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(K1) The Influence of Iron and Feed patterns of the influent for Sludge Reduction in the Cannibal^{TM} process

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Abstract

A laboratory study of a sludge reduction by the Cannibal process was performed to determine the variations of sludge reduction occurred infield installations. Two issues were thought to be important, the iron concentration in the feed and theprocess configuration. Laboratory sequencing batch reactors were operated-one of which was operated as aconventional activated sludge system (CAS) and the others included a side stream anaerobic reactor (Cannibalsystem). Initially, the iron content in the feed was varied. Later, the feeding cycles were varied. It was found thatIronoxidation/reduction cycling was influent the bioavailability of organic matter in activatedsludge flocs and played a role infloc destruction. In addition, the Cannibal process operated as a fast feed (5 minute feed) system generated up to 80% less solids than the CAS without any negative effect on the effluent quality or the settling characteristicsof the activated sludge. For the Cannibal system operated under slow feed (4 hour feed), solids production waslower than theCAS but remained higher than for the fast feed.

Keywords
Cannibal^{TM} process, anaerobic side-stream reactor, oxygen uptake, protein degradation

INTRODUCTION

A previous study by Novak (2007) demonstrated that the Cannibal process generated about 60% less solids than a conventional activated sludge system without any negative effects on the effluent quality. However, for some full-scale Cannibal processes, solids reduction does not meet expectations. Observations suggested that for plants operated at high SRT in a complete mix mode, solids reductions were much less than for plug flow systems. In addition, it was thought, based on studies by Novak (2007) that an important mechanism in solids reduction by the Cannibal process was iron reduction in the anaerobic (interchange) reactor which released iron-associated organics that could then be degraded. Therefore, this study was undertaken to examine the effect of iron in the feed and process configuration (feeding patterns) on the solids reduction by the Cannibal process.

MATERIAL AND METHODS

Two operational phases were used. In the first phase, two Cannibal systems and a conventional activated sludge were run. Each Cannibal system was operated as SBR with a sidestream anaerobic bioreactor. The control system was run as a SBR. The purpose was to evaluate the impact of iron concentration in the feed on the solids yield.For the second phase, two Cannibal systems were operated in the same manner as in the first phase without the control system. The first Cannibal system was fed over a 5 minute time period (fast feed) in order to produce a high initial substrate concentration during the feed cycle. The second system was fed over a period of 4 hours (slow feed) to provide a consistently low substrate concentration. More details for reactor configurations, feed composition, and analytical methods can be found from Novak (2007) and APHA (1999).In addition, some reactor and effluent samples were subjected to size separation to determine the molecular weight distribution of the soluble protein. For this experiment, an aliquot of centrate was individually filtered through 1.5- and 0.45-µm membrane filters and 30,000 and 1000 Dalton ultra filters. Ultrafiltration was performed at 414 kPa (60 psi). At the end of the second phase, the sludge in the anaerobic bioreactors was centrifuged at 9000 Xg for 30 minutes at ambient temperature (25^{o}C). The centrate was decanted and added to activated sludge from the SBR, and the oxygen uptake rate was measured using a dissolved oxygen meter. Oxygen uptake tests were conducted using 250 mL mixed liquor, 25 ml centratefrom fast and slow feed system respectively, and enough tap water to fill a 300-mL biochemical oxygen demand bottle.

RESULTS AND DISCUSSIONS

In the first phase, the total suspended solids (TSS) and soluble COD (sCOD) in the effluent were similar for all systems and remained between 20-24 mg/L and 12-18 mg/L, respectively once steady-state was reached as evidenced by low variability in sCOD and TSS in the effluent. It can be seen from Figure 1 that the Cannibal systems generated much less solids than the control system, as indicated by lower solid accumulation and observed yield for both Cannibal systems. In addition, the observed yield for the Cannibal system receiving lower iron in the influent was 0.14, and that for the high iron system was 0.09. The lower observed yield and less solid accumulation for the Cannibal system with higher iron in the influent indicate that iron plays a role in solids reduction in the Cannibal system. In the second phase, as illustrated in Figure 2, when the feeding time for the system with moderate iron in the influent was increased from 5 minutes to 4 hours, an increase in solids generation was found for the Cannibal system with moderate iron. However, when fast feed resumed, as shown in Figure 3, the solids generation returned to the lower level. For the low iron system, a similar response was seen to the conversion to slow feeding. As shown in Figure 4, conversion of fast to slow feed resulted in an increase in the yield from 0.14 to 0.31 mgTSS/mgCOD. Therefore, it can be seen that the fast feed mode gives better solids reduction than the slow feed mode. It is thought that fast feed operation provides an initial high F/M ratio and this makes the system performance similar to a plug flow operation. In contrast, slow feeding provides a low F/M ratio and is similar to a complete mix operation. The data show that the characteristics of the sludge from two Cannibal systems are different. The sludge produced under fast feed was more susceptible to the Cannibal configuration than that generated from the slow feed Cannibal system. The results of the oxygen uptake measurement are demonstrated in Figure 5. It can be seen that both the oxygen uptake rated and amount of oxygen used for the centrate from the fast feed system was greater than that in the slow feed system. These data show that the anaerobic bioreactor for the fast feed system contains more readily biodegradable material than that from the slow feed system. This indicates that the fast feed system generated the floc that was more susceptible to the Cannibal operation than the slow feed system. As can be seen from Table 1, the protein concentration increased for the sludge discharged from both of anaerobic bioreactors. This is consistent with the study by Novak et al (2003) and Park et al (2006) who found that Fe-associated EPS flocs disintegrated under anaerobic condition, resulting in deflocculation. The material that is bound to iron, primarily protein, is released and degraded. In addition, soluble protein in the anaerobic bioreactor of the fast feed system is higher than the system with slow feed. It appears that more Fe-associated EPS floc material was destroyed in the Cannibal system with fast feed operation. In addition, a higher portion of protein that passes through a 1 kDa ultrafiltration can be seen for the fast feed system compared to slow feed system. The protein fraction less than 1 kDa can be considered as readily biodegradable material. Therefore, it is clear that operating the Cannibal system with fast feed to achieve high substrate pressure allows the system to generate more soluble biodegradable protein. The data also show that the protein released in the anaerobic bioreactor in fast feed system is more readily degraded than that for slow feed system in an aerobic environment (protein degradation in the aerobic reactor is the difference between protein entering and leaving the SBR). These data correspond with the data from oxygen uptake test. That is, more substrate uptake as indicated by protein degradation in fast feed system resulted in a greater rate of oxygen utilization. The oxidation-reduction potential (ORP) in anaerobic bioreactor of the Cannibal system operated under fast and slow feed was -264 mV and -108 mV, respectively. These data are in accord with the research from Saby et al. (2003). These researchers operated a modified activated sludge system called the oxic-settling-anoxic process by recycling the settled activated sludge to an anoxic tank. They found that the amount of solid reduction was dependent on the ORP. That is, a lower ORP in an anoxic reactor was associated with a higher solid reduction.

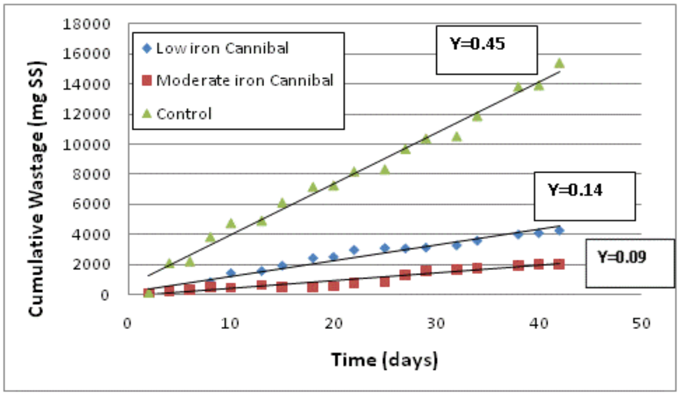

Figure 1 Cumulative Solids for Control, Low and Moderate Iron Systems

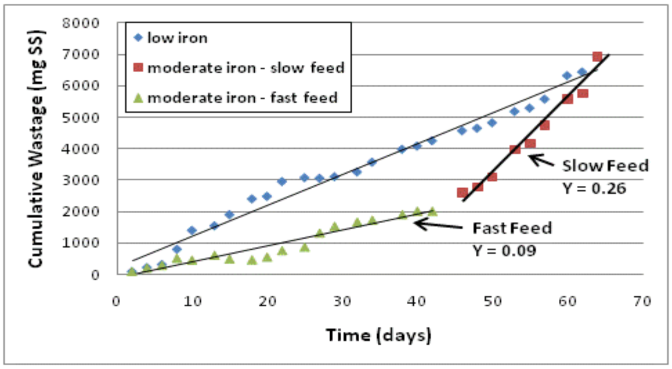

Figure 2 Effect of Feeding Pattern on Solids Production for the System with Moderate Iron in the feed

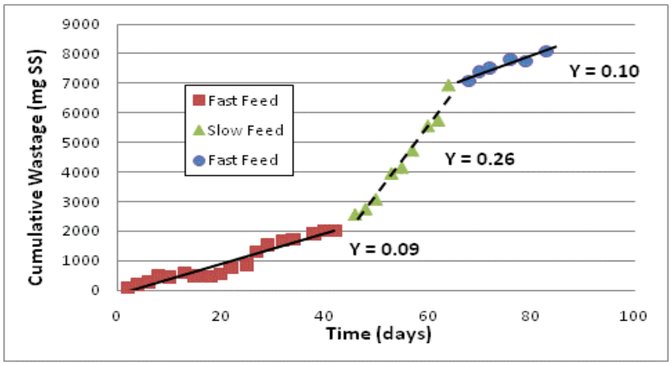

Figure 3 Effect of Feeding Variations on the Yield From a Cannibal System. Data are for Moderate Iron Concentration.

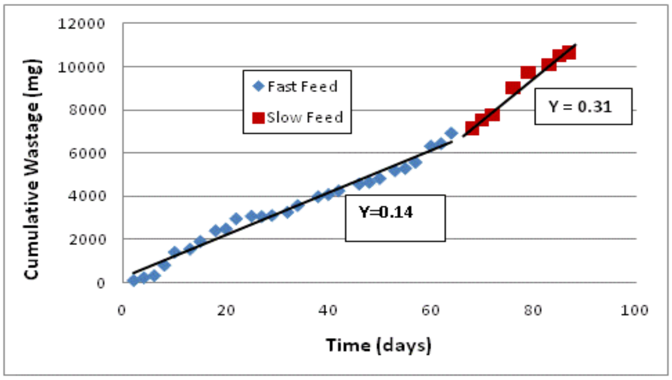

Figure 4. Effect of Feeding Variations on the Yield from a Cannibal System. Data are for the Low Iron Concentration.

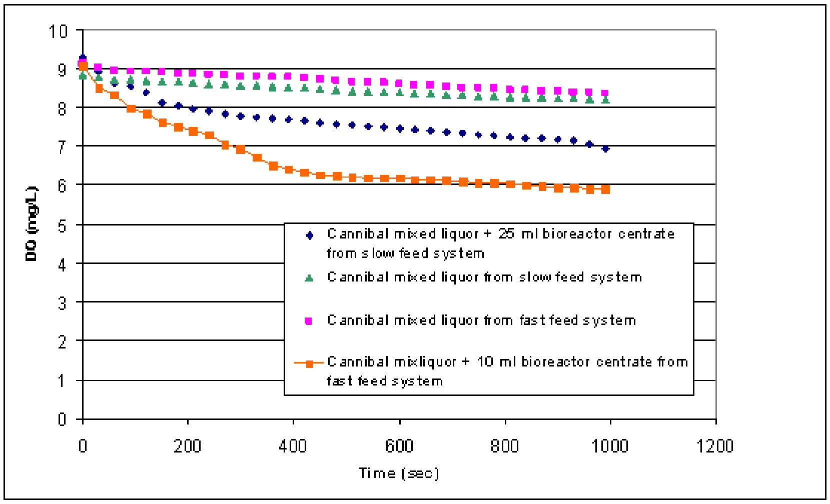

Figure **5**. Oxygen uptake for centrate from anaerobic bioreactors in fast and slow feed systems.

Table **1.** Protein data separated by molecular size at two different locations

LOCATION	FEED PATTERN	Protein Concentration (mg/L)			
		1.5 um	0.45 um	30kDa	1 kDa
Feed to aerobic reactor	Fast Feed Slow Feed	109 55	78 38	67 18	35 9
Feed to anaerobic reactor(settled activated sludge)	Fast Feed Slow Feed	17 13	12 8	9 6	5 3

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(P1) Anaerobic-Aerobic Digestion: Analysis of Process Performance for Secondary and Mixed Sludge

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Abstract

Sequential anaerobic-aerobic digestion has been demonstrated to be an effective alternative to enhance sludge stabilization: the basic motivation behind this approach is related to the different reaction environments provided for biodegradation of the different volatile solids (VS) fractions. In this paper, results of an extensive investigation on waste and mixed sludge from a full scale wastewater treatment plant are reported. Sequential digestion performance was evaluated in terms of VS removal efficiency, biogas production, and dewaterability of the digested sludge. High VS removal efficiencies (47% in the anaerobic phase and 25% in the aerobic one) were obtained for secondary sludge. Even higher performance was observed for mixed sludge with efficiency values of 50 and 45 % for the anaerobic and aerobic stage respectively. The aerobic stage was operated with alternate aeration so providing effective nitrogen removal and a consequent marked reduction of the nitrogen load recycled to the plant. The influence on sludge dewaterability was evaluated by determining the Capillary Suction Time (CST) and a significant positive effect due to the aerobic stage was observed. Biogas production (0.54 and 0.8 $Nm^3/(kgVS_{destroyed})$ for waste and mixed sludge respectively) was close in both cases to the upper limit of the range of values reported in the specialised literature so demonstrating that the low anaerobic sludge retention time of 15 days is still suitable for efficient energy recovery.

Keywords

Sludge stabilization; sequential anaerobic aerobic digestion; VS removal; secondary sludge, mixed sludge; nitrogen removal

INTRODUCTION

A promising strategy to improve the digestibility of sewage sludge is the application of a sequential anaerobic-aerobic digestion process. The basic motivation behind this approach arises from the different reaction environments (anaerobic and aerobic) provided to attain optimal biodegradability conditions for the different VS sludge fractions.

This point is well addressed in Kumar et al. (2006a, 2006b) reporting a simple classification for the sludge constituent fractions in terms of VS degradability: a fraction degradable only under anaerobic conditions, a fraction degradable only under aerobic conditions, a fraction degradable both under anaerobic and aerobic conditions, and a non degradable fraction.

It follows that conventional one stage digestion (aerobic or anaerobic) does not always provides efficient VS biodegradation. Moreover, the combination of the two digestion phases can be advantageous in that they can mitigate some of the drawbacks characterizing the two individual digestion methods.

Recently multi–step digestion has received increased interest and previous studies have demonstrated the potential of this approach to improve the performance of conventional digestion processing in terms of VS removal and improvement of the dewaterability characteristics of the digested sludge (Kumar et al., 2006a, Parravicini et al., 2008; Zupancic and Ros, 2008).

Another positive effect of the sequential anaerobic aerobic digestion is the ammonia nitrogen removal in the supernatant stream that can significantly reduce the nitrogen load recycled to the wastewater treatment plant as observed by Zupancic and Ros (2008) with nitrification efficiency up to 85% for mixed sludge stabilization.

The objective of the activity is to verify the applicability of sequential digestion to a real secondary and mixed sludges by evaluationg the process performance in terms of VS removal, ammonia nitrogen removal, biogas production, and dewaterability. In addition the possibility of achieving simultaneous denitrification by intermittent aeration was explored.

MATERIAL AND METHODS

Sludge

Primary and secondary sludges were provided by the Rome North wastewater treatment plant. The plant is a conventional activated sludge system including screening, primary clarification and secondary treatment, and serves about 700,000 P.E.

Reactors

Lab scale reactors utilized in this study were 7.4 litre cylindrical glass vessels equipped with mechanical stirrers fitted with helicoidal blades. The reactors were operated in series. The first reactor operated under anaerobic conditions and was equipped with a thermostatic jacket and a control device keeping the temperature at 37±0.5 °C. At the beginning of the start up phase it was filled with the inoculum and sewage sludge (ratio inoculum/sludge 1:1). The working volume was 7 L and the Sludge Retention Time (SRT) was controlled at 15 d. The inoculum was taken from a full scale anaerobic sludge digester.

The second reactor, operated under aerobic conditions, has a working volume of 4.5 L, and air was supplied by a compressor able to maintain the concentration of dissolved oxygen (DO) at levels of ~ 3 mg/L. The reactor was operated at room temperature at SRT of 12 days. Intermittent aeration (40 min ON and 20 min OFF) was applied in order to achieve simultaneous denitrification. As aerobic inoculum a mixed liquor sample from the aeration tank of a full scale plant was utilized.

Two series of tests have been performed with secondary and mixed sludge. Reactors were operated in semi-continuous mode for approximately 8 months (4.5 with secondary and 3.5 with mixed sludge) in order to have an extended work period, representative of real plant operation.

Analysis

Regular sample collection and analysis were initiated one week after start up. Feed, anaerobic digested and aerobic digested sludge were analyzed for volatile solids (VS), capillary suction time (CST), ammonia, nitrite and nitrate nitrogen. Biogas production rate and methane fraction were also measured. Analytical methods and devices are reported in the following.

Volatile solid concentration was measured according to Standard Methods (APHA, 1998). Ammonia, nitrites and nitrates were determined according to the standard methods (APHA, 1998).

CST was determined by a Triton Electronics apparatus, according to the Standard Method procedure (APHA, 1998).

The flow rate of biogas produced by the anaerobic reactor was measured by a volumetric counter and the measurement device was controlled by a Programmable Logic Controller that also provides the recording of signals.

Methane in the biogas was determined by a gas-cromatograph PERKIN ELMER AutoSystem equipped with a Carboxen 1000 (Supelco) column and a TCD detector.

RESULTS AND DISCUSSION

Two series of tests were performed at the same operating conditions with secondary and mixed sludge respectively, main results are reported in the Tables 1 and 2 for VS removal efficiency in the anaerobic and aerobic bioreactor, biogas production and nitrification – denitrification efficiency.

Table 1. Performance of the sequential digestion. Feed: secondary sludge OLR = Organic Loading Rate, SGP= Specific Biogas Production.

Anaerobic reactor			**Aerobic reactor**		
VS removal efficiency	(%)	47 ± 6	VS removal efficiency	(%)	25 ± 7
OLR	(kgVS/m^3·d)	1.42± 0.5	OLR	(kgVS/m^3·d)	0.83 ± 0.3
SGP	($Nm^3/kgVS_{destroyed}$)	0.54 ± 0.14	Nitrification efficiency	(%)	79
CH_4	($Nm^3/kgVS_{fed}$) (%)	0.24 ± 0.04 66	Denitrification efficiency	(%)	58

Table 2. Performance of the sequential digestion. Feed: mixed sludge OLR = Organic Loading Rate, SGP= Specific Biogas Production

Anaerobic reactor			**Aerobic reactor**		
VS removal efficiency	(%)	50 ± 9	VS removal efficiency	(%)	45 ± 6
OLR	(kgVS/m^3·d)	2.39 ± 0.5	OLR	(kgVS/m^3·d)	1.49 ± 0.2
SGP	($Nm^3/kgVS_{destroyed}$)	0.80 ± 0.35	Nitrification efficiency	(%)	95
CH_4	($Nm^3/kgVS_{fed}$) (%)	0.32 ± 0.1 67	Denitrification efficiency	(%)	46

VS were effectively removed in the anaerobic stage with percent removal efficiencies of 47 and 50 % for secondary and mixed sludge respectively. These values are in the range of values (27 - 71%)reported by Speece (1988) in a survey of 30 anaerobic sludge digesters of municipal WWTPs. The post aerobic stage significantly improved the stabilization efficiencies with additional VS removal of 25 and 45% for secondary and mixed sludge respectively. It is worth noting that performance of the sequential digestion is dependent on the OLR applied to the system i.e. removal increases with increasing OLR. This finding suggests the suitability of this technological solution for high loaded digesters or in the upgrading of WWTPs when an increase of the served population occurs. The better digestibility of the mixed sludge is confirmed by the higher SGP (0.8 vs. 0.54 $Nm^3/(kgVS_{destroyed})$ while the methane fraction (representative of potential energy recovery from the biogas) is comparable in the two cases. In any case the average specific biogas production is in both cases within the range of 0.19-1.6 $Nm^3/(kg/VS_{destroyed})$ reported in the literature (Speece, 1988; Bolzonella et al., 2005) for mesophilic digestion of sewage sludge. Methane fraction in the biogas was very similar for the two digested sludges i.e. equal to 66 and 67 % for waste and mixed sludge respectively which is consistent with literature data (Bousˇkova´ et al., 2005).

Results on nitrification and denitrification are of relevance if we consider that the supernatant from anaerobic sludge digestion is characterized by a high nitrogen content and can represent a significant fraction (up to 30%) of the nitrogen load of a wastewater treatment plant (Zupancic and Ros, 2008). The presence of an aerobic phase in which nitrification and/or (depending on the dissolved oxygen control) nitrification-denitrification can take place, is potentially able to significantly reduce this load. The aerobic SRT of 12 days was demonstrated to be suitable for achieving efficient nitrification (up to 95% ammonia nitrogen removal for mixed sludge) while the applied intermittent aeration was able to achieve remarkable denitrification efficiencies (46-58% for mixed and secondary sludge respectively).

A first assessment of the effects on sludge dewaterability was performed through CST measurement: data reported in Figure 1 show for both examined sludges an increase of CST after the anaerobic stage (i.e. negative effect on dewaterability) followed by a decrease after the aerobic phase. The positive effect is more evident for mixed sludge and confirm the data reported by of Kumar et al. (2006a).

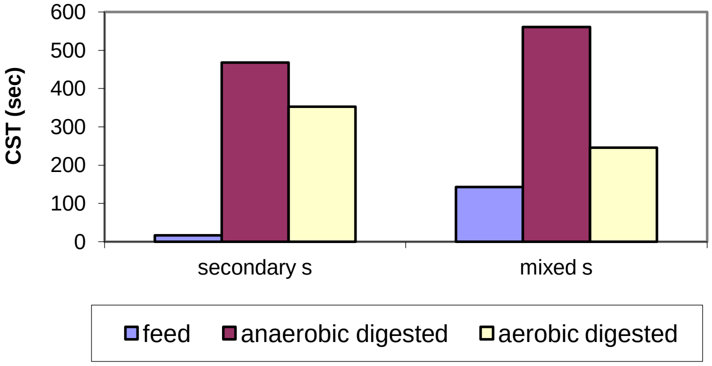

Figure 1. CST trend in the sequential digestion of secondary and mixed sludge.

CONCLUSIONS

Sequential anaerobic aerobic digestion confirmed the expected results in comparison to the single stage aerobic or aerobic stabilization in terms of improvement of VS removal efficiency and dewaterability characteristics of the digested sludge. Additional relevant feature is the demonstrated possibility of reducing the nitrogen load to the WWTP generated by the recycle of the supernatant from the digester by simultaneous nitrification-denitrification in the post aerobic digester.

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(P2) Sewage sludge and fruit wastes anaerobic co-digestion: Evaluation of the process when the co-substrate is changed

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Abstract

The low organic load and the non-used capacity of the sewage sludge digesters are the driving forces behind its anaerobic co-digestion. The present article, where sewage sludge is co-digested with three different fruit waste (seasonality), focus on the transitory state when co-digestion starts, co-substrate is changed and co-digestion is stopped. Two lab-scale digesters were operated during 280 days, one as a reference and the other as co-digester. Co-digestion beginning led to an increase of the organic loading rate and biogas production together with a rise of the volatile fatty acids concentration, which recovered previous levels in 5 days. Co-substrate change did not disturb process stability; however, both biogas production and alkalinity varied depending on the fruit waste and sewage sludge characteristics. Finally, when co-digestion was stopped, the parameters conveyed, at different rates, to the values recorded in the reference digester.

Keywords
Anaerobic digestion, Co-digestion, Transitory state, Fruit waste, Sewage sludge

INTRODUCTION

In Catalonia, 600 thousand tons of sewage sludge (SS), by-product of the physical, chemical and biological wastewater treatment, are annually produced by 340 municipal wastewater treatment plants (WWTP). Consequently, WWTP's require a good, economic and environmental, waste management and treatment such as anaerobic digestion (AD) (Metcalf and Eddy 2003). However, operational data have indicated some non-used capacity in SS anaerobic digesters, sometimes up to 30%. Therefore, it would be profitable to use these extra capacities by introducing additional components to conduct the co-digestion in the existing anaerobic system (Montusiewicz et al., 2011). Due to the high amounts of easily biodegradable organic matter, fruit wastes (FW) are ideal co-substrates for SS, substrate which is characterized by relatively low carbon-to-nitrogen (C/N) ratios and high buffer capacity(Bouallagui et al., 2009). Besides, anaerobic co-digestion (AcoD), the simultaneous AD of two or more substrates, is a feasible option to improve the economic viability of AD plants because of the higher biogas yields (Astals et al., 2011). Nevertheless, the seasonality of the fruit processing industry makes difficult to operate a co-digester under the same conditions during a long period of time, because waste supply can be frequently changed or stopped. The aim of the present study was to evaluate the performance achieved duringAcoD when the co-substrate was changed as well as when the co-substrate supply was stopped.

MATERIALS & METHODS

Two digesters with a working volume of 1.5L were operated during 280 days at mesophilic conditions (37 ºC) and with a hydraulic retention time of 20 days. The inoculum was obtained from a stable lab-scale mesophilic digester treating SS.The co-digester (R1), fed with SS and different FW (peach, banana and apple waste) had an organic loading rate (OLR) of 3.0 gVS L_R^{-1} day^{-1}, whereas the reference digester (R2), only fed with SS, had an OLR of 1.2 gVS L_R^{-1} day^{-1}. In R1, SS was used as a main substrate, while two kind of peach (PW1 and PW2), banana (BW) and apple (AW)waste were used as co-substrates. SS was obtained from a municipal WWTP of Barcelona metropolitan area (Spain), the two peach waste were obtained from a fruit processing industry in Lleida (Spain) and banana and apple were obtained from a grocery and then grinded in order to simulate real wastes.Total solids (TS), volatile solids (VS), volatile fatty acids (VFA), alkalinity, pH and methane percentage were determined following the Standard Methods for the Examination of Water and Wastewater procedures (APHA, 2005).

The study of the transitory state was divided into five stages.Initially (stage I), both digesters were only fed with SS(OLR 1.2gVSL$_R$$^{-1}$day^{-1}). Then (stage II), R1 started to co-digest SS and PW1, while R2 was kept as a reference digester. Ten days after the beginning of stage II, PW1 was changed by PW2. Later on, the co-substrate was change for BW (stage III) and then for AW (stage IV). Finally (stage V), the co-digestion was stopped and R1 was only fed with SS. The change from one stage to another one was done once the stationary conditions were achieved.It has to be noted that one batch of SS was used from the beginning until day 100 and another one since day 101 until the end.

RESULTS & DISCUSSIONS

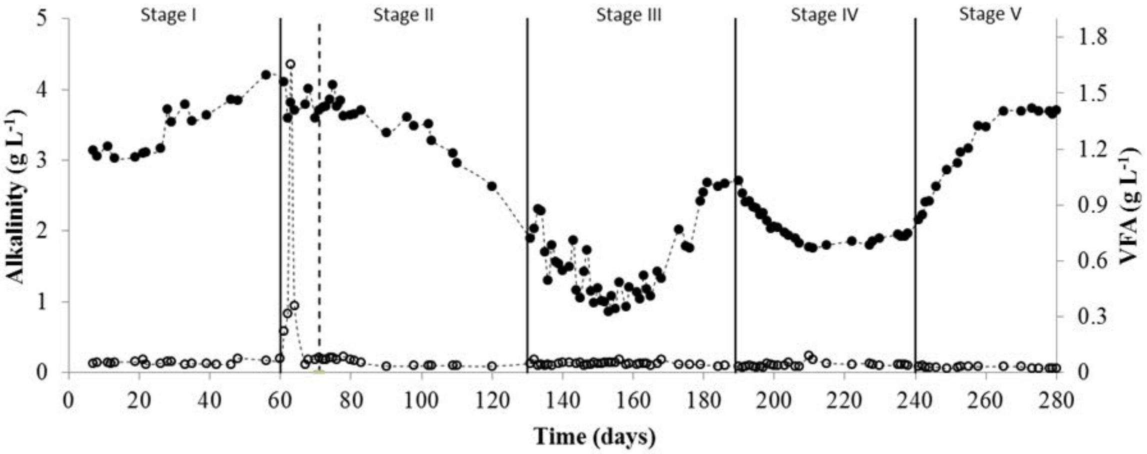

Fig. 1 VFA (○) and TA (●) levels from R1 effluent

In the figures the stages are divided by bars and the dotted line represents the change of PW1 by PW2. At Stage I both digesters were fed only with SS until they achieved similar stationary conditions (pH 7.3, TA 3.7 g $CaCO_3$ L^{-1}, VFA 0.06 g L^{-1} and constant methane production). Later on, co-digestion started with the addition of PW1 in R1 feedstock increasing the OLR from 1.2 to 3.0 g VS L^{-1} day^{-1} (Stage II). Those changes were reflected on VFA and alkalinity values during a short period of time (Fig. 1). On the one hand, the level of VFA rose up from 0.07 to 1.70 g L^{-1}in only three days, being propionic acid (1.35 g L^{-1}) the main VFA. When the maximum concentration of VFA was achieved (3 days after the perturbation), acetic and propionic acid started to decrease during five days until constant values were achieved (0.04 g L^{-1} for acetic and below 0.01 g L^{-1} for propionic). Although the propionic concentration was within the critical limit reported in the literature (0.9 – 2.2 g L^{-1}), from the prompt return of propionate to basal levels it can be understood that the system was not severely affected by the addition of PW1 as co-substrate (Nielsen et al., 2007). The same conclusion can be obtained from the evolution of the VFA/TA ratio. The ratio overcame the critical value for stable operation (VFA/TA > 0.4) three days after the co-substrate addition but returned to previous levels within two days (VFA/TA≈ 0.02). On the other hand, alkalinity values were also altered by the addition of PW1 as co-substrate due to the increase of the feedstock biodegradability (Fig. 1). At the 70th day PW1 was changed for PW2, presenting a high quantity of fibers and seeds. As illustrated in Fig. 1, the change of the PW composition did not significantly disturb R1 stability (3.6 g $CaCO_3$ L^{-1} for TA and 0.04 g L^{-1} for VFA), but reduced the production from 2.8 to 1.1 L$_{CH4}$ day^{-1} (Fig. 2). Even if the specific methane production (SMP) using PW2 was lower than that recorded in

R2 (0.22 and 0.23 L_{CH4} g^{-1}VS forR1 and R2 respectively), the methane production of R1 was about 110% higher than in R2 (Fig. 2). Contrariwise, at day 100th, when the SS was changed the alkalinity fell down from 3.3 to 2.1 g CaCO3 L^{-1} while the methane production was not highly influenced.

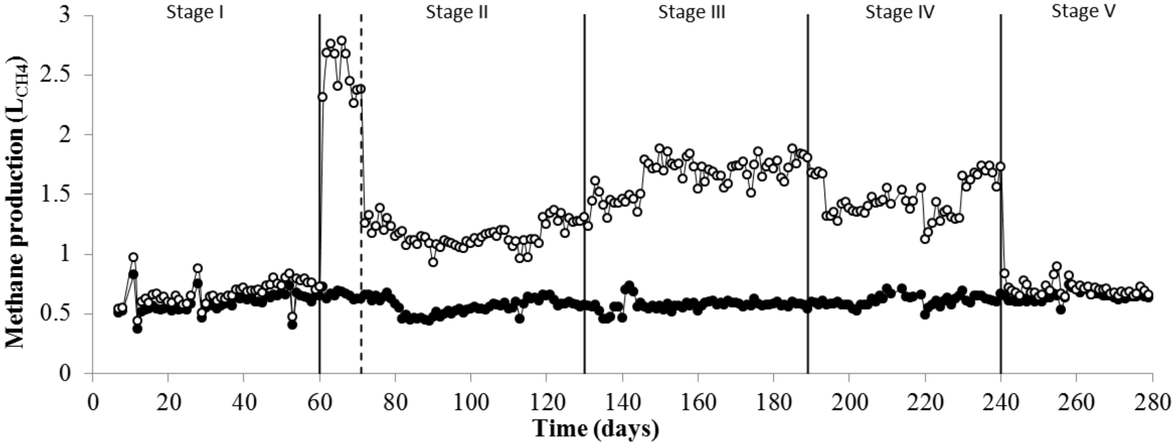

Fig. 2. Methane production of R1 (○) and R2 (●)

At day 131, PW2 was changed by BW which supposed a change in the feedstock composition while keeping the same OLR. As happened before, when PW1 was changed by PW2, the amount of VFA was not considerably affected by the change of the co-substrate (Fig. 1). However, the alkalinity in R1 presented an important change. TA decreased in R1 from 2.0 to about 1.1 g $CaCO_3$ L^{-1} (Fig. 1), likely due to the waste composition. In contrast to PW1 and PW2, BW was collected from the grocery so it did not suffer an industrial extraction process before it was fed to the digester. Therefore, the biodegradability of the BW was higher and its insertion led to a decrease in the TA. Bolzonella et al. (2003) also observed the same behavior when the most biodegradable waste was used in a semi-dry anaerobic digester. The variation of the stability parameters was higher and the TA was lower than before even if the reactor achieved stable conditions. It can be seen in Figure 1 that, at the end of the stage, the alkalinity rose up in both digesters because the alkalinity of the sewage sludge fed increased from 0.6to 1.4 g $CaCO_3$ L^{-1}. In that case the production last only one week to achieve the constant level of 1.8 L_{CH4} day^{-1} (SMP of0.30 L_{CH4} g^{-1}VS) being 180% higher than R2 (Fig. 2).

Similar behavior than in the transitory state between II and III was observed when BW was changed by AW while keeping the OLR. Again, a change in the co-substrate does not induce a rise in the VFA concentration.Nevertheless, TA decreased progressively in 20 days from 2.7to 1.8 g $CaCO_3$ L^{-1} and afterwards it remained at this value until the end of the stage (Fig. 1). As before, AW biodegradability was higher than PW biodegradability because it was also obtained from the grocery, but also, feedstock alkalinity of R1 was the lower than the other mixtures inducing that changes in alkalinity values. On the other hand, AW biodegradability seems to be less than the BW biodegradability since the registered SMP was only 0.26 L_{CH4} g^{-1}VSbeing very similar than that of R2, but, as stated in Fig. 2, the methane production in R1 was 133% higher (1.45 L_{CH4} day^{-1}) than that of R2 (0.63 L_{CH4} day^{-1}).

At the end of the study (Stage V), R1 was fed again only with SS and the OLR of R1 was decreased to 1.2 g VS L_R^{-1} day^{-1}. As expected, VFA did not present any change or fluctuation and remained at the same level (0.02 g L^{-1}). However, the levels of alkalinity presented a significant change. Due to the use of SS as a main substrate, alkalinity could increase in 25 days from 2.2 to 3.7 g $CaCO_3$ L^{-1}. Nevertheless, the system needs time to achieve the same alkalinity values of R2 since after 40 days the alkalinity was lower than that observed in R2. On the other hand, the methane production of R1 was slightly higher than that of R2 (0.70 L_{CH4} day^{-1}), probably because the methane potential from the remaining AW in the digester.

CONCLUSIONS

When co-digestion started, the VFA concentration rose up sharply. These changes only took five days and the rapid evolution of VFA and ratios to normal levels demonstrated that anaerobic biomass responded favorably to the co-substrate addition. However, when the co-substrate was changed while keeping constant the OLR, the VFA amount stayed constant but, due to the co-substrate biodegradability, the methane production changed and the alkalinity decreased. Finally, when co-digestion was stopped, the parameters conveyed, at different rates, to the values recorded in the reference digester.

AcoD between SS and FW has been identified as a successful tool to improve the methane production in WWTP even if the co-substrate is changed due to the fruit seasonality. Although some co-substrates did not present an improvement of the SMP, in all cases the methane production during AcoD was 110-180% higher than the production achieved during the SS mono-digestion. According to this study, the co-substrate change due to the harvesting season will not affect the digester stability. Nevertheless, to confirm the feasibility of this particular approach, further analyses have to be performed concerning the transportation costs or the digestate stability.

ACKNOWLEDGEMENTS

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(P3) Different strategies to enhance sludge stabilization:pre-treatment, temperature increase or dual-stage?

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Abstract

Sewage sludge processing is a key issue in wastewater treatment plants because of the assessed inadequacy of conventional treatments to produce high quality sludge to be safely used or disposed. This paper presents preliminary data on the performances of three different strategies in enhancing the conventional mesophilic digestion process (MAD), namely a) by adding an ultrasounds pretreatment (US-MAD), b) by increasing the temperature up to thermophilic conditions (TAD), and c) by adding a sequential thermophilic stage (MAD/TAD). For a feasible comparison, all the digestion tests have been carried out with the same substrate, i.e. real waste activated sludge and operated in semi-continuous mode at different organic loading rate. The innovative dual stage MAD/TAD permitted to achieve the highest organics removal (around 55%), but no biodegradability enhancement was evidenced. The best performances in terms of conversion rate was observed for US-MAD with average specific biogas production of 0.33±0.02 Nm^3 $kg^{-1}VS_{fed}$ against the 0.26±0.01 Nm^3 $kg^{-1}VS_{fed}$ of the conventional MAD. Increasing the temperature up to thermophilic conditions worsened noticeably the quality of the effluent, in particular as regards soluble COD and ammonia, whereas by integrating a pre-treatment as US-MAD, the high level of soluble substances in the pretreated was progressively removed up to a threshold value, and the effluent quality was similar to the one of the conventional reactor.

Keywords: advanced anaerobic digestion, sewage sludge, biogas, biodegradability

1. Introduction

Anaerobic digestion is widely accepted as a cost/effective alternative for sewage sludge treatment, because a large proportion of the organic matter can be converted into biogas (e.g., methane or hydrogen) or valuable products (e.g., organic acids), guaranteeing at the same time sludge stabilization. Advanced anaerobic digestion technologies allow not only to produce stable biosolids of exceptional quality but also to provide the following benefits: a) increased volatile solids reduction; b) improved biogas production rates; c) minimization of amount and volume of final product solids. Mesophilic ((35°C) anaerobic digestion is one of the most widely used process for the stabilization of sludge, defined as a conventional treatment. On the other hand, thermophilic (55°C) anaerobic digestion is considered as advanced treatment in the future European Directive, because at high temperatures the destruction of pathogens, increases, thus matching hygenization criteria which might be required for land application.

The objective of this work was to evaluate the performances of three advanced stabilization processes with respect to the reference mesophilic process. The investigated options were the following: a) addition of ultrasounds pre-treatment; b) increase of the temperature up to thermophilic conditions; c) addition of a second thermophilic stage.

The approach of the pre-treatment integration has the scope to improve the conversion of waste activated sludge, in which the particulate organics are recalcitrant to anaerobic bacterial hydrolysis, into a soluble, more biodegradable form (Braguglia et al, 2011). Modifications of anaerobic digestion usually involve introduction of thermophilic anaerobic digesters, whether it is thermophilic digestion by itself or in combination with mesophilic digestion (Bolzonella et al., 2012). With respect to mesophilic, thermophilic anaerobic digestion increases methane production, reducing the retention time needed for sludge treatment and providing sludge hygienisation. Although better digestion performances can be obtained from thermophilic digestion, the effluent quality and ability to dewater the residual sludge are poor, and require additional energy to heat the digester (De la Rubia et al., 2006).

The strategy of the dual stage approach by adding a thermophilic digester to a small mesophilic one brings together the advantages of both systems. In this perspective, the innovative process proposed here is based on a short mesophilic stage improving fatty acids production with a successive thermophilic stage acting as both methane fermenter, and polishing step.

In other words, the advanced anaerobic digestion processes evaluated here are grouped into the following classes: a) ultrasounds pretreated mesophilic digestion (US-MAD); thermophilic digestion (TAD) and c) mesophilic/thermophilic digestion (MAD/TAD). For the sake of comparison, all the digestion tests were carried out by feeding the same substrate, so that the enhanced stabilization processes could be directly compared with the more commonly used mesophilic one.

2. Materials and methods

2.1. Sludge

Waste activated sludge (WAS) was sampled from the municipal "Roma-Nord" wastewater treatment plant (about 700.000 p.e.). The WWTP includes screening, primary clarification and secondary treatment of activated sludge with a quite high sludge age (20 d). The secondary sludge was collected from the recycling stream before the thickener. The anaerobic inoculum was collected from the full-scale digester of the plant, which is fed with primary and secondary sludge.

2.2. Matter composition

Total and volatile solids (TS and VS) were determined according to standard methods (APHA, 1998). The soluble phase was analyzed by removing first the particulate sludge matter by centrifugation (10 min at 5,000 rpm); the resulting centrate was filtrated through 0.45 µm pore size membrane filters. Soluble COD, measured in duplicate, was determined with COD Cell Test by Spectroquant Merck (EPA method 410.4). Pre-thickening of sludge was performed by centrifugation for 5 min at 1,100 rpm. The ammonium ion was determined according to APAT IRSA-CNR (29/2003) methods 4030.

2.3. Digester system

Digestion of sludge was performed using anaerobic jacketed reactors (7 L), completely mixed and operated in semi-continuous mode. One reactor as control unit, was fed with untreated WAS and maintained at 37°C to perform the conventional mesophilic anaerobic digestion (MAD) process. A second reactor was fed with the same sludge, but was operated at 55°C to perform the thermophilic anaerobic digestion (TAD) process. Another mesophilic reactor was fed with sonicated sludge (US+MAD) and the last layout was a dual sequential stage mesophilic/thermophilic (MAD/TAD). The organic load was varied from 0.7 to 3.7 kgVS m^{-3} d^{-1}, which is a range usually adopted in sewage sludge digestion. For the MAD/TAD-1 the load to the first mesophilic reactor was 3.9 and to the successive thermophilic 1.2 kgVS m^{-3} d^{-1}, while for MAD/TAD-2 was increased up to 10 for the mesophilic and 2.5 kgVS m^{-3} d^{-1} for the thermophilic reactor.

Table 1 lists the operating conditions of the anaerobic digestion tests and the volatile solids removals obtained. Regarding the US-MAS, the operating conditions were the same as for the MAD tests, but the sludge was previously sonicated for 2-4 min, with energy inputs ranging from 0.35 to 1.4 kWh kg^{-1} dry solids (Braguglia et al., 2011).

Table 1. Operating conditions of the different anaerobic tests and the obtained VS removals (%)

Test #	MAD-1 (US-1)	MAD-2 (US-2)	MAD-3 (US-3)	TAD-1	TAD-2	TAD-3	MAD/TAD-1	MAD/TAD-2
Temperature (°C)	37°C			55°C			37°/55°C	
OLR (kgVS/ m^{3}d)	0.7	1.4	2.8	1	1.8	3.7	1.7*	3.2*
HRT (d)	20	10	10	15	8	8	5+10	3+10
VS removal (%)	37±1 (40±1.6)	33±0.9 (40±1.5)	30±1.3 (33±0.7)	43±1.5	42±1.4	38±1.1	55±3	47±3.5

*calculated as global organic loading rate

Data were collected during steady state conditions, i.e., after reaching constant specific biogas production. The produced biogas was collected by water displacement in a biogas collection unit.
The methane content was measured using a PerkinElmer Auto System GC-TCD.

3. Results and Discussion

For all the investigated stabilization processes, volatile solids removal decreased noticeably by increasing the operating OLR (Table 1). Nevertheless, it is important to highlight that while for the reference MAD process the VS reduction decreased progressively by increasing OLR from 37% to 30%, in the case of the enhanced stabilization processes, organics degradation was not affected by changing load in the range 0.7-1.8 kgVS/ m^{3}d, while decreased significantly at higher load. These results highlight the advantage of the enhanced stabilization processes to shorten the HRT of the process. In particular, best performances were obtained at medium OLR from the dual stage scheme, with surprisingly +67% gain in terms of VS removal. At the same time, by increasing OLR, the specific biogas production with respect to the fed VS did not change significantly indicating that the conversion rate was not influenced by load variation in the digester, both in mesophilic or thermophilic conditions. This result confirm the stability of the anaerobic tests in these conditions. Same trend was observed also by Ferrer et al. (2010) as regards thermophilic digestion of mixed sludge, where the specific biogas production with respect to VS fed remained constant in the OLR range 0.5-5.2 kgVS/m^{3}d.
The average mesophilic specific biogas production was 0.26±0.01 Nm^3 kg^{-1}VS$_{fed}$, according to the typical WAS digestion (0.15–0.30 Nm^3 kg^{-1}VS$_{fed}$), and increased slightly up to 0.29±0.02 Nm^3 kg^{-1}VS$_{fed}$ in thermophilic conditions, to 0.31±0.02 Nm^3 kg^{-1}VS$_{fed}$ for the dual stage, arriving up to 0.33±0.02 Nm^3 kg^{-1}VS$_{fed}$ with ultrasounds pretreatment.

The methane production was used to calculate the sludge biodegradability (Figure 1), determined by the ratio of the volume of methane produced per gCOD introduced divided by the theoretical methane production of 350 mL/gCOD at normal temperature and pressure conditions (Carrere et al., 2008). In the case of mesophilic digestion, the sludge biodegradability was significantly low (32±1%), independent on the OLR, whereas increased up to 42±1% after integration of the ultrasounds pretreatment (low-medium

OLR) or digester temperature increase (medium-high OLR). No enhancement effect of the dual stage was observed (the biodegradability was the same as the mesophilic reference system).

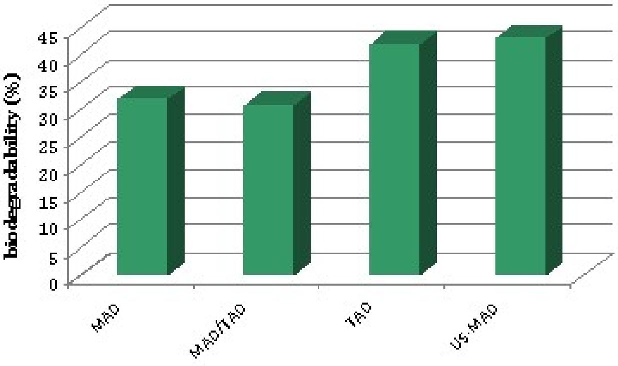

Figure 1. Sludge biodegradability (%) of the stabilization processes

Regarding the effluent quality at high loading rate, it was evident that the high temperature of the thermophilic digestion process (alone as TAD or coupled in dual stage MAD/TAD) generated highly concentrated effluent, in particular as regards soluble ammonia (1250-1350 mg N-NH_4/L) and COD in the range 1600-2200 mg/L), while in the case of mesophilic digestion the concentrations were noticeably lower (530 and 440 mg/L for N-NH_4 and COD, respectively). The integration of the mechanical pretreatment, did not affect the final effluent quality. It resulted therefore that by thermophilic digestion the quality of the effluent worsened, because of the typical intense hydrolysis process on the organic and proteic particulate matter, whereas by integrating a pre-disintegration, the high level of COD, ammonia of the pretreated feed was removed up to a threshold value, and the effluent quality was similar to the one of the conventional reactor.

Assessment of the options should be done on the economics of increased biogas production and solids removal against of the potential increased cost of treating the effluents, particularly ammonia. The available disposal route of the final sludge cake is potentially the most influential factor in the choice of advanced treatment process.

Acknowledgements

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(P4) Turn it up! High-load Contact Stabilization (HiCS) is a valuable activated sludge process for maximizing sludge production from sewage

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Abstract

The conventional approach of wastewater treatment is to maximize effluent quality and minimize operation costs, but this limits the amount of energy that could potentially be recovered. In order to proceed to an energetically self-sustaining wastewater treatment, engineers have taken renewed interest in pre-treatment processes that divert the organics present in the water into well-digestible sludge. In this study, we hypothesize that a High-load Contact Stabilization (HiCS) process is suitable for pre-treating domestic sewage to maximize sludge production. We compared the performance of HiCS to an established high-loadprocess, the so-called A-stage of the 'Adsorptions-Belebungsverfahren'. The HiCS reactor obtained an average removal efficiency of 34±10% total COD and 66±5% dissolved COD. The A-stage performed similarly, with a removal of 35±17% total and 77±3% dissolved COD. In both systems, specific oxygen utilization rates rose and dropped back to near baseline levels within 30 min.aerobic contact time, suggesting that aerobic substrate removal occurs primarily in the early stages of the contact period. Sorption experiments with HiCS sludge showed a fast removal of soluble and particulate substrate within the first min. of contact time. Conversely, sorption experiments with A-stage sludge showed a more gradual and variable pattern of substrate removal. These results indicate that the HiCS sludge is better adapted to quickly remove substrates via sorption than A-stage sludge and may therefore be more suitable for further optimization of sludge production for a maximal recovery of energy.

Keywords
AB process; Biosorption kinetics; Energy recovery

INTRODUCTION

Following adequate water purification, resource recovery is the new visionary goal for wastewater treatment, inspiring a search for technologies that not only remove energy and resources but make them available for reuse. Any technology that aims to recover energy from wastewater needs to (1) minimize energy loss by avoiding extensive oxidation of organic matter to CO_2, (2) facilitate efficient conversion of energy by fractionating the wastewater into a thick stream of concentrated organics and a diluted effluent stream and (3) operate in an energy-efficient manner and allow for close process control. In recent years, high-load activated sludge processes have gained attention because of their efficient concentration of organics into a well-digestible sludge, prior to further treatment of the water stream for nutrient removal. A well-known example of such a high-load system is the A-stage of the 'Adsorptions-Belebungsverfahren' or AB process (Böhnke, 1977), which is designed for rapid removal or organic materials at high sludge loading rates (2-10 gBOD $gVSS^{-1}$ d^{-1}) and low sludge retention times (hours to days). A short hydraulic retention time of less than 30 min. selects for rapid removal of organic matter and typical removal efficiencies range from 50 to 70%.

A novel promising technology for energy recovery from wastewater is a High-load Contact Stabilization (HiCS) process. In its original design at conventional loading rates, the Contact Stabilization (CS) process consists of a contact tank in which return sludge is mixed with influent for a short contact time – 15 to 60 min. – and substrate is removed via rapid degradation, sorption or storage. After settling, effluent is discarded and the sludge is sent to a stabilization tank where additional respiration occurs for at least 1.5 hours(Coombs, 1921). As a high-load version of the CS process, HiCS may provide advantages over other high-load processes such as the A-stage. CS has a high intrinsic resistance to toxic shocks and a low aeration tank volume(Bunch & Griffin, 1987). Whereas the contact tank may or may not be aerated, most of the oxidation occurs in the aerated stabilization tank, which gives a competitive advantage to micro-organisms adapted to quickly store or adsorb substrates for later metabolization after settling. Recent studies show a reappreciation of the CS processand it was suggested that HiCS performs better than the A-stage (Huang & Li, 2000), although a systematic experimental comparison has not yet been performed.

In this study, a HiCS system was developed and compared with the A-stage for the removal of organic substrates from black water. The two systems were operated at laboratory scale at high sludge loading rates and low sludge age, both with and without addition of iron chloride as flocculant to improve settleability and phosphate removal. Additional batch tests were performed to compare oxygen consumption rates, sorption kinetics and sludge digestibility. This paper demonstrates the feasibility of HiCS for wastewater treatment from an energy recovery viewpoint.

MATERIALS AND METHODS

Continuous and batch experiments

Black water was collected weekly for a period of 80 days (between May and July 2013), sieved (1 mm) and diluted to match average concentrations of chemical oxygen demand (COD) of Flemish wastewater. Average values and standard deviations were 270±70 mg L^{-1} total COD, 160±40 mg L^{-1} dissolved COD, 140±30 mg L^{-1} total BOD, 75±15 mg L^{-1} Kjeldahl-N, 71±15 mg L^{-1} NH_4^+-N, 6.4±1.5 mg L^{-1} PO_4^{3-}-P and pH7.7±0.2.A schematic representation of the HiCS and A-stage system is given in **Figure 1**. Average loading rates were 4.8 gCOD $gVSS^{-1}$ d^{-1} for HiCS and 3.3 gCOD $gVSS^{-1}$ d^{-1} for the A-stage.

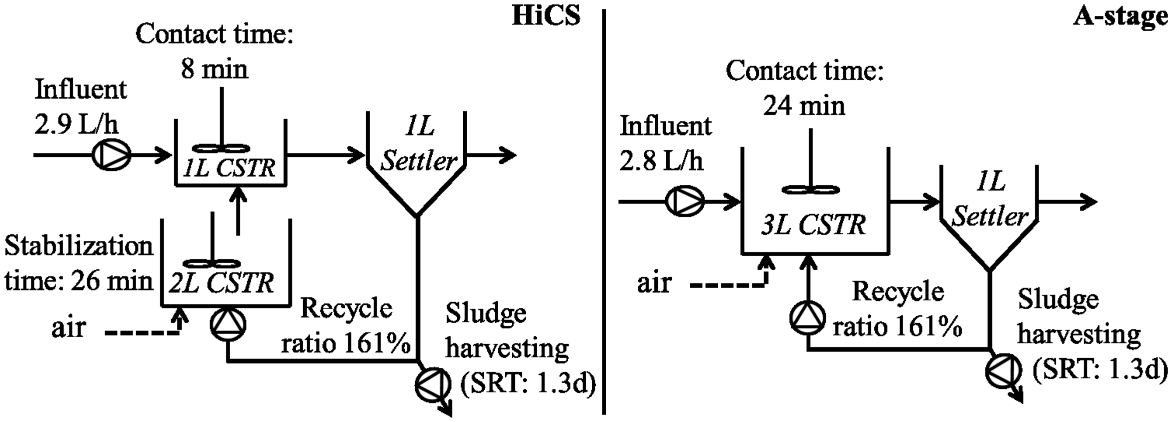

Figure 1. Scheme of the HiCS and A-stage reactor systems.

Sludge inoculum was obtained from the A-stage of the WWTP of Breda (NL). After 47 days, continuous addition of Fe_3Cl was started in both systems at a Fe:P molar ratio of 0.5.

For batch tests, HiCS and A-stage sludge were taken from steady-state reactors. To determine the specific oxygen uptake rate (SOUR), the sludge was continuously aerated and small samples were placed in a non-aerated sealed container every 10 min. Dissolved oxygen concentrations were measured at intervals of 30 sec, bothfor undiluted sludge (endogenous respiration) and with addition of substrate at a ratio of 2:1 substrate:sludge. The SOUR was calculated as the decline in DO per unit of time divided by the sludge concentration.For adsorption experiments, HiCS and A-stage sludge were centrifuged (2 min. at 2000 x *g*) and resuspended in distilled water at a pH of 8.5. The substrate consisted of reactor influent filtered over a 14 µm filter in order to distinguish substrate from sludge, since nearly all of the sludge particles had a size >14 µm (data not shown). The substrate was added to the sludge in a ratio of 2:1 in a stirred but non-aerated container. At different time points, samples were taken and immediately filtered over a 14 µm filter to determine the amount of free substrate and a 0.2 µm filter to determine the amount of soluble substrate.

RESULTS AND DISCUSSION

Reactor performances are given in **Table 1**.**Figure 2** represents the sludge yield of both systems before and after addition of flocculant.

Table 1. Volumetric COD removal rates ($g\ L^{-1}\ d^{-1}$)and standard deviations for the HiCS and A-stage systems.

		COD_{tot}	COD_{diss}
HiCS	No $FeCl_3$	2.46 (0.8)	2.93 (0.42)
	$FeCl_3$	1.37 (1.09)	2.06 (0.3)
A-stage	No $FeCl_3$	2.43 (1.45)	3.33 (0.46)
	$FeCl_3$	0.89 (1.01)	2.05 (0.32)

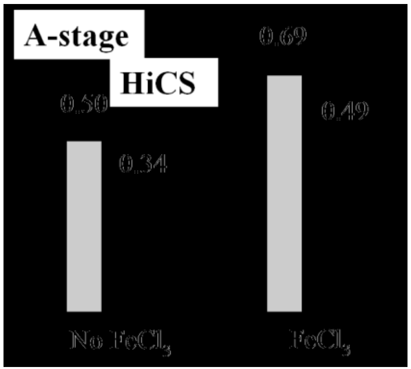

Figure 2. Sludge yields ($gVSS\ gCOD^{-1}$) for the HiCS and A-stage systems.

The removal rate of dissolved COD lay well within expectation and demonstrated the equivalence of the HiCS system with other high-load systems.The lower removal efficiencies for total COD were due to the periodic washout of non-settled sludge, indicating the importance of efficient sludge separation.As expected, nitrogen and phosphorus compounds left the reactors quasi unaltered, which potentially allows nutrient recovery in subsequent treatment stages.Addition of flocculant ($FeCl_3$) improved phosphorus removal at stoichiometric amounts.Sludge yields exceeded values encountered in conventional activated sludge systems (typically in the order of 0.15 gVSS gCOD^{-1}) by a factor two to five, indicating the subsequent potential for energy recovery by means of high-load wastewater treatment systems.The sludge volume index (SVI) did not notably decrease after flocculant addition, which shows that the sludge settleabilitywasmainly determined by other factors.

Batch experiments revealed that, upon addition of substrate, the SOUR increased by a factor five in the HiCS sludge and a factor nine in the A-stage sludge, and dropped back to near baseline levels after 30 to 40 min.of aeration (**Figure 3**). This suggests that aerobic substrate removal occurs primarily within the early stages of contact with the sludge. Sorption experiments (**Figure 4**) showed a fast removal of soluble and particulate substrate within the first min. of contact with HiCS sludge, followed by a slower removal during the remainder of the experiment. In contrast, substrate profiles for the A-stage sludge were more variable and showed a more gradually declining trend. These findings indicate that the HiCS sludge has a different substrate use strategy than A-stage sludge and is adapted to quickly remove substrates within the first min. of contact time, presumably via sorption or intracellular storage, before aerobic degradation occurs. Given a careful control of substrate contact times, the HiCS system may therefore be better suited than the A-stage sludge for the optimization of sludge production toward maximal recovery of energy.

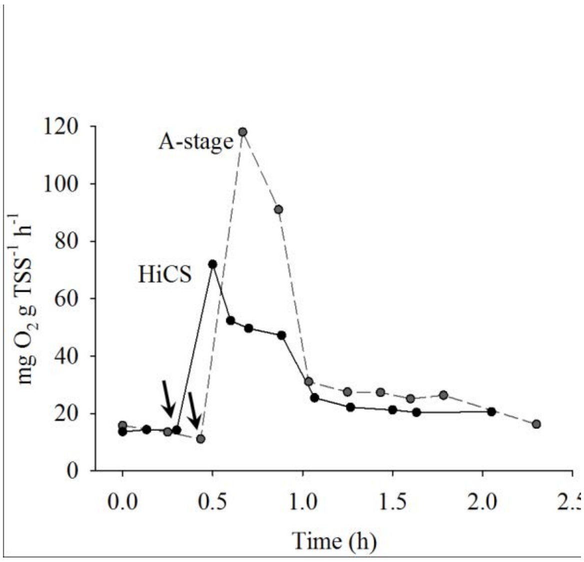

Figure 3.SOUR profiles for HiCS and A-stage sludge after addition of influent. The arrows indicate time of substrate addition.

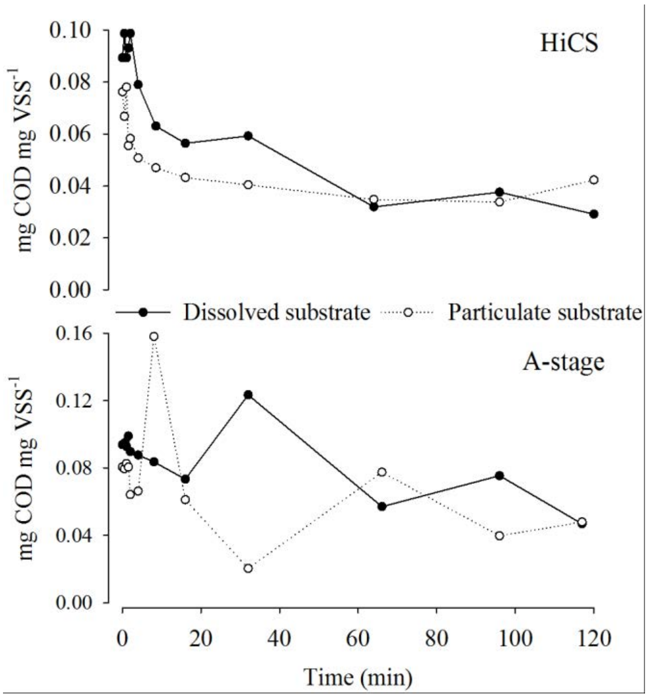

Figure 4. Adsorption profile of soluble and particulate substrate for HiCS and A-stage sludge.

In conclusion, our experiments demonstrate thepromising potential of HiCS as a high-load activated sludge system for pretreatment of wastewater to maximize sludge production and optimize conservation of chemical energy. Subsequent study will focus on further optimizing reactor performance and integrating this technology in an overall treatment scheme, thus advancing to an energetically self-sufficient wastewater treatment.

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(P5) Rotation generator of hydrodynamic cavitation for waste-activated sludge pretratment

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Abstract

The disintegration of raw sludge is very important for enhancement of the biogas production in anaerobic digestion process as it provides easily degradable substrate for microorganisms to perform maximum sludge treatment efficiency and stable digestion of sludge at lower costs. In the present study the disintegration was studied by using a novel rotation generator of hydrodynamic cavitation (CG). At the first stage the analysis of hydrodynamics of the CG were made with tap water, where the cavitation extent and aggressiveness was evaluated. At the second stage CG was used as a tool for pretreatment of a waste-activated sludge (WAS), collected from waste water treatment plant (WWTP). In case of WAS the disintegration rate was measured, where the soluble chemical oxygen demand (sCOD) and soluble Kjeldahl nitrogen (sTKN) was measured and microbiological pictures were taken. The sCOD increased from initial 50 mg/L up to 450 mg/L by exposing to 20 stages of cavitation.

Keywords
Disintegration of sludge, hydrodynamic cavitation, waste-activated sludge, wastewater treatment, biogas production

INTRODUCTION

Cavitation has despite its negative consequences as vibrations, noise, cavitation erosion etc., many beneficial features. It can be used in many different processes as a tool for water treatment, for cleaning, in medicine etc. As a phenomenon it is characterized by a formation, growth and collapse of bubbles within a liquid. The cavitation forms when the local pressure drops below the vaporization pressure. By ultrasonic cavitation acoustic waves cause the local pressure drop. By hydrodynamic cavitation the geometry of a system is the reason for velocity fluctuations in a liquid flow, which can cause local drop of pressure. Locally seen the cavitation bubble forms due to evaporation and gas expansion and therefore collects the energy from the surrounding liquid. By collapse, where the condensation and gas compression occurs, this energy is released. The energy can be released in forms of pressure impulses (order of several 100 bars), in so called micro yets (order of 100 m/s) and by very high temperatures (order of 1000 K). Such extreme conditions are adequate to rupture the cell wall of organic matter and consequently release the intracellular matter into the aqueous phase. These increase the biodegradability and enhance the anaerobic digestion, resulting in higher biogas production, less retention time and higher sludge reduction [1].

Wastewater treatment plants already use cavitation as a tool for sludge pretreatment to improve and accelerate the anaerobic digestion, which benefits in higher biogas production, mass reduction, pathogen reduction and odour removal [1]. Till now mostly ultrasonic cavitation (ultrasonication) is implemented in real processes, due to less complex installation as by hydrodynamic cavitation, where restrictions in shape of Venturi nozzle or orifice plates are needed, which causes great pressure losses and for that high power pumps are needed. Compared with hydrodynamic cavitation, ultrasonic cavitation disintegration generators found to consume significantly more energy [2].

In present paper a novel design of hydrodynamic cavitation generator is presented. In compare with other till today presented hydrodynamic generators [3-5], we believe, that it is most energy efficient. Due to all in one (cavitation generator and a pump) it does not require much space, it does not cause any additional pressure losses in existing system and it is easy to scale up. In order to determinate the applicability of the present cavitation generator for wastewater treatment, experiments with real wastewater were performed.

MATERIAL AND METHODS

Generator of hydrodynamic cavitation

On basis of knowledge and results from first designed cavitation generator [5], a novel rotation generator of hydrodynamic cavitation was built at Laboratory for Water and Turbine Machines (Faculty of Mechanical Engineering, University of Ljubljana). Based on centrifugal pump design it has a modified rotor and added stator in the housing of the pump (Fig. 1). The cavitation generator (CG) consists of an electric motor (1) with power of 4 kW, which drives the modified rotor (2) and the stator (3), which is placed opposite to the rotor in the front housing of the pump. The front housing of the pump preserves the original inlet (4) and outlet (5), to retain the possibility of standard installation. The front housing, the rear housing, the modified rotor (2) and stator (3) are forming the cavitation treatment chamber. In addition to treating wastewater with cavitation, the whole CG partly still preserves the pumping function, which means that the machine does not require an additional circulation pump to operate, and it does not cause additional pressure losses to the existing system.

Modified rotor and added stator have specially designed geometry, which causes periodically repeating pressure oscillations. The cavitation which is forming inside the treatment chamber is so called shear cavitation, where cavitation structures are formed due to opposite movement of two shear layers. The rotor has on its diameter of 190 mm a certain number of grooves. These grooves consequently form the so called teeth, which are sticking out of the main core of the rotor in axial direction. The stator, which has the same outer diameter as the rotor, has the same number of grooves. The difference is at the teeth geometry, where the stator teeth have inclination and they have barriers from three sides of each tooth. The purpose of these barriers is to prevent the high pressure to enter into the low pressure zone on the stator teeth.

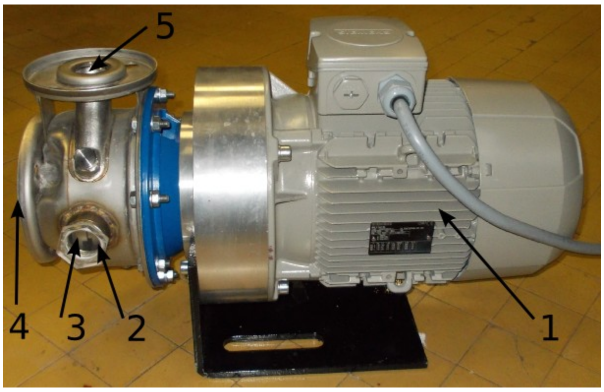

Figure 1: Rotation generator of hydrodynamic cavitation.

Wastewater

The WAS was collected at Domžale-Kamnik WWTP, Slovenia, where also chemical and biological analyses were conducted. WAS was taken from the secondary settler of aerobic biological stage treating municipal and industrial wastewater. Before performing experiments with the hydrodynamic cavitation, the sludge was settled in order to get at least 1 % thickened sludge.

Experimental set-up

Experiments were performed in two different set-ups. First the analyses of hydrodynamics were performed at laboratory conditions (Fig. 2, left) with tap water. The CG (1) was installed in a closed loop with a reservoir (2) and pipeline, where the volume of the test rig was approximately 100 L. The mass flow was measured by an electro magnetic flow meter (3), the temperature (4) and the absolute pressure (5) were monitored in the reservoir (2). To measure pressure oscillations, a hydrophone (6) was installed in the CG's treatment chamber. Also visualization by high speed camera (7) was performed.

Experiments with real wastewater (Fig. 2, middle and right) were performed at the Domžale-Kamnik WWTP, where two reservoirs (8) and (9) with a volume of 196 L each were used. The CG (1) was installed connecting these two reservoirs, where the flow rate was set to 65 L/min. The reservoirs and the CG formed an open loop, where "easy to connect" pipes were used to switch the pumping from the first reservoir to the second one and inversely. Only one reservoir was filled with thickened sludge and was systematically treated with cavitation. To compare the cavitation characteristic between the WAS and the clean tap water, also measurements with hydrophone were performed. Visualization could not be performed, due to very poor transparency of the WAS.

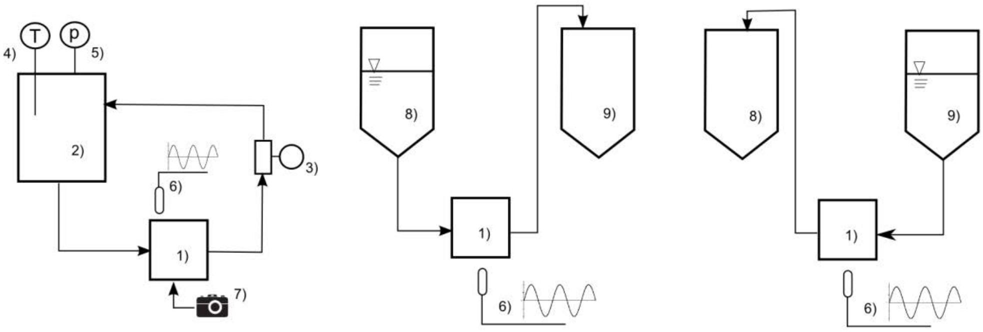

Figure 2: Schematic diagram of experimental set-ups (left – Faculty of Mechanical Engineering, middle and right – Domžale-Kamnik WWTP).

RESULTS

By hydrodynamic analysis, aggressiveness and the extent of hydrodynamic cavitation was evaluated by hydrophone and high-speed camera respectively. Two hydrodynamic parameters could be adjusted in the present configuration of the CG – the rotational speed of the rotor and the size of the gap between the rotor and the stator. The rotational speed of the rotor was controlled by frequency controller and the gap size was adjustable by positioning the stator in the CG's housing. Rotational speed was measured by digital tachometer and was set for 1740, 2290 and 2560 rpm respectively. The measurements were performed at the gap size of 3.5 mm, 1.5 mm and 0.5 mm. For each operating point the mean standard deviation of pressure inside the treatment chamber is calculated from three sets of measurements and shown on figure 3.

Standard deviation of the pressure inside the treatment chamber shows, that the pressure oscillations grows with rotational speed of the rotor and with the reduction of the distance between the rotor and the stator. Higher velocities mean higher pressure oscillations due to faster movement of the opposite teeth on the stator and rotor. Reducing the gap between the stator and the rotor is resulting in higher shear forces and consequently in higher pressure oscillations.

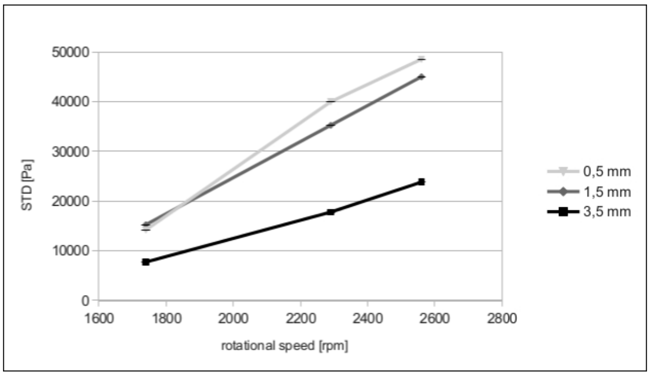

Figure 3: Mean standard deviation of the pressure inside the treatment chamber.

Figure 4 shows the cavitation between stator and rotor teeth. The images in Fig. 4 present the case for rotational speed of the rotor of 2290 rpm and the gap size of 3.5 mm. The time step between two images is ¼ ms and the recording speed was 8000 frames per second. The teeth of both stator and rotor are marked with dotted line for better perception. The stator tooth is kept still and is on the left side of the images, while on the right side of the images one can see, that the rotors tooth is moving upward. The series of images is shown for one passage of the rotors tooth by the stators tooth. As one can see, the cavitation is present all the time of the passage, which must be a consequence of a low pressure zone during the whole time.

By controlling the gap size between the rotor and the stator and the rotors frequency, we can regulate the cavitation extent and the cavitation aggressiveness. The extent of cavitation is increasing with the rotational speed, while the aggressiveness is increasing mainly with the reducing of the gap between the rotor and stator and also with increasing the rotational speed.

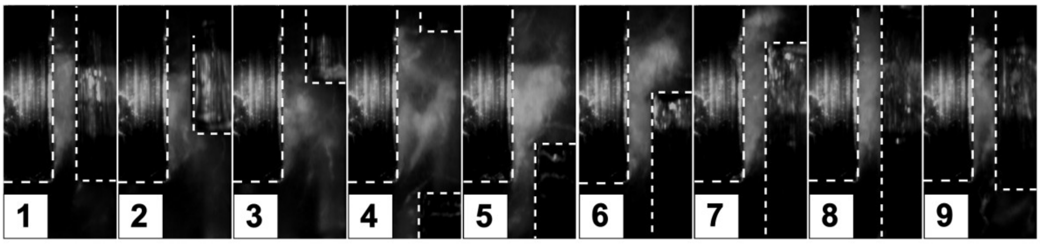

Figure **4:** Visualization of cavitation between stator and rotor in CG with time step between frames 1/4 ms.

In all samples (before and after different stage of cavitation) we performed the chemical analyses such as total dry solids, organic content, total COD, soluble COD (filtered through 0,45 µm filter paper), ammonia nitrogen, soluble Kjeldahl nitrogen (filtered through 0,45 µm filter paper) – all according to ISO standards, and microscopic analyses with 100 times magnification.

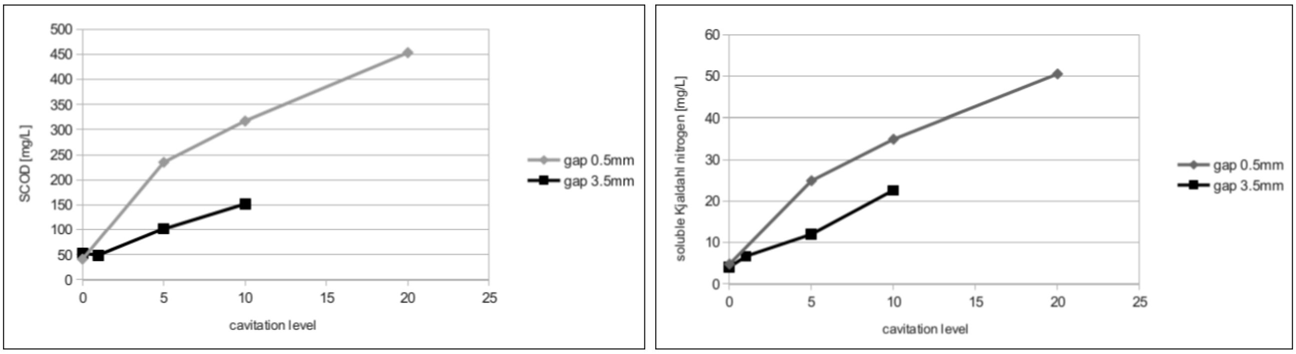

Figure 5: Soluble COD (left) and soluble Kjeldahl nitrogen (right) at different stage of cavitation and at two different gap size, for rotational speed of 2560 rpms.

As one can see on figure 5 (left) the sCOD is increasing with cavitation stage and reaches 453 mg/L from initial 41 mg/L in 20 passes through cavitation treatments in case of rotational speed of 2560 rpm and gap size of 0.5 mm. The sCOD indicates higher level of disintegration, which is very important for anaerobic digestion and consequently gas production.

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(P6) Energy balance and Life Cycle Assessment as a decision making tool for assessing sludge management concepts in emerging economies

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Abstract

Wastewater Treatment Plants (WWTP) in emerging economies need inexpensive and environmental friendly solutions for improving their sludge management. In Mexico, sludge production is continuously increasing due to the rapid growth in population. In addition, the new trend is to build up mega WWTP, which need to include a suitable sludge technology able to treat large amounts of sludge. Energy and mass balances, together with an Integrative Life Cycle Assessment (ILCA) would therefore be a suitable tool for selecting a holistic sludge management. The main objective of this study is to compare and evaluate the environmental impact and energy consumption/production of five possible scenarios that represent different sludge management systems. Using ILCA, the environmental impacts of the alternative sludge treatment systems are assessed and compared taking the local context into account.

Keywords
Emerging economies; energy balance; green energy; life cycle assessment; sludge management;

INTRODUCTION

Sludge is an unavoidable product from Wastewater Treatment Plants (WWTPs). Sludge management accounts for 49 to 53% of the total operation cost (Kroiss, 2004). The management of this by-product is still a challenge in many emerging economies, due to the lack of clear regulation, lack of a methodology for selecting a suitable sludge management system, high investment and operation cost for cutting age technology or simply, it is overlooked in the planning phase or optimisation of WWTP. Include economical, environmental, social, and political vectors in order to provide a cost-effective sludge management system, could be a better solution to address this growing problem in emerging economies. Therefore, the application of Life Cycle Assessment (LCA) for selecting suitable technologies in emerging economies is becoming more relevant than other methodologies. The LCA is a tool for evaluating the environmental performance not only of goods, but also of processes and/or services. ISO 14040 defines LCA as a compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a system through its life cycle, commonly known as cradle to the grave (ISO, 2000). LCA is designed to help practitioners to carry out integrated environmental health impact assessments.

Contextualizing the case study

Mexico has the 13th largest nominal gross domestic product (GDP) and ranks 14th in global greenhouse gas (GHG) emissions; however, GHG emissions per capita are relatively low. Mexico is the 5th largest country in the Americas and the 13th largest nation with an estimated population of over 113 million (INEGI, 2011). According to the Ministry of Energy (SENER), at the end of 2009, Mexico had an installed electricity capacity of 60.5 GW, which corresponds to technologies that use fossil fuel like natural gas, fuel oil, coal, and diesel (72.5%). Only, 26.7% corresponds to renewable energy such as hydropower. However, the National Energy Strategy “ENE 2013-2027” specified that Mexico must reduce its GHG emissions by 30% in 2020 and 50% in 2050. Indeed, Mexico must substitute 35% of its energy demand with renewable energies until 2024. These legally-binding goals are supported since2008 and 2012 through theLaw on renewable energy development and its energy transition funding (LAERFTE)and the General Law on Climate Change (LGCC), respectively (SENER, 2013). The LAERFTE was amended in 2013. In Mexico, the National Water Commission (CONAGUA) is the responsible for the wastewater management (WWM) in Mexico, which is centralized. There are three wastewater (WW) standards for industrial and municipal WW. Only one of it appoints heavy metals discharge limits. There are no specific local discharge limits. The WWM in Mexico is administrated by CONAGUA, while the regulations are provided by the Ministry of Environment (SEMARNAT) (CONAGUA, 2013; SEMARNAT, 2013).

SCOPE OF THE STUDY

The aim of this study is to select a holistic sludge management concept (SMC) which enhances the biogas production, reduces the amount of sludge to be disposed, and opens a new market for green energy production in municipal WWTPs, by performing an Integrative Life Cycle Assessment (ILCA). This SMC should include the so-called energy neutrality in WWTPs and should be replicable along the country. The ILCA will determine in which phase of SMC, a specific process causes the greatest harm to the environment in order to avoid or prevent it.

METHODOLOGY

Five scenarios of sewage sludge management in Mexico were compared using the ILCA methodology, which is in accordance with the ISO 14040/14044. The idea behind this is to present different holistic and suitable options for producing sludge class A and to accomplish the Mexican standards related to air, wastewater, and waste. The selection of the scenarios was based on conventional practices in this country and selected technologies which are available and probably suitable for Mexico. The life cycle inventory includes estimations on energy use, raw material, emission to air and water, and waste generation. The inventory includes data gathered from the case study itself, literature, and databases. The ecoinvent database (V2, 2010) was used to estimate the environmental impacts by categories, such as Global Warming (GWP). The data concerning electrical and energy mix was collected from the SENER, literature review, and information provided by a Mexican company (IEASA, 2012). The mass and energy balances were calculated using several technical sources and modelled with a specific excel spreadsheet. Technical data was taken from Tchobanoglous, G. (2003). The information related to typical operation conditions of WWTP and discharge limits was gathered from literature review and the National Water Commission (CONAGUA). The GaBi Software (version 6), developed by PE International, was used to model the scenarios and to evaluate their environmental impacts while using economic and environmental indicators. GaBi is a modelling, reporting & diagnostic software tool for LCA practitioners that drive product sustainability performance during design and planning. (PE, 2013).

LIFE CYCLE ASSESSMENT

Objective

Two objectives have been defined. The first objective was to evaluate different sewage sludge handling scenarios according to their environmental impacts. The second objective was to suggest a holistic sludge management concept, which potentially enhancing green energy production, in order to reach the so called energy neutrality at municipal WWTPs.

Functional Unit

A function unit (FU) is a comparison unit used in ILCA; expressed in terms of the system output. Since this study focuses specifically on sewage sludge management, the FU for this study has been described as one ton of dry sludge (DS) from the thickened sewage sludge process unit.

Scenarios

Figure 1 presents the five selected scenarios; each scenario considers a mix of primary and secondary sludge, which comprises the sewage sludge produced in a UASB reactor and a conventionalhigh rate aerobic reactor, without nutrient removal. The scenario one (S1) refers to the actual situation in Mexico, where biogas flare systems are installed in landfills and in anaerobic digesters. For scenario 5 (S5), composting refers to piles of sludge where sludge is conditioned for further use as soil amendment.After the approval and amendment of LAERFTE and LGCC in 2013, installation of co-generation equipments for energy production in-situWWTP has been facilitated; integration of electricity into the national grid has been approved, which will contribute to the national goal on renewable energy. The five scenarios show feasible options for final use or disposal of sludge, as well as the potential to produce green energy as methane gas in WWTPs.

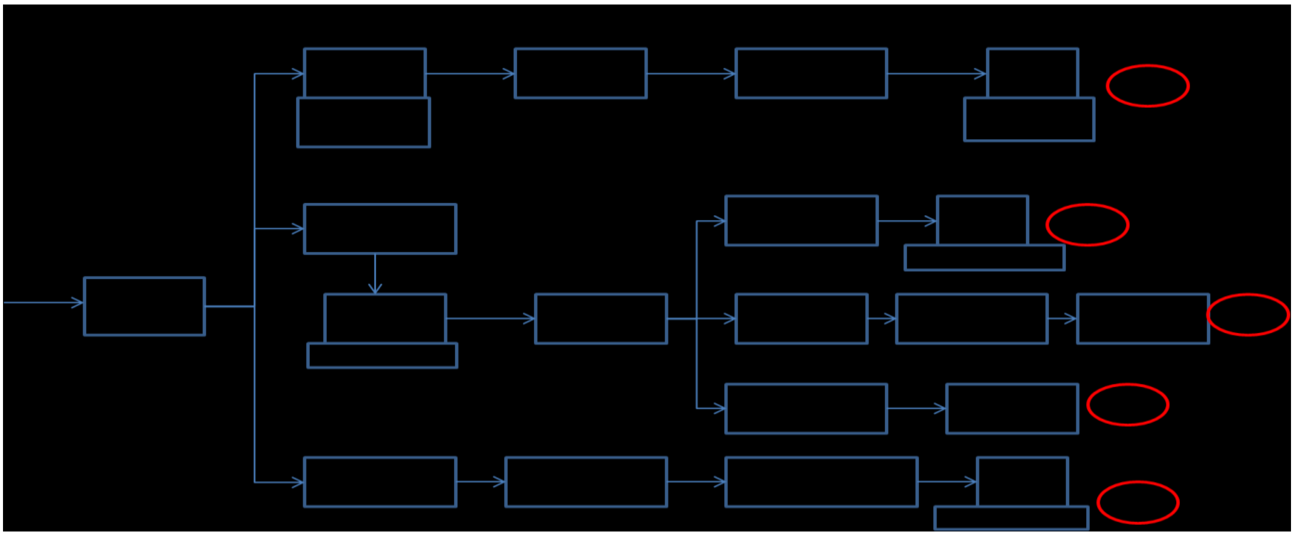

Figure 1. Flow chart of the different scenarios of sludge management for Mexican WWTPs.

Boundaries

The starting point of this study is the sludge thickener; no other process in the WWTP is considered. The boundaries for each scenario consider several points. The next lines describe some of them: (1) an average transportation distance of 25 km by trucks to either farms or landfills, (2) transportation and machinery work process, (3) direct emissions released to the environment during the train of treatment; including composting, incineration, anaerobic digestion and landfill, (4) avoided products resulting from the substitution of chemical fertilizers production by biosolids, (5) avoided energy production resulting from the substitution of conventional energy (fossil bases) by green energy (biogas), (6) avoided emission and environmental effects as result of open burning of agricultural residues, which could be used as bulking agent during the composting process of biosolids and (7) national energy mix. The latter includes the extraction of fossil fuels, resources, transportation, and electricity production. Further, the five scenarios comprised mechanical dewatering or/and sludge pre-treatment, anaerobic digestion (AD) and post treatment (landfill, incineration or composting). In addition, the following impacts, arising from these sections were not taken into consideration: (1) construction and operation of any kind of facility for sludge post-treatment and (2) construction and operation of the WWTP.

Description of the case study: Huejotzingo, Puebla, Mexico. Mexico has two WWTP operation conditions based on the climate season: humid season and dry season. In the State of Puebla the humid season is from June to October and the dry season is from November to May with an average precipitation of 1270 mm per year (INEGI, 2011). For calculating the design of the Huejotzingo WWTP and the FU the dry season was taken into consideration. Therefore, the WW flow is calculated as 5184 m^3/day. The WW flow is equivalent to 43,200 inhabitants if the average drinking water consumption is calculated as 120 l per capita per day (IEASA, 2012). In addition, the wastewater (WW) is a mixture of industrial and municipal flows.

The Huejotzingo WWTP is located in a Home Unit, a typical household arrangement in Mexico, and occupies an area of 132 ha. It should be noted that before the reinstatement, the Hujotzingo WWTP comprised of two trickling filters as main WW treatment, and three clarifiers and sludge beds as sludge post-treatment. There is no available information concerning the design parameters, operation conditions or energy consumption before the reinstatement.

After the reinstatement, the train of treatment comprises of conventional primary, secondary, and tertiary treatment. The latter includes disinfection with chlorine; common practice in Mexico (IEASA,2012). The secondary treatment includes a UASB reactor and high rate aerobic activated sludge. The UASB reactor was designed to treat 5184 m^3/d of wastewater with an organic load as 6221 kg/d. The following characteristics in the wastewater (WW) influent were reported (IEASA, 2012): BOD5: 523.3 mg/l; COD: 1085.4 mg/l; N total: 43.5 mg/L; P total: 13.03 mg/L. The sludge volume from the UASB reactor has been calculated as 726 kg per day, which after a thickening process could be reduced to 155.5 m^3 per day. The high rate aerobic reactor includes fine bubble diffusers. This unit will treat the outflow from the UASB with an expected organic load around 3110 kg of COD per day.

The selected sludge pre-treatment technology for scenarios 2, 3 and 5 is the CAMBI-THP. This process hydrolyses cell structure/organic materials into an easily digestible feed for anaerobicdigestion. In this way the sludge biodegradability increases and therefore yields more biogas. An energy and mass balance was performed for these 3 scenarios showing that after the hydrolysis of aerobic sludge from the high rate aerobic reactor the net sludge production is 726 kg per day, while for the UASB, the hydrolysed net sludge production has been calculated as 1443 kg per day. The carbon removal efficiency at the UASB has been calculated as 57%. It should be noted that this calculation is based on the assumption that the efficiency for this UASB is 43% (IEASA, 2012) and that only 72% of the COD is biodegradable in this type of wastewater mix.

RESULTS AND DISCUSSION

Five scenarios of sludge management in Mexico have been compared by applying ILCA methodology. For the five scenarios, emissions to air and to water, energy use, use of raw materials and waste generation were compared.The final results will be presented at the conference and in the final paper. Preliminary results indicate that the most important environmental impact is climate change, evaluated as Global Warming Potential (GWP). As part of preliminary result, scenario 5 (S5) shows a distinctive enhancement in some impact categories; especially the lowest GHG emissions. Based on the environmental impacts, we can foresee that the ranking of scenarios would be as follow: S5 → S3→S2→ S1→S4, where S5 indicates the most suitable option. However, we can foresee the use of incineration in the scenario 3 (S3) might required further research and benchmark on cutting age technology and air quality control regulations in Mexico.

The energy and mass balance shows that scenario 5 (S5) produces more electricity than is needed for all processes in the WWTP. The excess electricity can be integrated into the public electrical grid, since the LAERFTE has been approved. Indeed, the positive energy balance for S5 suggests that the application of sludge pre-treatment prior to a conventional anaerobic digestion could be feasible in Mexico. Some further discussion on investment and operation cost is needed, before the full application of this technology. As a recommendation for CONAGUA, an update on WW standards is needed. While the SENER, should define the mechanism for increasing and promote the investment on green energy in Mexico.

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(S1) Biogas Production from Anaerobic Digestion of DAF Sludge from Meat Industry

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Abstract

The high costs of waste disposal and the introduction of carbon tax in Victoria, triggered meat industries to seek alternative treatment methods for the wastes generated onsite. This study investigated the potential of using dissolved air flotation sludge (DAF-sludge) as a resource for energy through biogas production, hence alleviating the need for waste disposal. Anaerobic digestion of raw, diluted and polymer free DAF-sludge was evaluated at different organic loading rates (OLRs) and hydraulic retention times (HRTs) using mesophilic AD and temperature-phase AD (TPAD). The results showed the reactors fed with DAF sludge were overloaded and their biogas production was inhibited due to high concentrations of VAs and ammonia. For diluted DAF-sludge, TPAD showed 45% higher biogas yield compared to mesophilic AD at HRT of 23 days. The addition of polymers to the DAF-process had negative effect on biogas yield where 10% less biogass was produced from the polymer-free DAF-sludge and higher VS and COD reductions were observed.

Keywords

Meat wastes; DAF-sludge; two phase anaerobic digestion (TPAD); headings; layout; title page

INTRODUCTION

The high costs of waste disposal, energy and the introduction of carbon tax in Victoria, triggered meat industries to seek alternative sludge treatment methods for the wastesgenerated onsite.Woon& Othman (2011, 2012) determined the biochemical methane potential (BMP) for meat processing DAF-sludgeand concluded that ithas a good potential as a source for bioenergy. Girault et al.(2012) reported that results from BMP batch tests can be used to predict biogas yield under continuous conditions, as long as no inhibition occur in the reactors.The aim of this study was to assess the feasibility of biogas production from DAF-sludge under continuous conditions.

Temperature phase anaerobic digestion (TPAD) is a two phase digestion process which is carried out using two reactors in series. The first reactor is operated at thermophilic conditions (e.g. 55° C) and short hydraulic retention times (HRTs), e.g. 2-6 days, whereas, the second reactor is operated at mesophilic conditions (e.g. 35°C) and longer HRTs, e.g. 10-15 days. Compared with mesophilic ananerobic digestion (AD), the first reactor operates atthe conditions that promote enhanced hydrolysis and degradation of substrates rich in grease,fats and complex organics.Many studies reported that TPAD results inhigher VSand pathogens reduction and was associated with increased biogas production (Riau 2010;Ge et al. 2011;Woon 2012). The use of polymers to enhance WAS dewatering and thickening is very common but some polymers have shown negative effects on the AD of the thickened WAS (Rivard1992, Uyanik2002). Hence, associated objective for this study was to assess the effect of the polymer used to enhance the performance of the DAF unit on biogas yield from the DAF-sludge.

MATERIAL AND METHODS

Materials

The wastes used in this study were collected from a rendering plant located west Melbourne. The plant utilises dissolved air floatation (DAF) to treat the wastewater, where the supernatant is discharged into the sewer and the solids (DAF-sludge) are thickened then transported to landfill. The

DAF-sludge samples collected over the duration of experimental program had varied strength (egVS and COD). Tap water was used to prepare diluted DAF-sludge of lower VS and COD concentrations. Typically, a polymer is added to the wastewater in the DAF unit to enhance solids removal. Therefore, to assess effect of the polymer on the DAF-sludge samples of wastewater before being mixed with polymer were collected and thickened in the lab to prepare polymer-free DAF-sludge, then tap water was used to control the VS concentration. The seed (inoculum) was collected from mesophilic AD reactors at a municipal wastewater treatment plant in Melbourne

Methodology

DAF sludge samples were collected from a rendering plant in west Melbourne every 2-3 weeks. The DAF sludge samples collected over the duration of experimental program had varied VS concentrations, which was taken into account when calculating the yield. The raw DAF sludge samples were diluted with tap water to prepare DAF-sludge of lower strength to allow for lower for evaluation of performance at lower OLR. Therefore, the reactors that received diluted DAF-sludge received consistent OLR throughout the duration of the experiment unlike the reactors fed with raw DAF sludge. Samples of wastewater before the DAF unit (where a polymer is applied to enhance solids removal) were collected and thickened in the lab to prepare polymer-free DAF sludge then tap water was used to control the VS concentration. The seed (inoculum) was collected from mesophilic AD reactors at a municipal wastewater treatment plant in Melbourne.

The mesophilic AD reactors were operated at 35±2°C and HRT of 30 days (labelled DM30). The TPAD of DAF sludge was evaluated at total HRT of 23 and 28 days. The first phase reactors of the TPAD were operated at 35±2°C and HRT of 8 days (labelled DT8). The effluent from those reactors were fed into the second phase reactors, operated at 55±2°C, for another 15 or 20 days, which were labelled DTP15 and DTP20, respectively. All reactors were placed in shakers at 100 rpm. A summary of the experiments carried out is given in Table 1.

Analytical

The DAF sludge samples were characterised as soon as received then stored at 4°C prior to use as a feedstock. The total solids (TS) and total volatile solids (TVS) were measured according to the Standard Method 2540G (APHA 2005). The COD, TN, NH_3-N and VAs were measured using HACH spectrophotometer (DR5000)according to designated HACH methods..The biogas volume was measured daily through a water displacement unit at room temperature and 1 atm. Methane content was determined according to the method used by Demirer(2008).

RESULTS AND DISCUSSION

Biogas production from DAF-sludge

Daily biogas production from raw DAF-sludge both using mesophilic AD and TPAD showed strong correlation with the substrate strength, e.g. substrate VS and COD. The high production observed on day 60 to 80 was a response to the 20-30% drop in the raw DAF-sludge VS. Although all reactors showed stabilised performance during the period from day 100 to 130, daily biogas production from TPAD was more consistent than mesophilic AD rectors. This paper discusses biogas production during the stabilised period whereas the factors affecting biogas production for the two processes, mesophilic AD and TPAD will be reported in another paper. Mesophilic AD at HRT of 30 days produced on average 45 mL/gVS.day which is 100% and 33% higher than the production using TPAD at HRT of 23 and 28 days, respectively. The mesophilic AD reactors (HRT 30 days) were operated at an OLR of 2.66 kg/ m^3.day which is 7% less than the OLR received by the TPAD operated at HRT of 28 days, hence the high production using mesophilic AD compared to AD is not due to the OLR, rather it is due to the TPAD process conditions. The second phase reactors received substrates that were anaerobically degraded at 55 °C, i.e. the substrates were rich in soluble COD, VAs and NH_4. This suggests that the poor biogas production from DAF-sludge using the TPAD process was due to inhibition by the high levels of VAs and/or NH_4. Overall, the results obtained suggest that TPADtreating meat processing wastes are more susceptible to inhibition than mesophilic AD, under the conditions tested.

Table 1.Summary of the mesophilic and TPAD experimentscarried out

	Reactor Label	Temperature	HRT (days)	Average Loading Rate ($kgVS/m^3$.day)
Raw	DM30	Conventional AD	30	2.66
DAF	DT8	1st phase/ TPAD	8	3.47
sludge	DTP15	2nd phase/ TPAD	15	
	DT8	1st phase/ TPAD	8	2.85
	DTP20	2nd phase/ TPAD	20	
Diluted	HM23	Conventional AD	23	0.77
DAF	HM30	Conventional AD	30	0.59
sludge	HT4	1st phase/ TPAD	4	0.77
	HTP10	2nd phase/ TPAD	10	
	HT6	1st phase/ TPAD	6	0.59
	HTP17	2nd phase/ TPAD	17	
Polymer-	NM23	Conventional AD	23	0.62
free	NT4	1st phase/ TPAD	4	1.01
DAF	NTP10	2nd phase/ TPAD	10	
sludge	NT6	1st phase/ TPAD	6	0.62
	NTP17	2nd phase/ TPAD	17	

Biogas production from DAF-sludge of low TS

All AD reactors receiving the DAF-sludge of low TSshowedreasonably stabilised performance after 35 days, (i.e. after 2 cycles) but due the variable concentrations of the raw DAF-sludge biogas production fluctuated and stabilised only when DAF-sludge TSwas adjusted to maintain a constant level before being fed into the reactors. Eventually, stabilised performance was achieved after 80 days. The mesophlic AD reactors at HRTs of 23 (H23) and 30 days(H23 and H30, respectively), i.eOLR 0.65 and 0.5 kg/m^3.day, respectively, produced 64 and 87 mL/gVS.day, respectively (Figure 2). The mesophilic reactors at HRT 30 received one fifth the OLR applied onto the reactors receiving raw DAF-sludge at the same HRT, yet biogas production was about double that.The biogas from DAF-sludge of low TS using TPADat HRT of 23 days was 45% higher than production from mesophilic AD. The concentration of ammonia in these reactors was well below the inhibiting limits of 1,400 $mgNH_3/L$, hence the high yield obtained using TPAD is due to enhanced hydrolysis using the first phase AD at 55°C.

Polymer-free DAF-sludge

The daily biogas yield from polymer-free DAF showed similar trend to mesophilic AD of DAF sludge of low TS (HM23 and HM30). The biogas yield NM23 and NT6+NT17 reached stabilisedperformance around day 70. Biogas yield from the polymer-free DAF-sludge (OLR of 0.62 $kgVS/m^3$.day) was 10% higher compared to diluted DAF-sludge (of OLR of 0.77 $kgVS/m^3$.day) at HRT of 23 days. TPAD of the polymer at HRT of 14 and 23 showed same yield indicating that other factors played a major effect on performance of the reactors. The higher yield obtained for Diluted DAF-sludge (HT6+HTP17) compared to polymer-free DAF-sludge (Nt6+NTP17) wasduer to the use of water to reach to the desired TS for the former whereas supernatant from the AD reactor was used to dilute the latter.

The supernatant from reactors receiving polymer-free reactors was of better quality, ie lower strength.

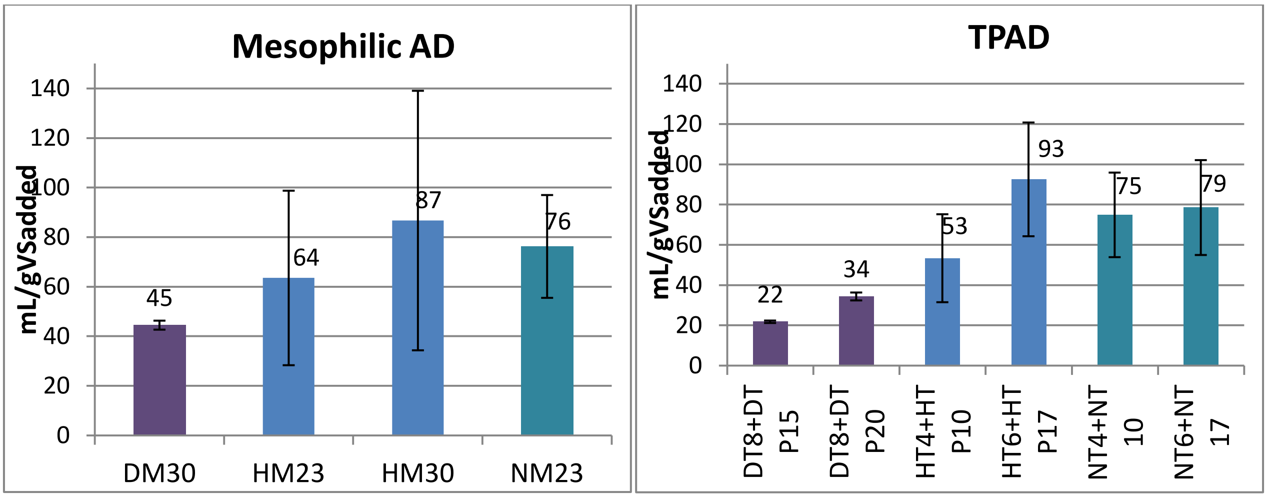

Figure 1. Biogas yield from DAF-sludge using mesophilic anaerobic digestion and two phase ananaerbic digestion

CONCLUSION

Meat processing DAF sludge has good potential as a substrate for biogas production. Mesophilic complete mix AD is not suitable for raw DAF-sludge being rich in VAs and nitrogenous matter. Biogas yield from meat processing DAF-sludge of low TS (ie diluted DAF-sludge) was doubled using TPAD compared to mesophilic AD.The polymer that was is used to enhance DAF performance had negative effect on biogas yield as well as VS and COD destruction.

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(S2) Examination on Alum Sludge for Rapid Phosphorus Adsorption from Municipal Wastewater Effluent

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Abstract

This study examined alum sludge as possible adsorbents for rapidly removing phosphorus from municipal wastewater secondary effluent. In a batch experiment, alum sludge required at least one week to reach equilibrium, and showed the maximum phosphate adsorption of 0.943 mg P/g DW and the pseudo-second-order rate constant of 1.27 g DW/mg P-d. A continuous filter column experiment indicated that the phosphate adsorption by alum sludge was kinetically limited at the filtration velocity of 108 m/d, while its adsorption capacity was fully used at the filtration velocity of 11.6 m/d. Considering the fact that most of phosphorus adsorbed to alum sludge can be recovered, the alum sludge filter column at moderate filtration velocities could be an alternative for the advanced phosphorus removal/recovery from wastewater effluent.

Keywords

Alum sludge; municipal wastewater effluent; phosphorus removal/recovery; rapid adsorption

INTRODUCTION

Since phosphorus can cause eutrophication in receiving water bodies and may be depleted as a resource in the near future, it is a general consensus that phosphorus should be removed and recovered from wastewater and waste, and more cost-effective methods should be developed. In recent years, the group of Zhao at University College Dublin has reported successful reuse of the alum sludge, usually as filter beds in constructed wetlands. The current authors also applied alum sludge beds for the advanced treatment of municipal wastewater and direct treatment of lake water at the filtration velocity of 0.1 – 0.9 m/d, and were able to produce superior effluents with total phosphorus below 0.03 mg/L and to recover 74 – 80% of phosphorus adsorbed to alum sludge by alkaline extraction (Takashima et al., 2013; Nagamune et al., 2013). In this study, alum sludge was examined as low-cost adsorbents for the advanced phosphorus removal/recovery from municipal wastewater secondary effluent. Particularly, this study focused on to operate the alum sludge filter column at higher filtration velocities than before, and to evaluate its performance.

METHODS

Alum sludge and municipal wastewater secondary effluent were collected from a water treatment plant (polyaluminum chloride, PAC, is used as the coagulant) and wastewater treatment plant, respectively, both located in Fukui City, Japan. As the phosphate phosphorus (PO_4-P) concentration was quite low in the wastewater effluent, KH_2PO_4 was added to raise its concentration to approximately 2 mg P/L. A batch experiment was performed to assess the adsorption rate and capacity of alum sludge for phosphate. 1 L of 1 mg P/L phosphate solution and about 1 g wet of alum sludge was added in a beaker, and mixed by a jar tester at a speed of 50 rpm, room temperature of 21 – 24 ^{o}C, and pH of 7.3 – 7.5. A continuous filter column experiment was conducted with the wastewater effluent as the influent. As schematically drawn in Figure 1, two acrylic-resin columns (the diameter of 2.4 cm and height of 50 cm) contained 12 g wet of acetylcellulose sponge media for suspended solids (SS) removal and 100 g wet of alum sludge (adjusted to 0.3 – 2.0 mm) for phosphate removal, respectively. Using a peristaltic pump, the flow rate to the columns was controlled at the filtration velocity of approximately 10 – 100 m/d. The influent and effluent were periodically analysed for phosphate and others.

RESULTS AND DISCUSSION

Batch experiment

Figure 2 shows the time course of PO_4-P concentration in the batch study, suggesting that at least one week was required to reach equilibrium. The batch data were analyzed with the pseudo-second-order equation, due to the highest correlation among major kinetic equations (R^2= 0.989): the amount of PO_4-P adsorbed by alum sludge at equilibrium of 0.943 mg P/g DW and the pseudo-second-order rate constant of 1.27 g DW/mg P-d. These results indicate that alum sludge is inferior in the adsorption capacity as well as in the adsorption rate to the reported synthesized adsorbents (Shimizu, 2011; Tsuji et al., 2012).

Continuous experiment

At the filtration velocity of 108 m/d (Figure 3(a)), the effluent PO_4-P concentration became close to that of the influent within only 4 hours, indicating only 18% exhaustion. This strongly suggests that the alum sludge adsorption was limited kinetically at the rapid filtration velocity employed. On the other hand, at the filtration velocity of 11.6 m/d (Figure 3(b)), the stable removal of phosphate lasted for about 10 days. This experiment was terminated at the effluent PO_4-P concentration of about 0.3 mg P/L, due to severe clogging of the filter column, although the effluent SS concentration from the first column was less than 1 mg/L. If the breakthrough PO_4-P of 0.2 mg P/L and the maximum adsorption capacity from the batch study are assumed, the breakthrough time is calculated to be 8.7 days, which is similar to that obtained in Figure 3(b). Therefore, the adsorption capacity of alum sludge is considered to be fully used, when operated at the moderate filtration velocity of 11.6 m/d.

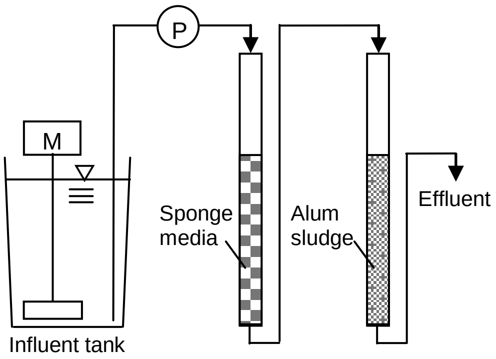

Figure 1. Experimental apparatus.

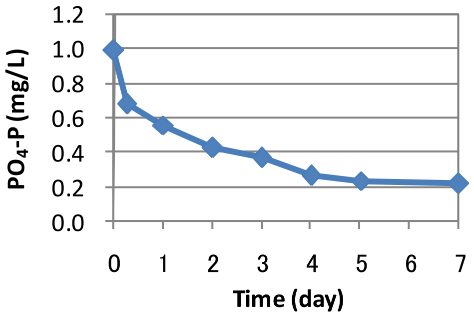

Figure 2. Time course of PO_4-P concentration in the batch study.

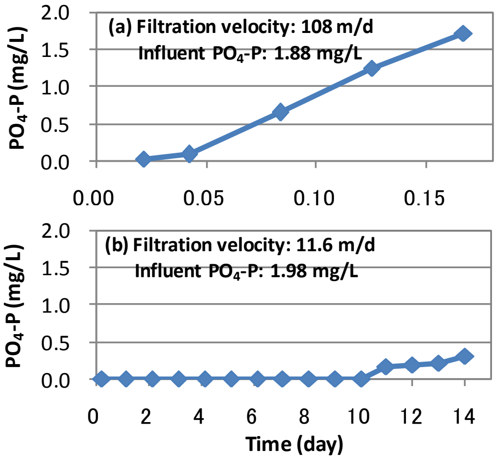

Figure 3. Time course of PO_4-P concentration in the continuous study.

CONCLUSIONS

Alum sludge showed a smaller adsorption capacity and rate than the synthesized adsorbents, but it has such advantages as the efficient recoverability of phosphorus adsorbed and beneficial reuse of the waste. Therefore, the alum sludge filter column can be an advanced phosphorus removal/recovery procedure, as far as moderate filtration velocities are employed.

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(S3) A New Approach for Sludge Disintegration&Minimization:Biomass Distortion using Nanoparticle Coated Surfaces

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Abstract

Abatement of the amount of mechanically dewatered sludge (MDS) using thin film (TF) method was investigated scientifically. TF coated glassslides(TFCGS) were prepared by sol-gel based dip coating method. MDS samples wereplaced between two TFCGSand irradiated by four different UV sources emitting around 240 nm, 310 nm, 380 nm and 450 nm individually. Obtained TF(s) were annealed at 550°C for 1h and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The effectiveness of the applied method was assessed observing the changes in physicochemical structure of sludge. In addition to the direct mass distortion (MD), variations in parameters including, lost on ignition (LOI), drying rate (SDR), and sludge bound water content sludge (BWC) were also critically investigated through the experimental period. Economics of the method were also discussed considering the energy demands of current dewatering/drying equipment. After 3 hours of irradiation period, MD and LOI (in volatile suspended solids-VSS) levels were 50%±5 (as weight) and 48.6%±3 respectively. Average BWC(s) of raw and photo-catalytically treated MDS samples were %52±1 and %30.6±1 respectively. Irradiation energies used through the experiments for photocatalysis and sludge drying were also measured during the experiments and average consumptionswere 1,142±10 Joule; 861 Joule $g^{-1}H_2O_{evaporated}$. Following the advanced oxidation period, sludge was irradiated at 450 nm and for 2 hours and the final moisture content in sludge was reduced from 60±1% to 10±6% depending on theapplied wavelengths.

Keywords

Sludge minimization, disintegration, TiO_2 thin film, nano-technology, dewatering, drying

1. INTRODUCTION

Increasing anthropogenic activitiesworldwide have resulted in huge amounts of sludge generation from wastewater treatment plants in recent decades. Sustainable management of this huge amounts of biomass isacriticalenvironmental concern.In addition, more and more strict regulations have been published on sludge disposal increasing the investment and operational costs. Furthermore removalof regulated persistent organic pollutantsfrom sludge matrix have become another concern for treatment plant operators. [Bennamoun et al., 2013; Abe et al., 2013; Tunçal et al., 2013].Improvement in reducing the volume of sludgeis beneficial from both economicand environmental aspects. Difficulties in dewatering/drying of sludge creates economic and environmental problems for wastewater treatment plants. Several methods have been proposed to overcome this problem. The advantages and disadvantages of different methods are described and the dominance of one over the others is discussed mostly with respect to energy requirement and environmental impacts [Lee et al., 2013; Mowla et al., 2013].

Pollution control using photocatalysis has gained significant attention over the past three decades (Hoffmann et al., 1995; Kolecka et al., 2013). According to the well-known theory of photocatalytic oxidation, photo-catalyser (TiO_2) absorbs a photon of light that has more energy than its band gap energy (≈3.2 eV), and then an electron (e^-) is excited from the valence band to the conduction band to form an electron–hole pair (e^-:h^+). Eventually, the charge carriers react with water and dissolved oxygen and strong oxidizing compoundslike hydroxyl radical ($OH^{\bullet}$) which have the ability to oxidise organic or inorganic pollutants are generated in situ(Öztürk et al., 2009; Parshetti&Doong, 2011).

In this study, mechanically dewatered sludge (MDS) was treated photo-catalytically using pure TiO_2 thin films (TFs) grown on ordinary glassslides (TFCGS). TF(s) were prepared using sol–gel dip coating technique. The resulting films were annealed at 550°C for 1h and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). Evaluation of the applied method was assessed observing the changes in physicochemical structure of sludge. In addition to the direct mass distortion (MD), variations in parameters including, lost on ignition (LOI), drying rate (SDR), and bound water content (BWC) were also critically investigated through the treatment method. Economics of the method were also discussed considering the energy demands of current dewatering/drying equipment.

2. Material and methods

2.1 Sol-gel preparation and photo-reactor configuration

TiO_2 TF(s) were prepared by the sol-gel dip-coating technique. The TiO_2 sol was prepared with titanium (IV) n-butoxide (Fluka) as precursor and ethanol as solvent. The ethanol was slowly added to titanium (IV) n-butoxide together with stirring. A secondary solution was prepared mixing glacial acetic acid with deionized water for an hour. This secondary solution was gradually added to titanium n-butoxide solution drop wise. As-prepared wet films were first dried at 300 °C for 10 minutes. Finally, the films were annealed at 550 °C for 1 h. The dimensions of TFCGS were 50x50x3 mm in length, width and thickness respectively. KSV Nima Medium Dip Coater Unit was used for TF fabrication. Luzchem ICH 2 photoreactor was used in the photocatalytic experiments. Power intensities were measured with a power meter supplied fromLuzchem.

2.2 Sample preparation and chemical analysis procedures

In order to provide homogeneity, samplings from different points of MDS are mixed mechanically in a teflon container before placing the sludge between two sealed GS(s). Coated surfaces are in contact with sludge and illuminated sides does not contain TF. As can be seen in Fig. 1 sealed GS(s) with MDS were placed into the photoreactor vertically and irradiatedwith 16x8 W, UV-A; UV-B, UV-C and UV-vis lamps individually.

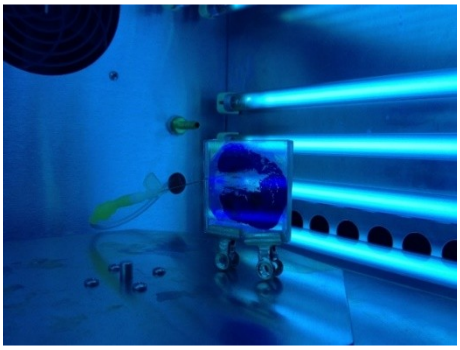

Figure 1a. Photoreactor configuration used in experiments

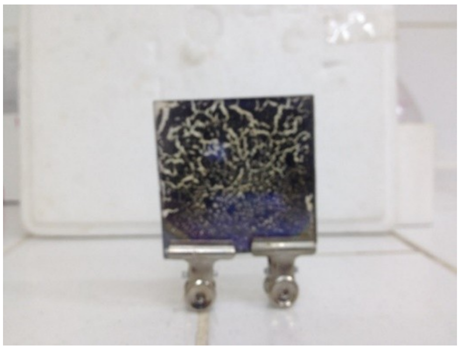

Figure 1b. Appearance of sludge after the treatment

Sludge moisture content and water fractions including free and bound water content (BWC) were determined using drying tests conducted with a Presica XM 60 Moisture Analyzer (Mowla et al., 2013). Total organic carbon (TOC), total nitrogen (TKN), LOI and DS andVSS content of sludge were determined according to the standard methods (APHA, 1998).

Appearance and structure of TF surfaces were studied by SEM that was carried out using JEOL JSM 6060. Before SEM analysis samples were coated with gold to increase the conductivity.

Electron micrographs from the surface were taken utilizing low voltage (5 kV) charge balance. The surface morphology of the TFs was studied using a Nanosurf Easy Scan Atomic Force Microscope (AFM). Crystallinity, crystallite size and phase relations of the TiO_2 TF(s) were characterized by XRD analysis. Diffraction data was collected with a Rigaku D/MAX-2200/PC diffractometer utilizing Bragg–Brentano geometry and Cu-Kα radiation source with monochromator in front of the X-ray detector. Ultraviolet–visible (UV–vis.) absorbance spectra was obtained using a SHIMADZU UV-1800 instrument. XPS measurements were performed on a Thermo Scientific K-ALPHA operating at 12.0 kV and 3 mA. The system was calibrated at 4f7/2 binding energy. Spot size and pass energy were 400 µm and 30 eV respectively.

3. Results and discussion

3.1. Structural characterization results

The surface morphology and surface texture propertiesof the films were investigated by SEM and AFM analysis. The TiO_2 crystals of TFs exhibit spherical shape having a particle size between 40-50 nm. These observations revealed that the film surface morphologies are very smooth, homogeneous, dense and having no cracks. The grains are also randomly scattered through the surface. Cu Kα X-ray diffraction patterns of pure TiO_2 TFs on GS(s) were also examined carefully. The XRD peak at about 25.28° suggested that the main crystalline structure of TiO_2 films is anatase. (Lim et al., 2009; Yang et al., 2012).XPS analysis was performed to investigate into the surface composition and the existing chemical states of Ti ions in nano-composite catalysts. Fig. 2ashows the typical XPS results of the TFs annealed at 550 °C for 1 h. The X-ray photoelectron spectroscopy survey spectrum indicates that the TF contains predominantly O, Ti and C elements. It is thought to be the residual carbon from the organic precursor solution and the adventitious carbon from the XPS instrument itself are the main reasonsexplaining the presence of C element (Yang et al., 2012).

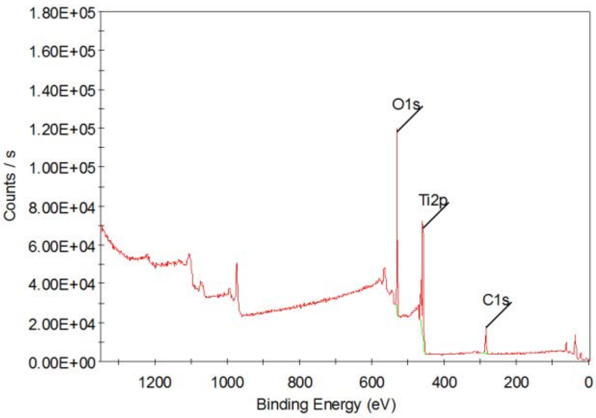

Fig. 2a. XPS spectrum of TiO_2 nano composite

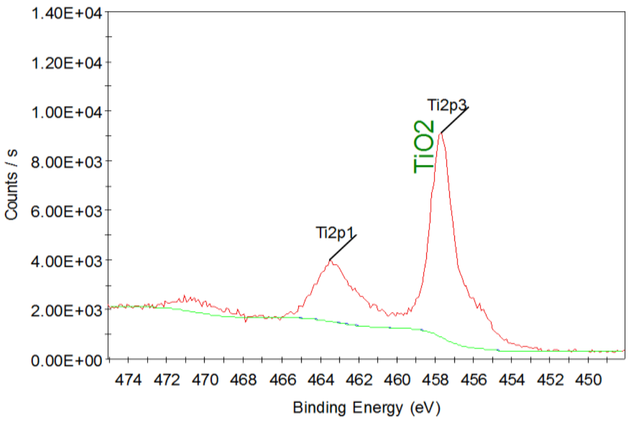

Fig. 2b. Ti2p scan results

As can be seen in Fig. 2b, the band located at the low binding energy (458.6 eV) is broad and asymmetric, demonstrating that there are at least two kinds of Ti chemical states. Besides the peak corresponding to the Ti^{+4}, the other peak at 464.48 eV were identified, suggesting the existence of Ti^{3+} in the composite catalyst and the formation of Ti^{3+} shows the presence of lots of oxygen vacancies during the doping process(Jing et al., 2006; Zhao et al., 2008).

3.2 Sludge characterization and performance of the proposed method

After 3 hours of irradiation period, MD and LOI (volatile suspended solids-VSS) levels were 50%±5 (as weight) and 48.6%±3 respectively. Average BWC(s) of raw and photo-catalytically treated MDS samples were %52±1 and %30±1 respectively. Irradiation energy used through the experiments was 1,142±10 Joule. Following to this advanced oxidation period, TF(s)were irradiated at 450 nm and for 2 hours (hypaethral) and the final moisture content in sludge was reduced from 60±1% to 10±0.6%. As can be seen in Table 1, increasing photon energy provided more efficient sludge treatment degree. However, UVA irradiation resulted with the highest final sludge dryness. Improvement in SDR could be attributed to increasing free water content in sludge matrix. From the legislative perspective, sludge is considered to be hazardous waste material if TOC concentration higher than 60%. Experimental results indicated that the applied method is capable to reduce TOC content of industrial sludge from 76±1% to 50±1% effectively. This low TOC levels also allow land application of sludge if the metallic content of sludge is low. Energy consumption of conventional dewatering/drying systems (belt, drum, flash, disc and paddle dryers) varies from 2.5 to 5.0kj g^{-1} MDS (Bennamoun et al., 2013). As it was indicated earlier, the energy consumptions measured during the experiments for advanced oxidation and drying were 1.1±0.3 and 0.9±0.2kjg^{-1} MDS. Therefore, total energy demand of the system is around 2±0.3kjg^{-1} MDS and this value is lower than the conventional methods.

Table 1. Physicochemical characteristics of raw and treated sludge

Parameter	Raw Sludge	Un-coated Surface*	After UV A Irradiation	After UV B Irradiation	After UV C Irradiation
TKN mg kg^{-1}	420±26	410±28	328±16	286±22	282±28
TOC %	76±1	76±1	52±1	48±1	44±1
LOI %	90±2	90±1	52±1	48±1	46±1
BWC %	52±2	52±2	36±3	28±3	28±1
SDR** g H_2O min^{-1}	0.07±0.01	0.09±0.001	0.05±0.008	0.04±0.008	0.04±0.008
DS*** %	25±1	76±1	86±1	78±1	76±1

Irradiated with UV A; SDR: Sludge drying rate measured after photocatalytic oxidation; ***After 2-hours drying period under irradiation at 450 nm*

CONCLUSIONS

In this study nano-technology based sludge disintegration-minimization alternative was investigated scientifically. Obtained results propose that significant amounts of sludge could be destroyed by the method in relatively short retention times. In addition, while organic content of sludge is decreased, sludge dewatering/drying could also be achieved simultaneously. Since the method is developed for MDS, retrofit costs of existing plants will be reasonable. Economics of the studied method was also evaluated considering the current dewatering/drying techniques and lab-scale test results indicatedcomparable energy consumption values with existing drying/dewatering technologies.

Acknowledgements

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Efficient Technologies – AnAmmOx

(Tuesday, 24 June 2014, Aula T1, Polo Zanotto)

(K2) Pilot Scale evaluation of Anammox based mainstream nitrogen removal from municipal wastewater

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Abstract

Autotrophic nitrogen removal in the main stream appears as a prerequisite for the implementation of energy autarchic wastewater treatment plants. Whilst the application of anammox related technologies in the side-stream is at present state of the art, the feasibility of this energy-efficient process at main-stream conditions is still under investigation. Lower operative temperature and ammonium concentration, together with required high nitrogen removal efficiency, represent the main challenges to face in order to reach this appealing new frontier of the waste water treatment field. In this study we report the evaluation of the process in a plug-flow granular sludge based pilot-scale reactor (4 m^3) continuously fed with the actual effluent of the A-stage of the WWTP of Dokhaven, Rotterdam. The one-stage partial nitritation-anammox system was operated for more than ten months at 19±1 °C. Registered N-removal and ammonium conversion rates were comparable or higher than those of conventional N-removal systems, with 310 and 180 mg-N L^{-1} d^{-1}, respectively. BOD was also oxidized in the system with average removal efficiency of 90%. Heterotrophic biomass was growing preferentially in flocs and was efficiently washed out of the system. Throughout the experimentation the main bottleneck was the nitritation process that resulted in nitrite limiting conditions in the pilot plant. Anammox bacteria were able to grow under main-stream conditions and new granules were formed and efficiently retained in the system.

Keywords: anammox; partial nitritation; actual wastewater; low temperature; A-stage; mainstream; WWTP; autotrophic nitrogen removal

INTRODUCTION

To date, most of the autotrophic nitrogen removal systems (including anaerobic ammonium oxidation (anammox)-related processes) reported in literature were operated at temperatures higher than 25 °C and influent nitrogen concentrations above 0.1 g-N L^{-1} (van Hulle et al., 2010). The application at lower temperatures and lower nitrogen concentrations would allow to extend the application of anammox-related processes to municipal sewage treatment opening new possible scenarios in designing energy producing wastewater treatment plants (Jetten et al., 1997; Siegrist et al., 2008; Kartal et al., 2010). In order to maximize energy recovery from municipal wastewater, removal of the organic carbon as a first step would be most advantageous. The remaining liquid contains ammonium that can be removed in an autotrophic process based on anammox (Jetten et al., 1997; van der Star et al., 2007; Wett, 2007; Joss et al., 2009; Abma et al., 2010; Kartal et al., 2010). This study aimed at demonstrating the feasibility of anammox based autotrophic nitrogen removal from pretreated sewage on pilot-scale. A plug-flow granular sludge based pilot-scale reactor (4 m^3) was continuously fed with the effluent of the A-stage of the WWTP of Dokhaven, Rotterdam (Kampschreur et al., 2008). A granular sludge process with integrated tilted plate settler (TPS) was chosen with the objective to achieve adequate biomass retention at short hydraulic retention time (HRT). A plug flow configuration was chosen to maximize the removal efficiency. The results obtained during 10 months of operation of the pilot plant at 19±1 °C are presented.

The pilot research is continued in a demonstration project. In the final presentation on going results, such as the effect of different temperatures (10-20°C), will be discussed as well.

MATERIALS AND METHODS

Dokhaven-Sluisjesdijk WWTP

The municipal wastewater treatment plant of Dokhaven (Rotterdam, The Netherlands) has a treatment capacity of about 560,000 p.e.. The wastewater applied for conducting this study originates from the main line of the treatment scheme. For a description of the sludge-line as well as the entire WWTP please see van der Star et al., 2007 and Kampschreur et al., 2008. The installation of Dokhaven was built entirely underground in the late 1970s and designed as an A-B system (Kampschreur et al., 2008).

Pilot set-up and operating conditions

Experiments were conducted in a plug flow reactor (working volume of 4 m^3) consisting of four equal compartments. The reactor was equipped with an external TPS for granular biomass retention operating at a surface loading rate of 5-15 m h^{-1}. Oxygen transfer and mixing were provided by fine-bubbles aerators. The dissolved oxygen (DO) concentration was controlled at 0-2 mg-O_2 L^{-1} by a gas recycle system, while maintaining a constant gas velocity and thereby mixing intensity. pH was controlled at 7.0-7.5 by addition of NaOH (0.1M). The influent of the pilot reactor was the effluent of the A-stage after settling. Before dosage to the reactor the influent was buffered in a 2 m^3 tank (HRT of 8±4 h) that was maintained at 19±1°C by a thermostat. The reactor was inoculated with granular biomass from the full-scale 1-stage partial nitritation/ANAMMOX® reactor of Olburgen (The Netherlands, Abma et al., 2010). Bio-augmentation was not performed during the experimental period.

Analytical methods

Analytical measurements for inorganic N-compounds were conducted as described by Lotti et al. (2012), while measurements for COD, BOD and biomass concentration (as g-VSS L^{-1}) according to standard methods (APHA, 1998).

RESULTS AND DISCUSSION

1-stage partial nitritation/anammox process was established in a plug-flow granular pilot-scale reactor (4 m^3) operated from July 2012 to April 2013. During the period of operations described in this study, the process experienced a number of setbacks due to technical issues. Ex-situ batch test results showed that the anammox biomass specific activity was maintained despite these temporary failures/disturbances throughout the experimentation (data not shown). Three periods of operation of 2-3 weeks in which no technical failures/disturbances occurred were analyzed and closely evaluated (Dec. 2012, Feb. and Apr. 2013). The reactor was continuously fed with the undiluted effluent of the A-stage of a municipal wastewater treatment plant, characterized by an average BOD/N ratio of 0.67. Throughout the whole experimental period (including disturbance periods) nitrogen removal rates fluctuated between 30 and 240 mg-N L^{-1} d^{-1} and amounted on average to 59±5 mg-N L^{-1} d^{-1}. The HRT of the system was 1.54-2.0 h while the SRT for granular sludge was estimated as 120±30 d. The biomass concentration in the reactor was 4±0.5 g-VSS L^{-1}, corresponding to an average biomass specific N-removal rate of 15 mg-N g-VSS^{-1} d^{-1}. Nitrite formation was found to be the rate limiting process during the whole experimental period. When nitrite was temporarily added to the influent wastewater (10-44 mg-NO_2-N L^{-1} added), higher N-removal rates up to 550 mg-N L^{-1} d^{-1} were observed. The DO was not changed in this period showing that Anammox bacteria where limited by nitrite and not inhibited by oxygen. Results from ex-situ anoxic batch tests conducted every 1-2 months at 20°C showed that the maximum nitrogen removal capacity was maintained over 300 mg-N L^{-1} d^{-1} throughout the experimentation (data not shown), confirming that anammox biomass was indeed always under substrate (nitrite) limiting conditions. The maximum biomass specific anammox activity (SAA) was regularly measured under anoxic conditions and values of 80±20 mg-N_2-N g-VSS^{-1} d^{-1} were found (data not shown). In a time period of 61 days (July-September 2012) SAA increased from 57 to 90 mg-N_2-N g-VSS^{-1} d^{-1}. Considering that for bacteria cultivated under certain conditions the biomass specific maximum activity is constant and that the biomass composition was rather constant during the same period (evaluated by FISH, data not shown), the observed increase of SAA in time indicated that anammox bacteria grew and were retained in the system . The average influent and effluent composition during periods of stable (undisturbed) operations are shown in Table 1. The average results during the same periods of stable operation are reported in Table 2.

Table 1. Influent and effluent average composition during periods of stable operations.

		NH_4^+ mg-N L^{-1}	NO_2^- mg-N L^{-1}	NO_3^- mg-N L^{-1}	P-tot mg-P L^{-1}	BOD mg L^{-1}	COD mg L^{-1}	TSS mg L^{-1}
Influent	Average	26.8	1.0	1.7	1.3	17.4	62.1	30
	Std.Dev.	5.3	0.7	1.8	0.6	7.3	17.0	10
Effluent	Average	6.8	2.3	9.1	1.2	1.7	26.1	30
	Std.Dev.	5.4	0.4	3.1	0.5	0.8	5.9	30

Table 2. Average reactor performance during periods of stable operation.

	NH_4 Conv. Rate [mg-N L^{-1} d^{-1}]	NH_4 Conv. Efficiency [%]	Tot-N Removal Rate [mg-N L^{-1} d^{-1}]	Tot-N Removal Efficiency [%]
Dec.				
2012				
Feb.				
2013	293	72	154	36
Apr.	319	86	189	47
2013	324	63	191	32

In order to compare the performance of the pilot with that of the B-stage of Dokhaven, in Table 3 are reported the averaged results of the latter obtained during periods when the wastewater temperature were comparable to the operative temperature in the pilot (20.0±1.7, May÷September 2012).

Table 3. Average performance of the B-stage in the period May÷September 2012. In this period temperature was 20.0±1.7 °C .

	NH_4 Conv. Rate [mg-N L^{-1} d^{-1}]	NH_4 Conv. Efficiency [%]	Tot-N Removal Rate [mg-N L^{-1} d^{-1}]	Tot-N Removal Efficiency [%]

May÷Sept. 2012	197.8	89.6	38.1	14.2

The active growth of biomass in the process and the achieved conversion capacity indicate that there is no need for bioaugmentation when developing a main stream anammox process. The volumetric specific ammonium conversion rates reported in this study (Table 2, 3) were in the same order of magnitude as a B-stage system and superior to a conventional activated sludge process (CAS, Metcalf & Eddy, 1991). Furthermore, considering the biomass concentration in our system (~200 mL L^{-1}) and the much higher potential biomass concentration in granular systems (~600 mL L^{-1}, Abma et al., 2010), the reported results appear even more promising for full scale application.

CONCLUSIONS

The reported results show that the proposed reactor configuration with granular sludge had the potential to be successfully applied for the completely autotrophic nitrogen removal from the mainstream of WWTPs. The system was shown to efficiently retain granules. Evidence for anammox growth at main-stream conditions was reported. Throughout the experimentation the main bottleneck was represented by the nitritation process since anammox activity was always present in overcapacity due to the nitrite limiting conditions experienced in the pilot. Observed N-removal and especially ammonium conversion rates were higher than those of conventional N-removal systems. Furthermore, considering the higher biomass concentration obtainable in granular systems, kinetics much higher than conventional systems appeared to be feasible.

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(P7) ELAN®, an anammox based process, to treat industrial effluents from fish canning industry

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Abstract

The autotrophic nitrogen removal by the ELAN® process (partial nitrification and anammox) appears as a good option to remove nitrogen from saline effluents, like those of the seafood industry. A nitrogen loading rate of 0.2 g N/(L·d) was treated with a removal efficiency of 80% when concentrations of 4.3 g NaCl/L were present. The obtained effluent fulfilled the discharge requirements for this industry (outlet total nitrogen concentration has to be lower than 100 mg N/L). However, a punctual salt concentration increase, from 3.8 to 15.9 g NaCl/L, provoked partial inhibition of the ammonia oxidation (40%) and total inhibition of the anammox process. This inhibition was reversible and could be avoided with a progressive adaptation of the biomass to high salts concentrations. The treatment of agro food industrial effluents combining anaerobic digestion for organic matter removal and ELAN® for nitrogen removal would minimize the energy demand of the wastewater treatment.

Keywords: Anammox; granular sludge; industrial; partial nitrification; salinity; seafood.

INTRODUCTION

The treatment of saline wastewaters, characteristic of some types of industries (like seafood processing, fish canning, textile dyeing, oil and gas production and tanneries) by biological processes is sometimes difficult. High salinity conditions result in high osmotic pressures which might cause severe inhibition or death of microorganisms (Jin *et al.*, 2012). In this sense, the use of granular biomass could be adequate, because the granulation process increases the concentration of biomass into the reactor and improves the resistance to toxicity (Moussavi *et al.*, 2010). Furthermore, the granule matrix acts as a mass transfer barrier that produces lower local concentrations of toxics on cells than in the bulk liquid (Adav *et al.*, 2008).

The effect of salts concentration has been studied separately in nitrification (Li *et al.*, 2011) and anammox (Dapena-Mora *et al.*, 2010) systems. The adaptation of both types of microorganisms, ammonia oxidizing bacteria (AOB) and anammox, to high salt concentrations was possible. To assess the treatment of saline wastewaters by a combination of both types of microorganisms in one unit is of interest. This potential application will broaden the field of application of the partial nitrification-anammox based systems for the nitrogen removal in saline industrial wastewaters. In this sense Liu et al. (2008) tested the effect of NaCl addition in a partial nitrification-anammox single system and observed an enhancement on the total nitrogen removal rate from 425 (without salt) to 637 mg N/L·d (10 g NaCl/L). Although they used a synthetic wastewater, the results obtained showed the possible application to industrial saline wastewaters of the partial nitrification-anammox single unit system. The ELAN® process, developed by Aqualia with the know-how of the University of Santiago de Compostela, is a system of this kind performed in a single granular sequencing batch reactor (SBR).

The objective of this work is to test the possible application of the ELAN® process to treat an industrial effluent coming from a fish canning industry. This type of industry is very common in the northwest of Spain (Galicia) and the produced effluents are characterized by high fluctuations on ammonia and salts concentrations.

MATERIALS AND METHODS

A laboratory scale SBR with a useful volume of 1.5 L was operated in cycles of three hours distributed as: 5 min of feeding, 160 min of aeration, 10 min of settling and 5 min of withdrawal. The SBR was fed with the effluent from an anaerobic digester treating a fish canning industrial wastewater (Table 1). The temperature was maintained by a thermostatic bath around 24±1 ºC, which is the expected value for the reject water of a mesophilic anaerobic digester. The hydraulic retention time (HRT) varied from 1.0 to 1.5 days along the operation. The nitrogen loading rate (NLR) applied was around 0.20-0.25 g N/(L·d). The dissolved oxygen concentration was maintained between 2-3 mg O_2/L to achieve an adequate balance between the partial nitrification and the anammox processes. The reactor was inoculated with 7.5 g VSS/L of granular biomass from an ELAN® pilot plant (200 L) treating the supernatant of a sludge anaerobic digester of a municipal WWTP (Vázquez-Padín *et al.*, 2013). This granular biomass had both, the specific ammonia oxidation and anammox activities, of 0.19 g N/(g VSS·d) at 25ºC, while nitrite oxidation activity was not detected.

Table 1. Characteristics of the different batches of industrial wastewater fed to the reactor and operational conditions for the different stages.

Parameter	Stage I	Stage II	Stage III	Stage IV	Stage V
Days of operation	0-30	31-40	41-75	76-130	131-155
pH	7.8±0.1	7.7±0.1	7.8±0.1	7.6±0.1	7.6±0.1
Conductivity (mS)	9.7±0.9	21.2±0.4	9.3±0.2	6.1±0.2	9.8±0.8
NaCl (g/L)	3.8±0.2	15.9±0.8	3.5±0.3	1.9±0.3	4.3±0.4
NH_4^+ (mg N/L)	280±37	269±38	344±28	206±22	211±19
NO_x^- (mg N/L)	1.4±0.5	3.1±0.4	1.5±0.8	1.1±0.8	1.9±0.7
Inorganic carbon (mg C/L)	339±33	360±25	347±31	284±35	340±29
TOC(mg C/L)	51±6	52±5	53±9	47±10	53±11
Na^+ (mg/L)	1575±30	6467±102	1447±128	807±82	1724±194
Cl^- (mg/L)	2182±22	9360±470	2046±80	1029±178	2616±275
PO_4^{-3} (mg/L)	124±16	ND	39±17	96±21	48±12
SO_4^{-2} (mg/L)	77±4	165±18	69±49	77±18	156±46
HRT (days)	1.22±0.24	1.47±0.01	1.32±0.15	1.10±0.02	1.10±0.02
NLR (g N/(L·d))	0.24±0.07	0.19±0.03	0.23±0.06	0.19±0.02	0.20±0.01

RESULTS AND DISCUSSION

Nitrogen removal and salinity

During the first 30 days of operation (Stage I) the fed industrial wastewater had a conductivity of 9.7

mS/cm and a salt concentration around 3.8 g NaCl/L (Table 1). The achieved efficiencies of ammonia oxidation and total nitrogen removal were 100 and 85%, respectively; similar to the values obtained in the pilot plant origin of the inoculum. This pilot plant was fed with the effluent of an anaerobic sludge digester with a salt concentration around 0.5 g NaCl/L, although the ammonia concentration was higher (around 1000 mg NH_4^+-N/L) than in the industrial effluent of this study. This implied that the granular sludge inoculated was already adapted to treat values of conductivity around 8.5 mS/cm, similar to the values used at the beginning of this experiment.

After day 31, the new batch of feeding presented a conductivity of 21.2 mS/cm and a salt concentration of 15.9 g NaCl/L (due to a change from tuna to mussels on the material processed) which caused the failure of the process, with a value of total nitrogen removal of zero. However, even if the ammonia oxidation decreased, it was maintained around 60%, which means that the salt inhibition had a higher effect on anammox bacteria than on AOB. Dapena-Mora et al. (2007), working in batch tests, demonstrated that NaCl did not affect anammox activity at concentrations below 8.78 g/L, and they determined that the IC_{50} was of 13.46 g NaCl/L. The adaptation of anammox bacteria to high salinity is possible, as it was demonstrated by Yang et al. (2011). These authors treated a NLR of 5.2 g N/(L·d) with 30 g NaCl/L in an anammox system fed with synthetic wastewater and they pointed out as crucial the progressive adaptation to the high salinity after observing two episodes of inhibition due to corresponding sharp increases of salinity. However, no adaptation strategy was used in the present research. That is due to the fact that in the seafood industry it is common to change the raw material from one day to another, which implies also sharp changes on the wastewater composition, mainly in the salt concentrations. In this sense, the salt concentration around 3.8 g NaCl/L (stage I) was related to the manufacture of tuna, while values around 15.9 g NaCl/L (stage II) were related to the manufacture of mussels.

On stage III (day 41), the conductivity of the wastewater fed was of 9.3 mS/cm. The nitrogen removal efficiency was restored to values around 80% (Figure 1.a). This means that the inhibition by salinity in that case was reversible. During the rest of the operation, the nitrogen removal efficiency remained around 80%, while the conductivity and the salt concentrations ranged between 6-10 mS/cm and 1.5-4.7 g NaCl/L, respectively.

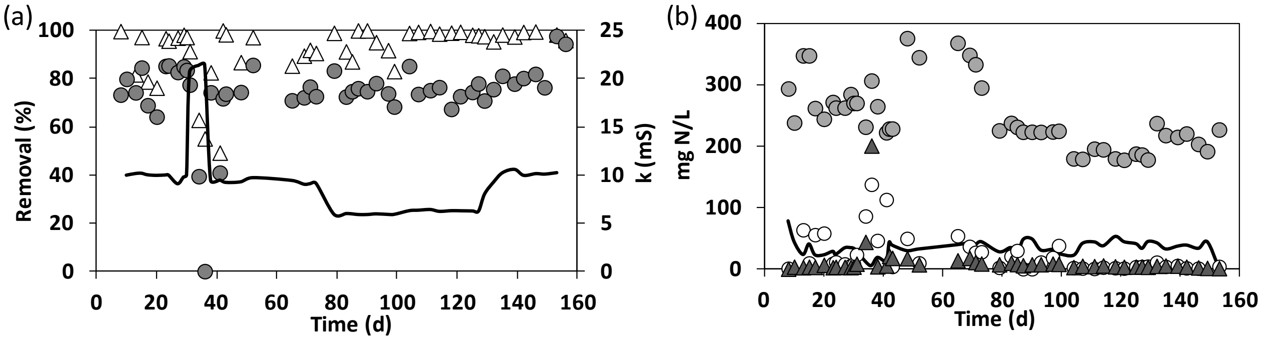

Figure 1. (a) Percentage of NH_4^+oxidation (△) and TN removal (●) and conductivity (□); (b) Profile of nitrogen compounds concentrations: NH_4^+ in the influent (●); NH_4^+ (○), NO_2^- (▲) and NO_3^- (□) in the effluent.

Effluent quality

The ammonia concentration in the influent varied between 180 and 400 mg NH_4^+-N/L according to the batches of wastewater collected in the industry. The values of the total nitrogen concentration in the effluent (ammonia, nitrite and nitrate) achieved in the experiment (Figure 1.b) were in a range below 100 mg N/L, which was the limit value for discharge required by the industry. Only between days 35-40, due to the inhibition of the process by high salt concentrations, this limit was exceeded.

The nitrate and nitrite concentrations in the effluent were stable during the operational time, with average values of 30 mg NO_3^--N/L and 5 mg NO_2^--N/L, respectively. No accumulation of nitrite was observed. Only a punctual value around 200 mg N-NO_2^-/L was measured when the anammox process failed, on days 35-40. Furthermore, the nitrate concentration measured in the effluent coincided with the expected value for the anammox stoichiometry, which indicates a negligible nitrite oxidation activity, since it is reported that the presence of NaCl causes the inhibition of nitrite oxidizing bacteria (Liu *et al.*, 2008).

Granular sludge characteristics

The VSS concentration in the reactor was maintained around 7 g VSS/L. The concentration of solids in the effluent had an average value around 40 mg VSS/L. Values up to 130 mg VSS/L were punctually obtained due to the flotation of some granules caused by the entrapment of the N_2 gas produced in their internal core. The average diameter of granules increased during the experimental time from 2.5 to 3.6 mm, as shown by their size distributions (Figure 2).

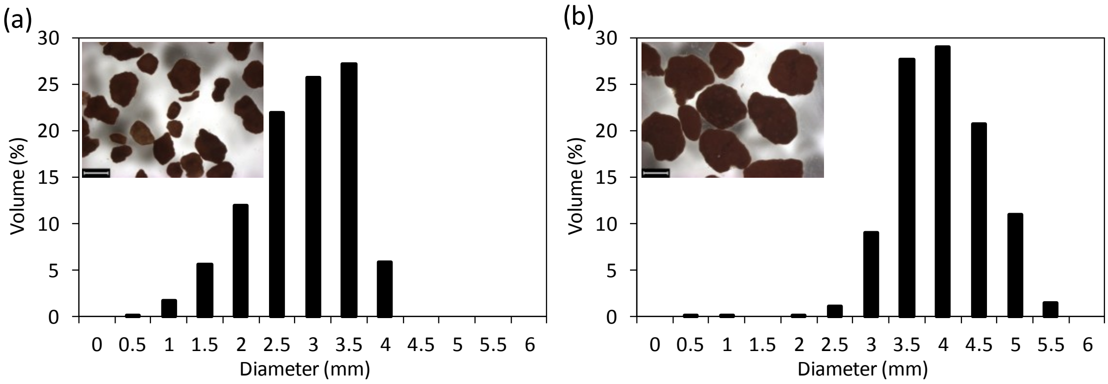

Figure 2. Images and size distributions of granular sludge in percentage of volume respect to the total volume: on day 0 (a) and on day 146 (b). The size bar represents 2 mm.

CONCLUSIONS

Nitrogen removal from effluents produced in the fish caning industry was feasible with the ELAN® process (a partial nitrification-anammox process in single unit). The total nitrogen removal achieved was high (80%), but dependent on the salt concentrations. The complete inhibition of anammox bacteria by salt occurred after the sudden increase of its concentration from 3.8 to 15.9 g NaCl/L. This caused one-day break down of the process, although it was reversible. With long-term operation at high salts concentrations a possible alternative should be the adaptation of anammox bacteria but further studies are required. The fact that the ELAN® reactor reached the performance required opens the possibility to use this process for nitrogen removal as a post treatment of an anaerobic digester which would be used for organic matter valorisation. This combination is the future of the agro food industry in terms of wastewater treatment since it lowers the energy demand and the sludge production compared to the classic nitrification-denitrification pathway.

ACKNOWLEDGEMENTS

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(P8) Treatability of digested piggery/poultry manure by anammox bacteria

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Abstract

The liquid fraction of digested material is rich in ammonium and may require nitrogen removal. The aim of this research was to evaluate the applicability of the anammox process for the biological N removal from a supernatant coming from the anaerobic digestion of a mixture of piggery manure, poultry manure, and of agro-wastes. The supernatant was pre-treated in a partial nitritation pilot-scale reactor located at the farm. A batch procedure for testing the short term effect of high-strength wastewaters on anammox activity is presented. The anammox process was successfully applied for the first time to undiluted digestate, and the average N removal efficiency achieved during 350 days of experimentation in a SBR lab-scale reactor was 91%.

Keywords

Anammox, activity test, digestate, manometry, piggery manure, poultry manure

INTRODUCTION

Anaerobic digestion (AD) can effectively treat livestock wastewater and produce renewable energy as biogas. The liquid fraction of the digested material is rich in ammonium and its disposal on agricultural soil is regulated by the European directive on nitrates (91/676/CEE). Therefore N removal may be required in intensive breeding farms. This aspect has prompted attention toward advanced biological processes such as the nitritation-denitritation process (Scaglione et al. 2013), and the completely autotrophic process (partial nitritation and anammox) that are cost effective thanks to lower aeration and external carbon source requirements (Van Hulle et al. 2010). Most studies regarded digestates from piggery manure (Dosta et al. 2008) or diluted wastewater in lab-scale reactors (Yamamoto et al. 2008). Literature documented the treatment of neither digestates from mixed animal wastes nor undiluted agricultural digestate (Magrì et al., 2013). This work is part of a two-years project (BRAIN) funded by the Italian Ministry for Agriculture, whose aim was to evaluate autotrophic N removal processes applied to digested liquid fraction coming from the anaerobic digestion of a mixture of agro-wastes, mainly piggery and poultry manure. In this paper some lab-scale results are presented, namely: (i) activity batch tests, to assess anammox activity of digestate supernatant after partial nitritation stage and the effect of different salinity concentrations; (ii) report the results of a 350-day operation of an SBR treating digested supernatant.

MATERIALS and METHODS

Characteristics of the supernatant

The supernatant from a full-scale anaerobic digester (solid/liquid separation by centrifugation), located in a piggery farm in Northern Italy, was used. The digester was fed on thickened piggery manure, poultry manure and agro-wastes. The supernatant showed a high variability in its chemical composition during the course of the experimentation (pH =8.0±0.1, Conductivity =14.2 ± 2.1 mS cm^{-1}; NH_4^+-N =1151 ± 251 mg L^{-1}; COD = 2634 ± 1178 mg L^{-1}; TSS = 430 ± 220 mg L^{-1}; Alkalinity = 7128 ± 2932 mgCaCO$_3$ L^{-1}). The supernatant was treated in a partial-nitritation 650-L SBR. The NO_2/NH_4 molar ratio of the effluent from the partial nitritation pilot plant was slightly adjusted to remain within 1.25±0.25, thus suitable for feeding the subsequent anammox reactor.

Soluble COD concentration in partial-nitrified supernatant was 853±257 mg/L while BOD_5 and BOD_{20} were 25±15 mg/L and 49±26 mg/L respectively.

Manometric batch tests

The assessment of the N_2 production rate from the anammox reaction was performed by means of an OxiTop® Control system. This is a manometric device consisting of a pressure transducer and data logger located inside a measuring head that is mounted on a glass bottle of 1140 ml volume, filled with anammox biomass suspension. The bottle has got two lateral openings; one is sealed by a rubber septum and is used for substrate injections, the second one is sealed by a teflon airtight valve for gas discharge. During the course of the batch test, the overpressure due to N_2 production by the anammox reaction is automatically registered by the measuring heads. Manometric determinations of Anammox activity were performed according to the following procedure. Each bottle was filled with 30 ml of granular anammox biomass and 700 ml of either mineral medium or a blend of real-wastewater and mineral medium, depending on the test type. Sodium bicarbonate (1g/L) was added and the headspace was flushed with 95%N_2 and 5% CO_2 to ensure anaerobic conditions and to keep the pH around 7.8. Bottles were thermostated at 35±0.5°C and stirred by a magnetic mixer. Substrates were added by spike injections through the rubber septum. Then, the gas volume of cumulatively evolved N_2 was calculated from overpressure data according to the ideal gas law. At the end of the test, concentrations of ammonium, nitrite and nitrate were measured. For each test, the maximum N_2 production rate, the maximum specific Anammox activity, SAA_{max} (mgN_2/gVSS/h) and the nitrogen mass balance was verified.

Lab-scale anammox reactor

To test the stability of the anammox process, a thermostated (34-36°C) 3-L lab-scale reactor was used. It was equipped with time-controlled feeding/discharging pumps, mechanical mixing, and with a pH control unit. The reactor was operated in a SBR mode with a 8 h cycle (5 h of FILL, 2.5 h of REACT, 0.5 h of SETTLE/DRAW).

RESULTS AND DISCUSSION

Manometric batch tests

A first set of manometric tests were performed to evaluate the effect of exposing granular anammox biomass sample to the effluent of a partial nitritation reactor. However, the high concentration of nitrite in this wastewater (around 500 mgN/L) would have caused anammox inhibition. Therefore, the wastewater was first pretreated by adding activated sludge and a stoichiometric amount of sodium acetate to remove nitrite by heterotrophic denitrification. After 24h of reaction, the supernatant was centrifuged and the clarified fraction used, either as such or after dilution with a mineral medium, for testing its effect on anammox biomass. The ammonium concentration was yet high (around 190 mgN/L) so that only nitrite was spiked to achieve an initial concentration of 50 mgN/L. Soluble COD concentration was 1018 mg/L while BOD_{20} and BOD_5 were 80 and 30 mg/L respectively. The first set of activity tests aimed at evaluating the response of a non-acclimated anammox biomass to the pre-denitrified digestate. To this purpose, a granular biomass sample was used, having a specific activity of 0.11 gN_2/gVSS/d. Results are reported in Figure 1. No inhibition was observed when the wastewater was blended with 50% mineral medium, while activity showed an 85% decrease after 24h exposure to a blend containing 75% wastewater. For the last two samples, anammox activity recovered with time, more significantly for the less concentrated blend. The results confirmed that the inhibition increases with the fraction of wastewater in the blend and that a long term adaption may take place.

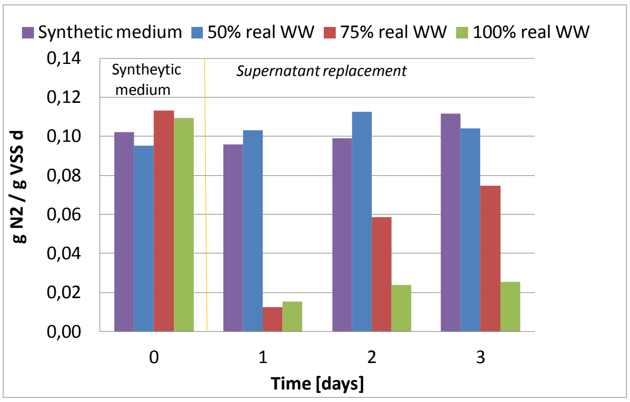

Figure 1: Results of the first set of inhibition tests

Table 1: Results of the second set of inhibition tests

Days	Activity loss		
	Unacclimated biomass	Acclimated biomass	
	7 g/L NaCl	7 g/L NaCl	13.5 g/L NaCl
1	0%	0%	0%
2	62%	57%	60%
3	57%	80%	87%
4	86%	66%	77%

A second set of tests were used to evaluate whether the previously observed anammox inhibition could be due to the high salinity of the digested supernatant. In these tests, salinity of the mineral medium was modified by NaCl addition. The NaCl concentrations tested were 7 and 13.5 g/L, while salinity of the digested supernatant corresponded to around 5 g/L as NaCl. As inoculum, two type of biomass were used: (1) the unacclimated granular sludge, and (2) an acclimatised sample drawn from the anammox. Results are reported in Table 1. For the unacclimated sludge the activity decreased during time with a final inhibition of 86%. At the same salinity concentration, the acclimatized sludge showed a faster adaptation with an activity recovery trend after 3 days of incubation. By doubling the salinity level a slightly higher inhibition was observed.

The inhibition level obtained are slightly higher than the one reported by Dapena Mora et al. (2007) who found a IC50 value of 13.5 g/L of NaCl in similar manometric batch tests on granular anammox biomass.

Lab scale anammox SBR

The SBR reactor was inoculated with granular anammox sludge coming from a full-scale anammox reactor located in Rotterdam (NL). The SBR was operated at an HRT of 2 d. A synthetic feed was used initially, at an average nitrogen loading rate (NLR) of 0.5-0.6 gN L^{-1} d^{-1}, kept constant during the experimentation. Then a blend with increased fractions of real wastewater were used (10%, 25%, 33%, 50%, 70%, 100%), adjusting the NLR and the NH_4/NO_2 molar ratio by $NaNO_2$ and NH_4Cl additions. The reactor was operated for 350 days; during a 40 days stop in summer, the biomass was kept at 4°C. Batch tests were periodically performed to assess the maximum anammox activity (NRR_{max}). In figure 2-right influent and effluent nitrogen compounds are reported. The average N removal efficiency was 91±10% with an average nitrite removal efficiency higher than 97%. NO_2-N/NH_4-$N_{removed}$ ratio was 1.28±14% while NO_3-N/NH_4-$N_{removed}$ ratio was 0.10±72%. In Figure 2-

left, the NRRmax is plotted together with the percentage of supernatant in the feed. During the initial start-up and restart after the first break, the activity increased from values between 1 and 2 kgN/m^3/d up to values between 3 and 4 kgN/m^3/d in about 30 days, suggesting an increase of the active biomass. In contrast, after each increase in blending real wastewater in the influent, the activity decreased, suggesting that real wastewater had an inhibitory effect on the anammox bacteria, similarly to what had been observed in the manometric batch tests. While working at 75% of wastewater in the feed and also during the first days of operation with undiluted wastewater, a minimum value of 0.14 kgN/m^3/d was achieved. In these low-activity phase, temporary but significant increase in nitrite concentration in the effluent was observed. After 30 days of operation with undiluted wastewater, the anammox activity began to recover and continued to rise until the end of the experimentation, achieving values greater than 1 kgN/m^3/d. The trend observed in the last two months of operation at 100% real wastewater suggests the ability of anammox bacteria to adapt to inhibitory substances that may be present in the agricultural digestate. Three particle-size tests were carried out at day 0, 260 and 350 of operation, and showed that the average diameter of granules increased from 775µm of day 0 to 1003µm and 1033µm of day 260 and 350 respectively.

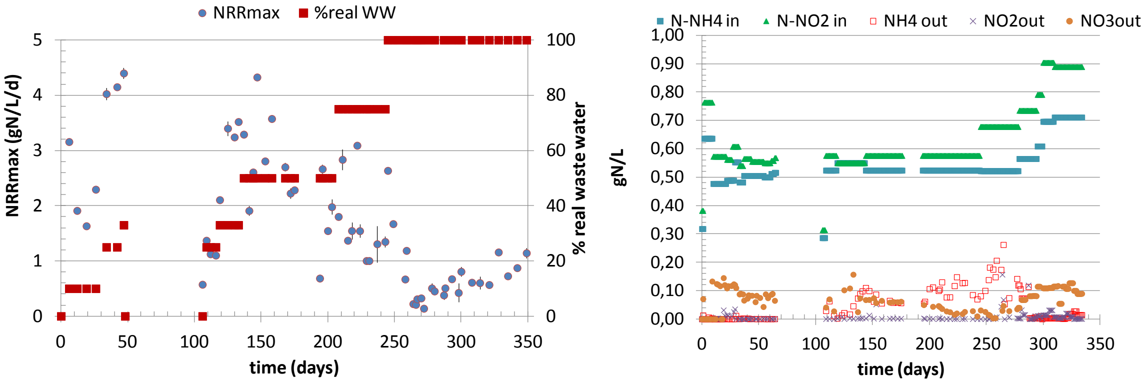

Figure 2: Maximum anammox activity in the SBR reactor during the experimentation and fractions of real wastewater blended in the feeding (left) and influent and effluent nitrogen compound (right).

CONCLUSIONS

The following main conclusions can be drawn:

- a procedure to perform short-term batch tests to assess inhibition of anammox activity in presence of high-strength wastewaters was developed and tested successfully;
- inhibition in presence of undiluted digestate supernatant from piggery/poultry manure processing with not acclimatized biomass; was as high as 85%;
- salinity concentration of 7 gNaCl/L caused 68% activity reduction in the test with acclimated biomass and 86% in the test with non- acclimated biomass;
- in the first days of operation with undiluted supernatant, the maximum anammox activity in the SBR decreased sharply, but recovered afterwards, suggesting that biomass acclimated to the wastewater;
- in the long term, the anammox SBR proved successful in treating undiluted supernatant, with N removal efficiencies higher than 90%.

Acknowledgements

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(S4) Single-stage Nitrogen Removal using Double-Layered Gel Beads Entrapping AOB and ANAMMOX bacteria

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Abstract

The completely autotrophic nitrogen removal process based on aerobic and anaerobic ammonia-oxidizing bacteria (AOB and ANAMMOX bacteria) saves upto 90% of operational costs due to the reduced aeration intensity in completely autotrophic conditions (no need for the extra organic carbon sources). In this study, the entrapment of autotrophic bacteria was applied to enhance nitrogen removal performance through maintaining a long bacterial retention time. For the effective cooperation between two autotrophic ammonia-oxidizers, AOB and ANAMMOX bacteria were physically localized in shell and core layers of poly vinyl alcohol (PVA)/alginate gel, respectively. The thickness of the shell layer was manipulated for possible needs for the thicker outer layer. The mechanical strength of the shell layer depends on the PVA concentration. The effective total nitrogen removal using the core-shell structure of PVA/alginate was proven in a continuous experiment.

Keywords
Entrapment; completely autotrophic nitrogen removal over nitrite; PVA/alginate; double-layered gel beads

INTRODUCTION

The entrapment of AOB and ANAMMOX bacteria in the form of artificial biofilm would offer superior mechanical stability to that of natural biofilm. The co-immobilization system having different functional microorganisms in an entrapping matrix is the effective method to facilitate the interactions of multi-stage reactions. The co-immobilization has been applied to removal processes of toxic chemicals and ammonia which require multiple reactions, typically for aerobic and anaerobic bacteria. The conventional incorporation of aerobic ammonia oxidizers and heterotrophic denitirifiers results in uniform microbial distribution within the gel polymers, such as alginate [Uemoto and Saiki, 2000] and PVA [Morita *et al*., 2008], without the border between the aerobic and anaerobic zones. However, the novel immobilization in double-layered gel beads exhibits well-defined aerobic and anaerobic zones for AOB and denitrifiers. It has been developed [dos Santos *et al*., 1996a] and characterized regarding to substrate diffusion and distributions of nitrogen compounds [dos Santos *et al*., 1996b]. However, the polymeric matrix of double-layered gel beads was restrained to alginate [dos Santos et al., 1996a; 1996b] even though PVA was proven as the suitable polymeric compound to entrap microorganisms for better durability [Leenen *et al*., 1996]. In this study, the double-layered PVA/alginate gel beads were fabricated to co-culture AOB and ANAMMOX bacteria within well-defined aerobic and anaerobic zones, respectively.

MATERIALS AND METHODS

Fabrication of double-layered gel beads

The PVA/alginate gel bead containing pre-cultured ANAMMOX bacteria was prepared before the fabrication of double-layered gel beads. The cross-linking agents of $B(OH)_3$ and $CaCl_2$ were diffused into 100 core ANAMMOX beads in a 250 ml solution of saturated $B(OH)_3$ and 1% $CaCl_2$ (w/v) for 5 min. 250 ml/L of solution containing 25 % PVA (w/v) (with a polymerization degree of 2000, Wako, Japan) and 2.0% of sodium alginate (w/v) (Showa, Japan) was autoclaved at 121 ^{o}C for 30 min. The AOB biomass, which was produced by the selective cultivation, was concentrated by gravity settling for 1 hr. After cooling to 40 ^{o}C, one portion of AOB biomass was slowly added into the PVA/alginate solution. The ANAMMOX core beads containing the cross-linking agents were immersed in the mixture of PVA, alginate and AOB. By the diffusion of the cross-linking agents towards the bulk phase, the interfacial cross-linking of the outer layer occurs. The beads were kept in the $B(OH)_3$-$CaCl_2$ solution for 1 hr for hardening. Then, the beads were transferred to a 0.5 M orthophosphate solution (KH_2PO_4) and immersed for 1 hr. Finally, the fabricated double-layered PVA/alginate gel beads were washed with a large amount of distilled water.

Mechanical strength of the outer layer

The mechanical strength of the outer layer was measured using a high speed agitation unit with four blades (4 cm in length and 2 cm in width). The internal diameter of the cylinder was 14 cm. The intensive agitation speed of 1,000 rpm was applied. The number of beads, which survived the various agitation speed, were counted to compare the mechanical strength of the outer layer. The test was triplicated for 25 beads. Before the test, distilled water was filled up to 10 cm from the bottom in the cylinder.

Single-stage removal of ammonia

The continuous reactor of 500 ml for single-stage removal of ammonia was packed with 40 ml of double-layered PVA/alginate gel beads, i.e., 8% packing ratio. The core ANAMMOX beads had a diameter of 3.72±0.41 mm. 12,610 mg-VSS/L of AOB was entrapped in the outer layer and the thickness of the outer layer was 3.2±0.4 mm. The reactor was operated in the dark condition at a high agitation rate of 500 rpm with a magnetic bar to prevent the possible accumulation of dinitrogen gas inside the core gel beads. The temperature was maintained at 35 ^{o}C with a water jacket. The aeration intensity of 100 ml/min was applied to maintain low DO concentration of less than 0.5 mg/L.

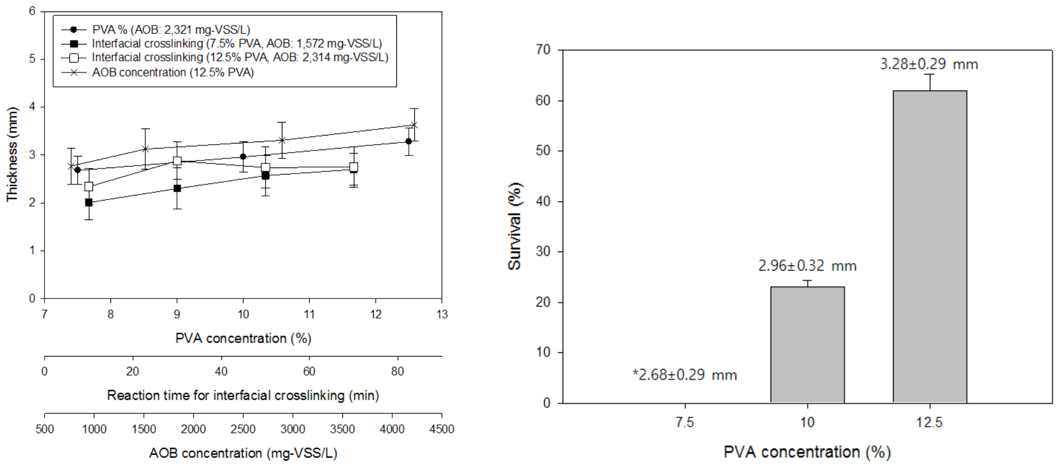
RESULTS AND DISCUSSION

Thickness and mechanical strength of the outer layer

The effects of various conditions during the fabrication of the outer layer on the mechanical strength were tested (Figure 1(a)). The thickness of the outer layer was proportional to PVA concentration. The additional reaction time for the interfacial cross-linking reaction also resulted in the increase in the thickness of the outer layer at a PVA concentration of 7.5%, but the thickness of the outer layer was less sensitive to the interfacial cross-linking reaction time at a PVA concentration of 12.5%. It was expected that the high concentration of PVA contributed to the rapid termination of the cross-linking and the additional reaction has no significant effect on the increase in the thickness. The reason for the positive effect of AOB concentration on the thickness is not clear, but it was speculated that the steric hindrance caused by high concentration of AOB contributes to the increase in the thickness of the outer layer. The factors in this test can be used to extend the anaerobic zone of the double-layered gel beads by increasing the thickness of the outer layer.

The mechanical strength of the outer layer depends only on the PVA concentration. At a 7.5% PVA concentration, all double-layered beads were broken at a agitation speed of 1,000 rpm, but 12.3±1.4 and 62.1±3.2% of double-layered gel beads were survived at PVA concentrations of 10 and 12.5%, respectively (Figure 1(b)). As a result, a PVA concentration of 12.5% was selected as the optimal concentration for the best mechanical strength of the outer layer. The concurrent increases in thickness of the outer layer from 3.68±0.29 to 4.28±0.29 mm and in the mechanical strength of the outer layer was observed in this test. Therefore, it was hypothesized that the mechanical strength is proportional to the thickness of the PVA.

No enhancement of the cross-linking between PVA molecules by AOB was found in the test of different AOB concentrations (data not shown). Even though the thickness of the outer layer was increased with high concentration of AOB, the mechanical strength showed no difference. Thus, it is concluded that the thicker outer layer has an insignificant role in enhancing the mechanical stability. Unfortunately, comparison of the mechanical strength of the outer layer with regards to the interfacial cross-linking reaction period was not possible because all beads were broken or exhibited no difference at 7.5% and 12.5% PVA concentrations, respectively (data not shown).

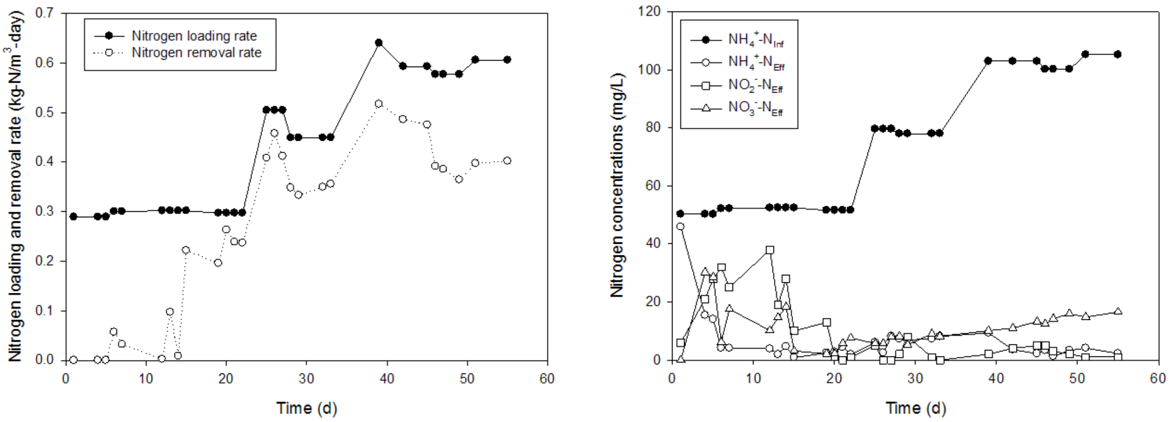


(a) (b)

Figure 1. The thickness of the outer layer according to the PVA %, interfacial cross-linking reaction time and AOB concentration (a) and effects of PVA concentration on the survival ratio of the outer layer at the intensive agitation of 1,000 rpm (b). (*Thickness of the outer layer was indicated.)

Single-stage removal of ammonia

The total nitrogen removal rate was gradually increased from Day 13 (Figure 2(a)). The ANAMMOX activity was recovered from the inhibition and the nitrogen removal rate reached to 80.0-88.5% on Day 22. Note that the theoretical value of the total nitrogen removal efficiency is 87% because ANAMMOX bacteria produce the by-product of nitrate through the anaerobic ammonium removal pathway [Chen *et al.*, 2009]. Thus, it was concluded that the nitrogen removal efficiency was reached to the maximum. The maximum nitrogen removal rate of 0.24 to 0.26 kg-N/m^3-day was observed on Day 22. The total nitrogen removal performance was stable in extended reactions with NH_4^+-N concentrations from 79.6 to 105.2 mg/L with low concentrations of residual ammonia, nitrite and nitrate (Figure 2(b)). In this phase, the total nitrogen removal rate responded immediately to the increase in the total nitrogen loading rate of 0.47±0.03 kg-N/m^3-day (80.3±5.2%), and a total nitrogen removal of 0.38 kg-N/m^3-day was achieved. With the increased total nitrogen loading rate of 0.59±0.01 kg-N/m^3-day, the performance of single-stage removal of ammonia was increased to 0.43 kg-N/m^3-day on Day 28. The ANAMMOX activity was still active by exhibiting nitrite concentrations of lower than 4.8 mg/L. However, the reactivation of NOB, which is responsible for the steady increase in NO_3^--N, resulted in the lower total nitrogen removal efficiency of 71.6±7.9% at the end of the operation. In this study, it is suggested that the inter-correlated reactions between AOB, NOB and ANAMMOX should be thoroughly simulated in dynamic conditions of NH_4^+, NO_2^- and NO_3^- to inhibit the NOB activity in the single-stage ammonia removal reactor.



(a) (b)

Figure 2. Nitrogen loading and removal rates (a) and the nitrogen compositions (b) during the operation of the single-stage ammonia removal process using double-layered PVA/alginate gel beads.

CONCLUSIONS

The mechanical strength of the outer layer dominantly depends on the PVA concentration and a 12.5% was preferred to enhance the durability of the double-layered gel bead. The double-layered PVA/alginate gel bead was fabricated based on the interfacial cross-linking of PVA on the surface of the core ANAMMOX bead. The AOB obtained from the selective cultivation was successfully entrapped in the outer layer. During the start-up of the single-stage ammonia removal process, the nitrification activity was dominant over the ANAMMOX reaction possibly due to the inhibition of ANAMMOX activity during the fabrication procedures. However, the single-stage ammonia removal process showed stable nitrogen removal performance of 80.3 and 71.6% at nitrogen loading rates of 0.47 and 0.59 kg-N/m^3-day, respectively. The lowered nitrogen removal rate at the end of the operation was caused by the production of NO_3^- by NOB.

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(S5) Influence of COD input and aeration regime on the NOB out-selection and the competition between denitrification and anammox during mainstream deammonification

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Abstract

This research was aiming to identify the effect of organic carbon content availability and aeration frequency on the out-selection of nitrite oxidizing bacteria (NOB) in aerobic phases and competition between heterotrophic organisms and anoxic ammonia oxidizing bacteria (AnAOB) in anoxic phases. Two 10 L lab-scale sequencing bath reactors (SBRs) were operated at 25°C in the study. After 514 days of operation, with daily performance analysis and ex-situ activity tests, we were able to conclude that lower COD feeding (secondary effluent) and higher aeration frequency favors AnAOB over denitrifiers, as a result, about 86% of the total nitrogen removal was contributed by AnAOB and a total nitrogen removal efficiency of 29% could be achieved in mainstream SBR.

Keywords

Sequencing Batch Reactor, NOB out-selection, nitrite competition

INTRODUCTION

Wastewater treatment plants in the Chesapeake Bay region, USA are challenged to meet very low nitrogen and phosphorus discharge limits due to eutrophication issues. Deammonification is a two-step process where aerobic ammonia oxidizing bacteria (AerAOB) aerobically oxidize approximately half of the ammonia to nitrite and the anoxic ammonia oxidizing bacteria (AnAOB) organisms anoxically oxidize the remaining half of the ammonia with nitrite produced in the first step to nitrogen gas without the need for organic carbon. This process which shows potential in cost savings on carbon and aeration as instead of only 20% of the nitrogen load (sidestream), all nitrogen is send to this process when applied in mainstream (Al-Omari et al, 2012). It is widely used for the treatment of nitrogen rich wastewater streams with limited carbon source all around the world (Wett. 2007).

The goal of this research is to identify the impact of organic carbon difference in the influent on controlling nitrite oxidizing bacteria (NOB) and competition between heterotrophic organisms and AnAOB. Moreover, different aeration regimes (oxygen as competitive factor) were tested to favor AerAOB rate over NOB in aerobic phases.

METHODOLOGY

Two 10 L lab-scale sequencing bath reactors (SBRs) were operated at 25°C, and the operation cycle time was 6 hr. The reactor was fed during the first 7 minutes of the cycle using secondary effluent (phase SE) or primary effluent (phase PE) from DC Water Blue Plains wastewater treatment plant (WWTP) after storage of the feed at 25°C and UV disinfection. Influent total nitrogen concentration was corrected to about 22 mgN/L, with an ammonia concentration of 20 mgN/L. Influent alkalinity and phosphorus was maintained at about 180mg$CaCO_3$/L and 0.1 - 0.2mg PO_4-P/L, respectively. Influent soluble COD (sCOD) to total nitrogen ratio ranged from 1.5 to 3.0, and total COD (tCOD) to nitrogen ratio ranged from 1.5 to 6.2, when treated with secondary and primary effluent, respectively.

Every cycle began with a 4hr reaction phase where dissolved oxygen (DO) concentration was controlled at a DO set point of 1.5 mg O_2/L using a DO controller and LDO probe (HACH, Düsseldorf, Germany). To achieve intermittent aeration in the reactor, aeration was also controlled using a timer at a frequency of interest. An anoxic phase (30 min) followed the aeration period, and after the settling phase (65 min) and decanting phase (15 min) finished the cycle. During the whole cycle, pH was controlled between 7.00 and 7.20 using a pH controller and probe (Eutech Instruments, Singapore). AnAOB were seeded to the SBRs initially from the DEMON reactor in Strass WWTP (Wett 2006) (phase SE 1-2), and later from a sidestream bench-scale DEMON (PE 1-3, SE 3-5) to maintain the AnAOB activity in the mainstream system. The influent flow rate was 21 L/day resulting in hydraulic retention time (HRT) of 0.47 d. The total sludge retention time (SRT) was maintained at about 30 days, and wasting was done through a screen (212 um) technique to retain the AnAOB biomass (De Clippeleir et al. 2013). The latter allowed for higher AnAOB SRT compared to NOB and AerAOB. Reactor Influent and effluent samples were taken daily for ammonium, nitrite, nitrate, total COD, and soluble COD analyses. Moreover, activity and kinetics tests were done separately to quantify maximum conversion rates and half saturation.

RESULTS AND DISCUSSION

The impact of influent COD over N ratio on the performance of mainstream deammonification SBR reactor in terms of competition for nitrite between AnAOB and NOB and between heterotrophs and AnAOB was studied in two SBR systems at high (1 min air on in 15 min) and low (7 min air on in 45 min) aeration frequency, referred to later as reactor A and B, respectively.

NOB out-selection

Keeping a higher AerAOB to NOB ratio in aerobic phase is always the goal since it will result in more nitrite availability for AnAOB in anoxic phases. It was shown that when switching from Secondary effluent to Primary effluent for influent feeding of the SBRs, AerAOB rate had a decreasing trend for both SBR A and B (Table 1), and vice versa. Although NOB rates were also a little lower during primary effluent phases, the influence of extra COD was not as big as AerAOB (Table 1). In other words, the ratio of AerAOB to NOB rate was also lower, so out-selection of NOB decreased when sCOD increased. Nitrite accumulation at the end of aerobic phases could also be seen as a sign of NOB out-selection. There was no nitrite when fed with primary effluent, but when switching from primary effluent to secondary effluent, nitrite accumulation up to 0.4 mg N/L and 0.6 mg N/L for reactor A and B was detected. The reason could be rates of AerAOB decreased when switching from secondary to primary effluent (Table 1) while effects on the NOB rates were lower (Figure 1). This result indicated that NOB out-selection was more efficient during secondary effluent treatment compared to primary, and this also correlates well with AerAOB to NOB ratios in different phases shown in Table 1.

Table 1. Operation summary of for reactor A (high frequency aeration) and B (low frequency aeration).

Reactor A	SE 1		SE 2		SE 3		PE 1		PE 2		SE 4		SE 5	
Time duration (d)	19		78		28		53		81		69		89	
Aerobic SRT (d)	5.66	± 1.11	2.51	± 0.90	2.36	± 1.47	2.55	± 1.08	5.21	± 4.13	1.73	± 0.72	1.30	± 0.31
Overall SRT (d)	33.95	± 6.69	32.81	± 10.66	31.84	± 19.80	34.42	± 14.52	41.73	± 33.47	30.39	± 11.93	32.73	± 8.39
Influent loading rate (mgN/L.d)	47.47	± 3.77	44.94	± 5.95	47.77	± 4.29	44.34	± 5.18	47.00	± 3.58	45.54	± 6.13	43.94	± 42.82
Relative NO3 production (%)	40.01	± 4.71	38.86	± 22.84	75.65	± 40.28	-8.97	± 20.94	9.97	± 11.96	53.89	± 14.71	61.45	± 25.46
sCOD/N ratio (-)	1.47	± 0.22	1.55	± 0.38	1.38	± 0.37	2.69	± 0.38	2.58	± 0.60	1.32	± 0.34	1.06	± 0.88
NH4 removal rate (mgN/L.d)	44.68	± 5.18	33.60	± 9.05	24.56	± 27.73	27.09	± 14.25	35.09	± 8.58	40.91	± 8.53	36.73	± 8.40
Ntot removal rate (mgN/L.d)	26.60	± 3.06	19.80	± 8.39	8.97	± 11.01	12.25	± 12.96	30.99	± 6.69	18.84	± 7.12	12.93	± 5.29
Ntot removal efficiency (%)	57.53	± 4.23	43.18	± 17.15	17.98	± 22.76	27.09	± 26.38	66.20	± 14.56	40.87	± 11.92	28.61	± 8.52
sAOB rmax (mg N/gVSS.d)	235.78	± 220.45	248.37	± 71.86	314.56	± 142.65	149.56	± 108.49	136.76	± 48.61	167.16	± 50.54	303.39	± 187.58
sNOB rmax (mg N/gVSS.d)	63.06	± 41.84	142.87	± 80.86	219.52	± 52.35	141.44	± 68.50	168.63	± 63.13	147.52	± 51.74	236.34	± 150.08
sAnAOB rmax (mg N/gVSS.d)	295.52	± 88.1	120.64	± 32.60	170.04	± 28.34	82.98	± 91.58	57.81	± 27.03	56.94	± 24.57	71.68	± 21.61
AnAOB seeding activity (mg Ntot/gVSS.d)	2.69		3.96	0.97	5.38		5.22	± 2.95	9.87	± 10.22	10.01	± 2.65	20.39	± 9.86

Reactor B	SE 1		SE 2		PE 1		PE 2		PE 3		SE 3	
Time duration (d)	98		28		55		59		33		158	
Aerobic SRT (d)	6.53	± 2.87	6.93	± 3.16	7.82	± 4.06	5.81	± 4	4.77	± 0.69	1.46	± 1.43
Overall SRT (d)	29.39	± 12.9	31.17	± 14.23	35.18	± 18.25	48.43	± 33	27.53	± 2.36	26.80	± 26.36
Influent loading rate (mgN/L.d)	45.51	± 5.6	47.77	± 4.29	44.34	± 5.18	47.32	± 3.28	46.59	± 3.97	46.02	± 51.8
Relative NO3 production (%)	41.05	± 18.63	55.85	± 18.33	-11.57	± 27.73	2.62	± 13.18	6.04	± 16.74	67.60	± 25.43
sCOD/N ratio (-)	1.54	± 0.35	1.38	± 0.37	2.69	± 0.38	2.35	± 0.53	2.93	± 0.53	0.94	± 0.67
NH4 removal rate (mgN/L.d)	37.83	± 5.59	40.64	± 9.32	15.23	± 14.3	22.80	± 7.97	38.00	± 6.31	40.40	± 9.64
Ntot removal rate (mgN/L.d)	21.42	± 6.53	16.03	± 5.8	14.77	± 12.93	22.29	± 5.46	36.24	± 5.47	12.94	± 7.02
Ntot removal efficiency (%)	46.45	± 13.07	33.47	± 11.46	32.64	± 20.29	43.60	± 18.04	78.58	± 14.04	28.21	± 14.24
sAOB rmax (mg N/gVSS.d)	294.58	± 160.69	242.33	± 110.77	131.94	± 48.45	135.55	± 54.61	130.39	± 15.31	245.72	± 128.29
sNOB rmax (mg N/gVSS.d)	134.64	± 99.02	240.92	± 53.17	195.14	± 77.31	154.17	± 53.08	112.80	± 31.94	213.73	± 169.09
sAnAOB rmax (mg N/gVSS.d)	219.49	± 112.91	305.88	± 9.67	122.88	± 55.98	64.41	± 23.62	64.85	± 30.36	72.16	± 24.9
AnAOB seeding activity (mg Ntot/gVSS.d)	3.67	± 1.01	5.38		5.22	± 2.95	3.67	± 1.046	18.55	± 11.14	17.43	± 9.65

Aeration frequency difference between the two reactors resulted in different NOB out-selection. For higher aeration frequency reactor (reactor A), it was easier to keep a higher AerAOB to NOB ratio than the lower frequency reactor (reactor B) for the first couple of secondary effluent phases (Table 1). When it comes to primary effluent phases, the difference gets smaller for both reactors and no clear impact could be observed. It could be conclude that since the primary effluent had more negative influence on AerAOB activity than NOB activty, the distinct created by aeration regime was subtle.

AnAOB contribution

In anoxic phases a competition between AnAOB and denitrifiers will determine the degree of ammonium removal in the anoxic phases. In the whole operation period, AnAOB activity kept decreasing, although the seeding rate kept increasing and SRT was the same (Table 1). During the last secondary effluent phase there was some nitrite accumulation for both reactors (0.4 mg N/L for reactor A, 0.6 mg N/L for reactor B) as mentioned above, which was very close to the half saturation constant for nitrite of AnAOB of 0.6 mg N/L (measured value in this study). But this did not necessarily result in a higher deammonification rate (Figure 1). The reason could be because of much lower AnAOB rate compared to the inocula (Table 1). A minimum of 86% for A and 82% for B of deammonication was achieved in total nitrogen removal for all the secondary effluent phases. Although it seems the lower frequency reactor (B) has a higher maximum AnAOB rates, it did not show the advantage in performance (Table 1, Figure 1). The reason could be higher NOB rates in reactor B than reactor A which gave AnAOB less opportunities in competition for nitrite. Reactor A has a higher total nitrogen removal rate and efficiency than reactor B in secondary phases overall (Table 1), which was probably related to the better NOB out-selection. When it comes to primary phases, AnAOB showed lower activity during primary effluent phases than secondary effluent phases for both reactors (Table 1) due to less nitrite availability. Deammonification percentages in total nitrogen removal decreased to 20% during the primary phases for both reactors overall (Figure 1). But even with low nitrite and AnAOB activity, it was possible to achieve a significant contribution of AnAOB (63% and 61% for reactor A and B) to the total nitrogen removed when reached stable operation (Figure 1). The total nitrogen removal rate increased 250% and 225%for reactor A and B respectively, but it was mainly attributed to higher denitrification rate (Figure 1). The maximum deammonification rate was about 6-7 times higher under ideal conditions than actual nitrogen removal rate through deammonification route measured in the reactor overall (data not shown). This showed that the AnAOB rate was limited by NOB out-selection thus by and nitrite limitation.

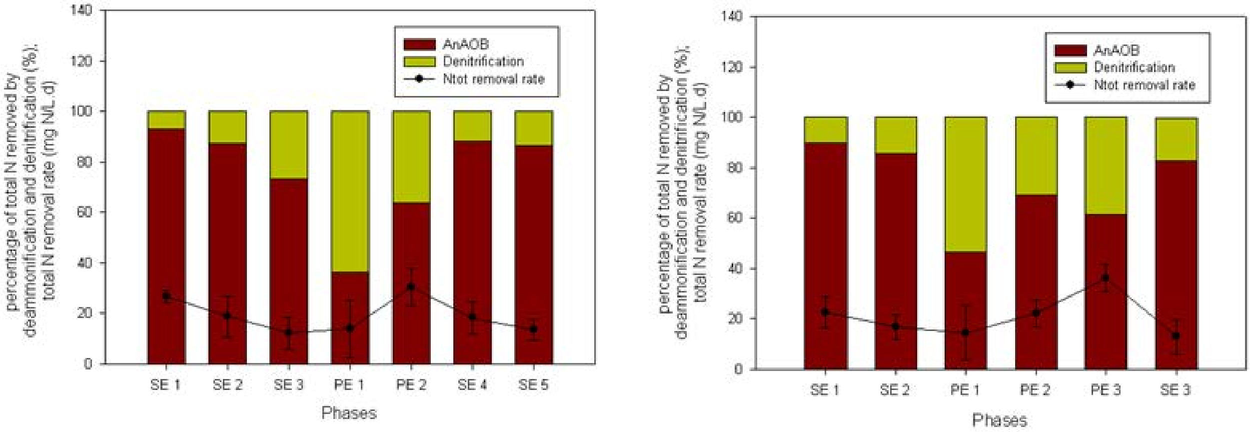

Figure 2. Total nitrogen removal rate and ammonium removal efficiency of deammonification and denitrification comparison for all the operation phases in reactor A (left) and reactor B (right). Data was interoperated in percentage of total nitrogen removal. This calculation is based on aerobic COD loss of 50% for primary effluent, and 75% for secondary effluent to allow for equal mass of COD loss.

To conclude, higher aeration frequency gave more advantage for AerAOB over NOB and thus better NOB out-selection in secondary effluent phases, but did not in primary effluent phases. Higher COD to nitrogen ratio in primary effluent phases resulted in lower AerAOB to NOB ratios and AnAOB rates, and as a consequence higher denitrification rates. Overall, secondary effluent feeding and higher frequency favors AerAOB and AnAOB over NOB, as a result, about 86% of the total nitrogen removal was contributed by AnAOB in mainstream SBR. During primary phases an AnAOB contribution of 60% to the total nitrogen removal could be maintained despite the higher competition with denitrifiers for nitrite.

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Efficient technologies - Novel processes

(Tuesday, 24 June 2014, Aula T1, Polo Zanotto)

(P9) Environmental assessment of biological treatment of washing waters from cheese production

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Abstract

Life cycle assessment (LCA) is a tool for evaluating environmental burdens related to a product, process or activity throughout its entire life cycle. In wastewater treatment, LCA can provide, for example, guidance for improving the environmental performance of existing treatment plants. In this study, we applied LCA to assess the environmental impacts of treating washing waters from cheese production by nitrification/denitrification and simultaneous phosphorus precipitation. Wasted sludge was applied as organic fertilizer to farmland to recycle nutrients. LCA results revealed that emissions from biological treatment to air and water, electricity consumption, and consumption of ferric chloride contributed most to the environmental burdens at the level of the treatment plant. Sensitivity analysis of the LCA results regarding the choice of precipitating agent showed that the use of ferrous sulphate instead of ferric chloride reduces the environmental impacts in all impact categories.

Keywords

Industrial wastewater; Life Cycle Assessment (LCA); phosphorus precipitation; organic fertilizer; wastewater treatment

INTRODUCTION

Life cycle assessment (LCA) is a methodology for evaluating environmental impacts associated with a product, process or activity covering all stages of its life cycle from cradle to grave. With respect to wastewater treatment, LCA allows identifying processes at the treatment plant level or beyond that contribute most to the environmental burdens of wastewater treatment. LCA results can provide guidance for improving the environmental performance of existing treatment plants. During the design of a treatment plant, LCA can be used to compare the environmental performance of different plant configurations.

In this study, we used the LCA methodology to evaluate the environmental impacts of treating washing waters from cheese production by nitrification/denitrification with simultaneous phosphorus precipitation. Washing waters from cheese production originate from cleaning pipelines, tanks and equipment, and can contain different fractions of cheese whey. For this study, we assumed that the lactose and protein rich cheese whey is valorised, for example, by drying it and using it as feedstock for animal feeding. The remaining washing waters are, nonetheless, characterized by high organic loads of readily biodegradable organics (Carvalho *et al.* 2013) and need to be treated prior to discharge to receiving waters. Waste activated sludge from biological treatment of the washing is applied to farmland in order to recycle nutrients.

MATERIALS AND METHODS

Goal and scope

The aim of this study was to assess the environmental impacts of treating washing waters from cheese production by nitrification/denitrification and simultaneous phosphorus precipitation. The studied system included application of waste activated sludge as organic fertilizer on farmland, replacing the use of mineral fertilizers. Cheese production and pretreatment of washing waters (sieving and degreasing) is excluded from the study. The functional unit of the system is the treatment of 1 m^3 washing waters from cheese production.

System description

The treatment system under study is designed for treating 250 m^3/d washing waters from cheese production and is depicted in Figure 1. The characterization of the washing waters in the influent of the treatment plant and imposed effluent limits are given in Table 1. The washing waters are treated by nitrification/denitrification and simultaneous phosphorus precipitation using ferric chloride as precipitating agent. The aeration basin is intermittently aerated with two surface aerators. Sludge is recycled from the clarifier to the aeration basin. The effluent from the clarifier is discharged to receiving waters. Waste activated sludge is thickened, conditioned with a polymer solution, and dewatered in a belt filter press. The dewatered sludge is stored, transported for 50 km and spread on farmland as organic fertilizer. The air from the sludge thickener, the dewatering hall and the sludge storage silo is treated with an activated carbon filter.

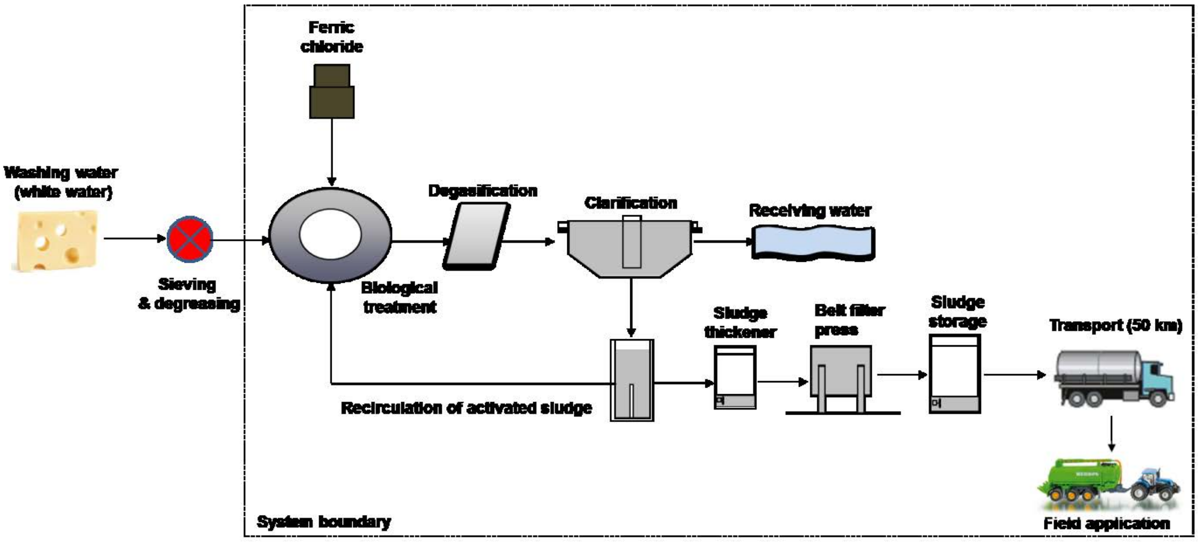

Figure 1. Schematic of the treatment process for washing waters from cheese production.

Field application of biological sludge replaces mineral fertilizer application at equivalent nutrient and fertilizer values. The nitrogen mineral fertilizer equivalent (MFE) of waste activated sludge was determined using the plant available nitrogen (PAN) calculation method (Water Environment Federation 2005). MFE values for phosphorus and potassium were fixed at 0.95 and 1.0, respectively, as both phosphorus and potassium are primarily available in mineral form. N_2O emissions from biological treatment as well as emissions to water from the discharged effluent were accounted for. Direct emissions to air, water and soil from mineral and organic fertilizer application were calculated using different emission models. Overall, ammonia (NH_3), nitrous oxide (N_2O), and nitrogen oxide (NO_x) emissions to air, nitrate (NO_3^-) and phosphorus emissions to water, and heavy metal emissions to soil were considered. Heavy metal contents of mineral fertilizers were taken from Dittrich and Klose (2008) and Nemecek and Schnetzer (2012). Heavy metal contents of the waste activated sludge were assumed to be similar to those of activated sludge from municipal wastewater treatment plants and were taken from Oliva *et al.* (2009). A detailed description of the applied emission models and the PAN calculation is given in Brockmann *et al.* (2013).

Impact assessment

Environmental impacts of treating washing waters from cheese production were assessed at midpoint with the ReCiPe Method (version 1.07) (Goedkoop *et al.* 2013) using the ecoinvent v2.2

database and SimaPro 7.3.3 software.

Table 1. Wastewater characterization of the washing waters from cheese production and imposed effluent limits**.**

Parameter	Unit	Influent	Effluent
Q_{in}	m^3/d	250	250
COD	g COD/m^3	2,000	125
BOD_5	g BOD_5/m^3	1,500	25
TSS	g TSS/m^3	500	35
TKN	g N/m^3	100	(2)
NO_3-N	g N/m^3	40	(13)
N_{tot}	g N/m^3	140	15
P_{tot}	g P/m^3	50	2
Grease	g/m^3	300	-

RESULTS AND DISCUSSION

Figure 2 shows the results of the environmental impact assessment of treating 1 m^3 washing waters from cheese production. Emissions from the biological treatment step had large impacts on climate change (N_2O), freshwater eutrophication (phosphorus), and marine eutrophication (NO_3^- and NH_4^+). Electricity consumption (French electricity mix) at the wastewater treatment plant significantly affected 11 of 18 impact categories (76-320% of the total impact). The consumption of consumables at the treatment plant, in particular ferric chloride (84% of the impact of consumables), had a large influence on 12 impact categories (27-196% of the total impact). In addition to the processes at the treatment plant, direct field emissions from organic fertilizer application and the amount of replaced mineral fertilizers had large impacts on the environment. Field emissions from sludge spreading had negative environmental effects on human toxicity (heavy metals), particulate matter formation and terrestrial acidification (NH_3 and NO_x), freshwater eutrophication (phosphorus), marine eutrophication (NH_4^+ and NO_3^-), and terrestrial ecotoxicity (heavy metals). In contrast, substitution of mineral fertilizers by produced sludge resulted in large environmental benefits. Recycling nutrients from washing waters from cheese production significantly reduced the environmental burdens of the treatment. Levers for improving the environmental performance of the wastewater treatment plant are 1) emissions from biological treatment to air and water, 2) electricity consumption, and 3) consumption of ferric chloride.

Impact of choice of precipitating agent

Due to the large environmental impact of ferric chloride consumption, the sensitivity of the LCA results with regard to the choice of precipitating agent was evaluated. Besides ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$) and aluminium sulphate ($Al_2(SO_4)_3$) were chosen as precipitating agents. Aluminium chloride ($AlCl_3$) was not considered as precipitating agent, because it is not inventoried in the ecoinvent v2.2 database. Using ferrous sulphate instead of ferric chloride for simultaneous phosphorus precipitation reduced the environmental impacts for all impact categories by 2-145% (median 22%). The use of aluminium sulphate (instead of ferric chloride) resulted in reduced environmental impact for 14 of the 18 regarded impact categories. But the environmental impacts increased for four categories (photochemical oxidant formation, particulate matter formation, terrestrial acidification, and water depletion). Thus, from an environmental perspective, the use of ferrous sulphate instead of ferric chloride should be favoured.

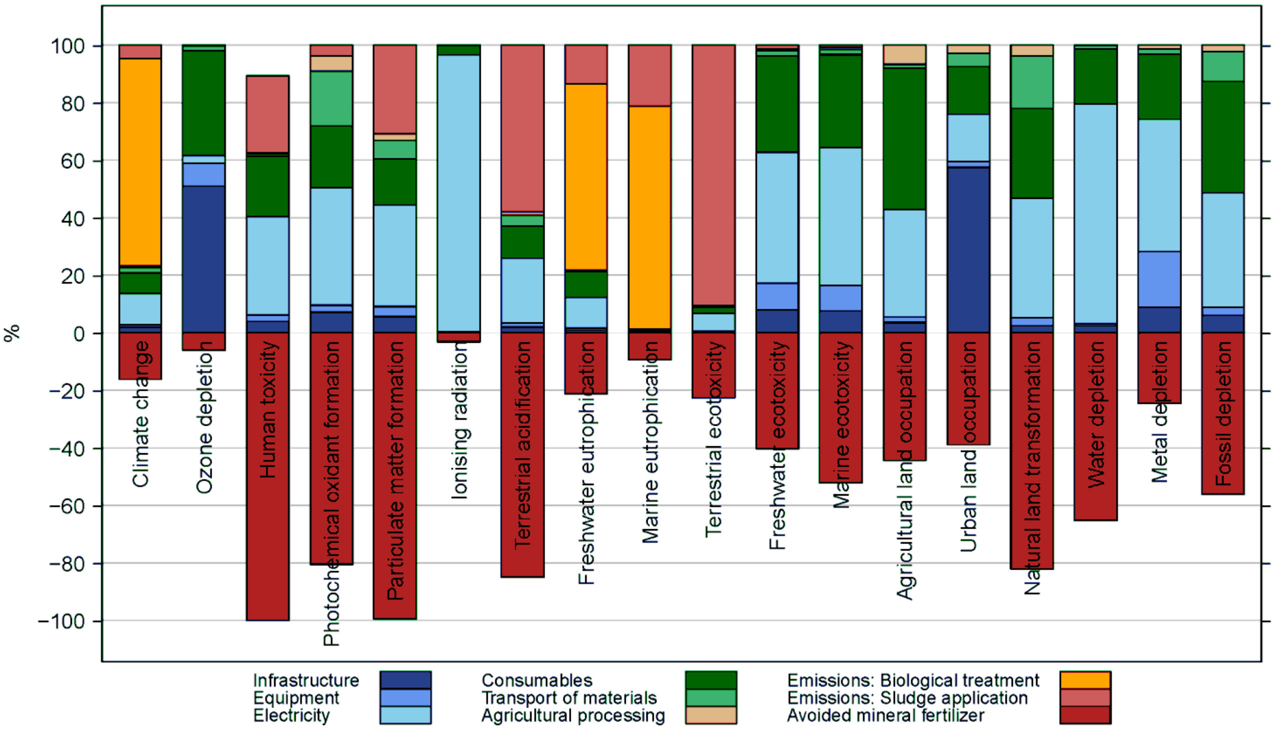

Figure 2. Impact assessment for treating 1 m^3 washing waters from cheese production. ReCiPe Midpoint (version 1.07) was used for characterization at midpoint.

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(P10) When more means better? How to assess the wastewater treatment chain by means of a global evaluation tool

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Abstract

It is the aim of this work to present an innovative methodology to judge the eco-suitability of wastewater treatment processes on the basis of the damage on human health produced/avoided, expressed as an economic value. In particular, the benefits on effluent quality obtained by treatment technologies can be weakened by the negative effects on air quality, when energy consumption and related pollutants emissions are taken into account. While for air pollution a set of established external costs was applied, for water pollution the rates of the impacts on human health have been evaluated in terms of Global Burden of Disease and measured in units of DALY (Disability-Adjusted Life Years), then converted into costs based on Gross Domestic Product. This procedure was used for assessing three paradigmatic scenarios: the (hypothetical) lack of treatments, a conventional biological process, and a tertiary oxidation stage (ozonation). The results showed how the WWTP is able to increase the health status of citizens, but also that the reduction of water pollution achieved by means of ozonation might be beneficial for human health at an extent which is in the same order of magnitude of damage caused by air pollution, emphasizing that the question if the use of advanced (energy-intensive) treatments is a proper solution to remove organic micropollutants from wastewater remains still open.

Keywords

Cross-media effects; DALY; eco-suitability; tertiary oxidation treatments; wastewater

INTRODUCTION

If, on the one hand, chemicals are part of our daily lives, on the other hand, they may cause diseases. Which fraction of the current disease burden do chemicals however cause? This is an important question for decision-makers in order to prioritize efforts to protect us from the harmful effects of chemicals (Prüss-Ustün *et al.*, 2011). As far as contamination from sewage is concerned, secondary biological treatment of wastewater significantly reduces the concentrations of many substances, but does not provide their complete elimination (see, among others, Clara *et al*, 2012). In order to prevent this kind of water pollution, an advanced treatment downstream the biological process can be implemented, e.g. a final ozonation stage (Koester *et al.*, 2012). However, also the most promising technologies for trace pollutant removal have still to be assessed with regard to their environmental sustainability, e.g. considering energy consumption (Jones *et al.*, 2007).

A paradigm of wastewater treatment can plainly explain the situation: namely, an increase in effluent quality can only be environmentally beneficial. In fact, when subjected to a wider analysis, the benefits of improved effluent quality are balanced by the negative effects on air quality, when energy consumption and related pollutants emissions deriving from the advanced treatment technologies are taken into account. Basically, there is a conflict of interest between two contradictory goals, but current environmental policy has not fully recognized the cross-media effects of improving water quality. The critical point is the determination and quantification of the damage caused by different kinds of pollution on different media, and its translation in a common parameter (e.g. an economic value) to make the comparison possible. It is the goal of this work to present, first of all, an innovative methodology based on an order-of magnitude calculation of damage on human health expressed as an economic value; secondly, three paradigmatic scenarios were assessed: the (hypothetical) lack of treatments, a conventional biological process, and a tertiary oxidation stage (ozonation). In particular, while for air pollution the established external costs have been applied, for water pollution, on the contrary, the rates of the impacts on human health have been evaluated in terms of Global Burden of Disease (GBD). Its quantification was carried out, in order to compare the effects on a linear scale, in units of DALY (Disability-Adjusted Life Years, i.e. a health gap measure comprising the potential years of life lost due to premature death and the equivalent years of 'healthy' life lost by virtue of being in states of poor health or disability), as developed by the World Health Organization, WHO (Murray and Lopez, 1996), and then converted into costs based on Gross Domestic Product (GDP).

MATERIALS AND METHODS

Damage on human heath for air emissions

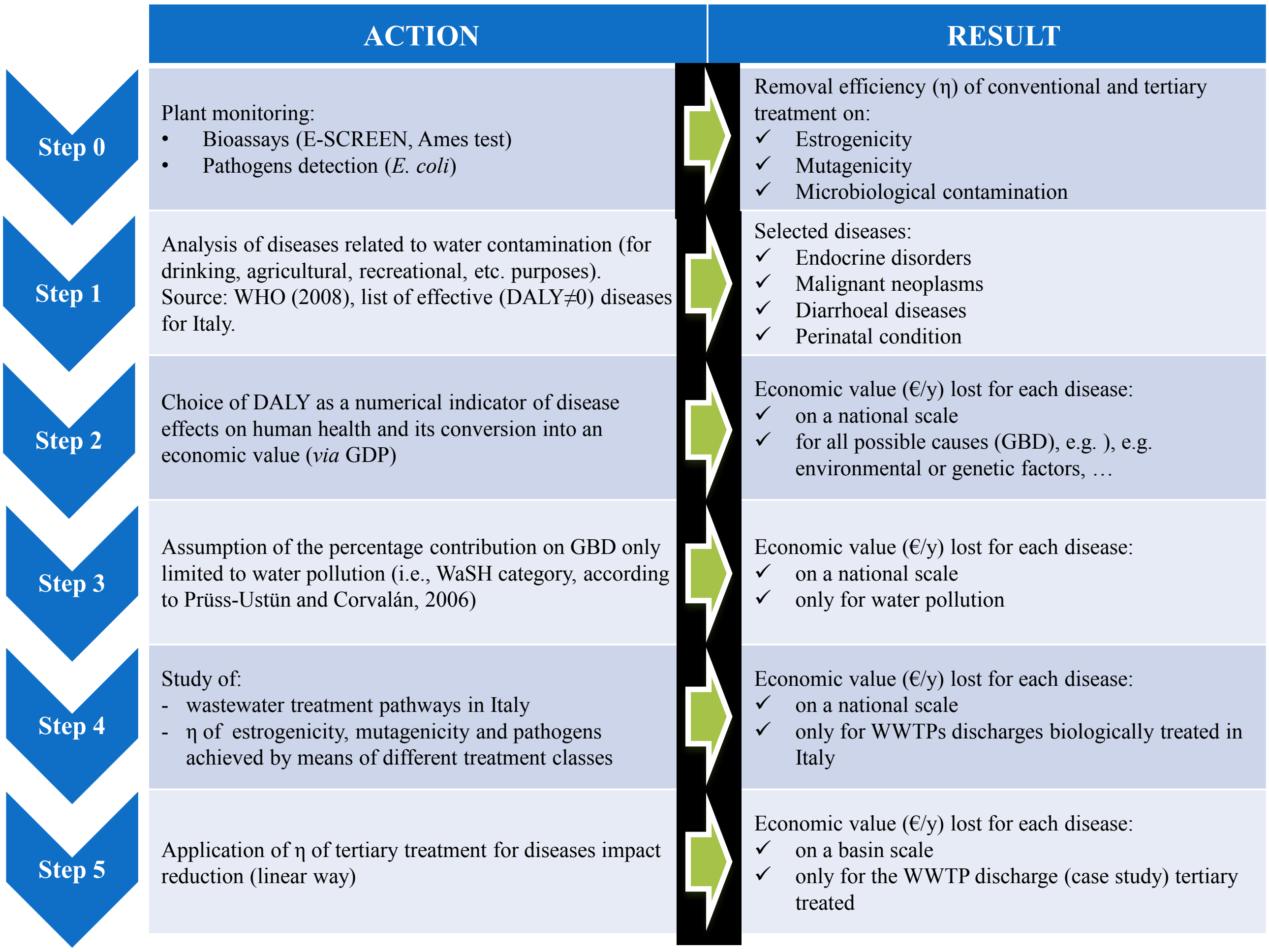
Several methodologies have been developed to derive economic values for the effects of atmospheric pollution: all of them are characterized by a direct approach, i.e. the straight attribution of a cost to each emission. In particular, the European Environmental Agency derived external costs for some air pollutants, as part of the development of cost benefit analysis (EEA, 2011).

Damage on human heath for water emissions

The calculation of damage factor for water emissions was performed, on the contrary, via an indirect approach (i.e., calculating the Environmental Burden of Diseases (EBD)). The flow-sheet diagram in Figure 1 summarizes the adopted methodology, hereinafter described. After plant monitoring (labelled as "step 0" in Figure 1), the main diseases linkable to water contamination were selected (step 1) from WHO list reporting all possible diseases, with the help of an expert in the field of Hygiene and Public Health. Other water-related infectious and parasitic diseases (such as intestinal nematode infections) were not accounted for, as they have no impact in Italy (the Country of the case study). Then (step 2), the weight of each disease was evaluated by means of a specific indicator, the DALY (Disability Adjusted Life Year). Furthermore, the money value of the economic loss of one productive year of life (or one DALY) was considered equal to the national Gross Domestic Product per capita per year: in this way, it is possible to attribute an economic quantification to the damage on human health. The overall DALY values were reduced only to the ones directly linked to water pollution in step 3: Prüss-Ustün and Corvalán (2006) estimated, for each disease, the environmental attributable fraction and an indicative value for the specific risk factor (the WaSH - *Water, Sanitation and Hygiene* – category, in the current case-study). In order to focus on the damage due to WWTP discharge, in step 4 the wastewater treatment pathways in Italy were considered, focalizing on the respective percentages of *uncollected/untreated*, *only partially treated* and *biologically treated* sewage; the quantification of microbiological and biological activity reduction exerted by a secondary treatment and, considering gradually lower efficiencies, by the other treatment categories was performed (literature review) in order to determine each class contribution on the overall damage. Finally (step 5), the damage related to the final ozonation was decreased on the basis of the ozonation removal efficiencies obtained from real data obtained on an ozonation plant (Bertanza *et al.*, 2013), in particular the biological (estrogenic and mutagenic activity) and microbiological (disinfection) assays.

RESULTS AND DISCUSSION

The impact on endpoint categories (quantified in terms of social cost due to the damage on human health and expressed in €/y) is displayed in Figure 2: first of all, a clear improvement of the health status of citizens can be highlighted through the adoption of proper actions for wastewater treatment (i.e., a conventional WWTP with a biological process), as expected. On the contrary, quite surprisingly, similar global effects (considering the inherent methodological approximations) were recorded for two analyzed treatment options: secondary (biological) and tertiary (ozonation).



	ACTION	RESULT
Step 0	Plant monitoring: • Bioassays (E-SCREEN, Ames test) • Pathogens detection (*E. coli*)	Removal efficiency (η) of conventional and tertiary treatment on: ✓ Estrogenicity ✓ Mutagenicity ✓ Microbiological contamination
Step 1	Analysis of diseases related to water contamination (for drinking, agricultural, recreational, etc. purposes). Source: WHO (2008), list of effective (DALY≠0) diseases for Italy.	Selected diseases: ✓ Endocrine disorders ✓ Malignant neoplasms ✓ Diarrhoeal diseases ✓ Perinatal condition
Step 2	Choice of DALY as a numerical indicator of disease effects on human health and its conversion into an economic value (*via* GDP)	Economic value (€/y) lost for each disease: ✓ on a national scale ✓ for all possible causes (GBD), e.g.), e.g. environmental or genetic factors, …
Step 3	Assumption of the percentage contribution on GBD only limited to water pollution (i.e., WaSH category, according to Prüss-Ustün and Corvalán, 2006)	Economic value (€/y) lost for each disease: ✓ on a national scale ✓ only for water pollution
Step 4	Study of: - wastewater treatment pathways in Italy - η of estrogenicity, mutagenicity and pathogens achieved by means of different treatment classes	Economic value (€/y) lost for each disease: ✓ on a national scale ✓ only for WWTPs discharges biologically treated in Italy
Step 5	Application of η of tertiary treatment for diseases impact reduction (linear way)	Economic value (€/y) lost for each disease: ✓ on a basin scale ✓ only for the WWTP discharge (case study) tertiary treated

Figure 1. Flow-sheet diagram of the proposed methodology for health impact assessment concerning water pollution.

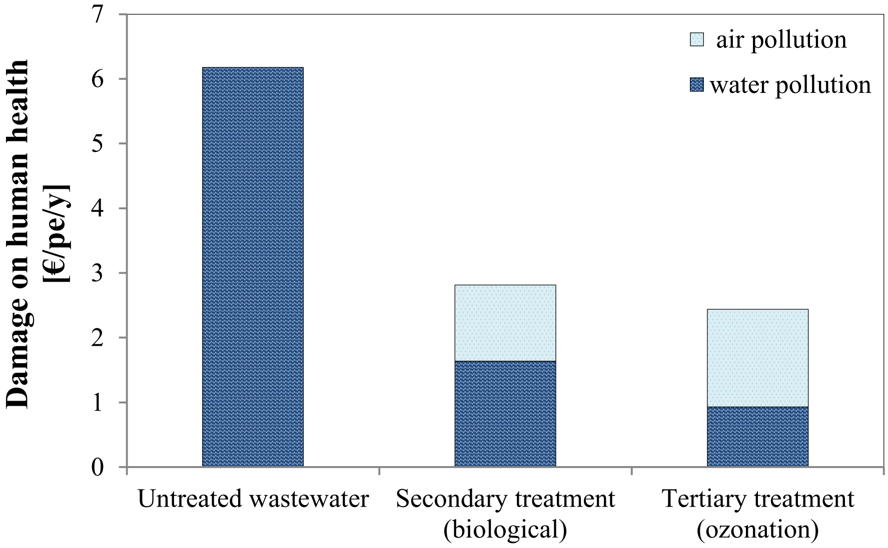


Figure 2. Damage on human health (as Euro per person equivalent per year) for assessed scenarios.

CONCLUSIONS

In this study, an innovative appraisal framework aimed at evaluating the environmental suitability of the wastewater treatment chain was proposed. It allowed weighing both the avoided impacts for the water receiving body and the consequent induced atmospheric pollution, quantifying the effects on the basis of a common endpoint category (identified in the damage on human health and expressed as economic value). Actually, while for air emissions rough but accepted data on the damage generated by specific atmospheric pollutants to human health and the relative economic impact are available in literature, for water pollution conventional tools, such as LCA, are unsuitable, due to the difficulty in assigning a common parameter to different environmental factors and in accounting for all the negative effects on human health, which can be estimated only by means of appropriate bioassays. Therefore, this study proposed a health impact assessment through the measurement of the environmental burden of disease (for WaSH category), attributable to a specific emission source (WWTP discharge) and taking into consideration the health status of citizens (measured by means of DALY values).

Its application confirmed that the implementation of WWTPs is able to decrease the damage on human health, but the increase of their complexity (e.g., with a tertiary chemical oxidation) is not always as beneficial as hoped: for example, the reduction of water pollution achieved by means of ozonation might be advantageous for human health at an extent which is in the same order of magnitude of damage caused by air pollution.

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(P11) Leachate Remediation at Closed Solid Waste Landfill using Permeable Reactive Barrier with Vegetation

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Abstract

This research was conducted to investigate leachate treatment efficiencies by using permeable reactive barrier (PRB) with guinea grass (Panicum maximum TD 58). Pilot scale PRB was examined at hydraulic loading rate of 0.028 m^3/m^2d and hydraulic retention time of 10 d. Two different types of media in PRB were used i.e. system 1: clay and sand mixture of 40:60 %w/w and system 2: clay, ferric chloride sludge and sand mixture of 30:10:60 %w/w. The results showed that the performance of system 2 was better in terms of pollutant removal efficiencies. Average BOD, COD and TKN removals were 76.1, 68.5 and 73.5% respectively. Greenhouse gas (GHG) emissions during the treatment of PRB were 8.2-52.1 $mgCH_4/m^2.d$, 69.1-601.8 $mgCO_2/m^2.d$ and 0.04-0.99 $mgN_2O/m^2.d$. The use of system 2 with vegetation resulted in lower GHG emissions. The results show that PRB with vegetation could be effectively used to remediate leachate from close landfill site.

Keywords
Leachate treatment; permeable reactive barrier; site remediation; vegetation

INTRODUCTION

Leachate is a highly concentrated wastewater generated as by-product from municipal solid waste landfill. It poses a threat to the environment in terms of air, surface water and ground water pollution. Conventional leachate treatment systems available in developing countries are generally low-cost technologies such as stabilization pond, aerated lagoon or land treatment. Nevertheless, those treatment technologies are usually implemented only during the operation stage of solid waste disposal site. After site closure, most of the treatment systems are not well operated or poorly maintained due to lack of post-closure operation and maintenance cost. The control of leachate migration off the site after landfill closure is not an easy task because of high variations of leachate quantity and characteristics with time. Subsurface flow constructed wetland which utilizes coarse media with high permeability and vegetation has been proven to be an efficient treatment method for landfill leachate treatment (Chiemchaisri et al., 2009). Its main treatment functions include biological treatment using attached growth on the media and plant root and plant uptake of nutrients. Meanwhile, permeable reactive barrier (PRB) technology using low permeable media like clay and sand mixture has been also successfully applied for reducing groundwater pollution from solid waste disposal site (Dong et al., 2009). PRB utilizes reactive media to prevent contaminated water pollutants by physical, chemical and/or biological processes. The treatment processes can include precipitation, sorption, oxidation/reduction, fixation or degradation to remove the contaminants from the water (McMahon et al., 1999). This research is carried out to investigate the possibility of utilizing PRB containing high permeable reactive media and plant as an in-situ pollution control technology for close landfills. The concept is to construct PRB surrounding the waste disposal area so that infiltrated leachate can be treated until it is safe for discharge off-site. It is also anticipated that vegetation could also enhance the performance of PRB by improving soil porosity and oxygen diffusion for the microbial activities. In our previous investigations, vegetation has provided positive effect on leachate treatment in soil-plant system while also helped reducing greenhouse gas emission during it treatment (Suwunpukdee et al., 2013).

MATERIALS AND METHODS

Two pilot-scale permeable reactive barrier (PRB) units of 1 m width, 2 m length, and 1 m depth, as the schematic shown in Fig. 1, were used. The inlet and outlet zones of the experimental unit were filled with 30-60 mm gravel of 0.80 m depth. PRB media made of clay: sand mixture at 40:60 (%w/w) was provided in system 1 and clay: ferric chloride sludge: sand mixture at 30:10:60 (%w/w) was provided in system 2. Clay was obtained from local soil and ferric chloride sludge was brought from sludge storage pond of an advanced leachate treatment system at the same solid waste disposal site. The main purpose for introduction of ferric chloride sludge in reactive media was to investigate its effect on suppression of methane production during the treatment (Sylvia and Schnell, 2000). Guinea grass (Panicum maximum TD 58) was used as vegetation in both units with an initial plant density of 20 rhizomes/m^2. Leachate was fed into the system at a hydraulic loading rate (HLR) of 0.028 m^3/m^2.d, equivalent to a hydraulic retention time (HRT) of 10 d.

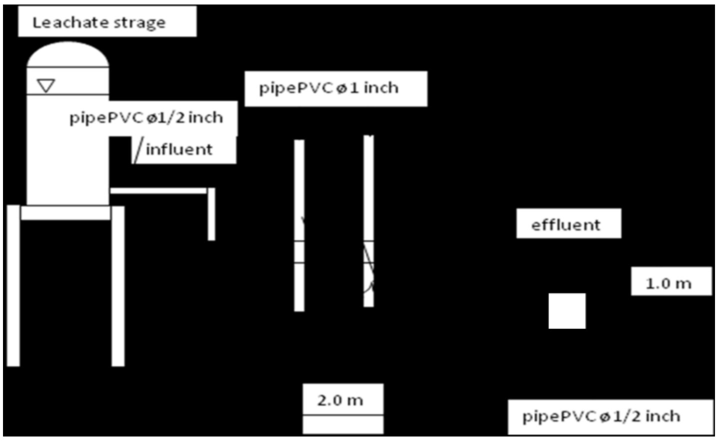

Figure 1. Schematic of pilot-scale permeable reactive barrier (PRB) with vegetation

The characteristics of leachate are shown in Table 1. The water qualities were monitored over 257 days for pH, EC, BOD, COD, SS, TDS, NH_4^+, TKN, NO_2^-, NO_3^- and TP. Soil samples in the media were analyzed for pH, EC, organic carbon, NH_4^+-N, NO_3^--N, TKN and TP. The growth of plant was determined in terms of height, number of leaves and shoots and total dry weight.

Table 1. Characteristics of leachate used in this study.

Parameter	Range	Average±SD
pH	7.5-8.8	8.3±0.4
EC (ds/m)	11.5-25.9	19.2 ± 4.3
BOD (mg/l)	704-1,434	922±211
COD (mg/l)	2,200-3,145	2,694±480
SS (mg/l)	230-810	575±192
TDS (mg/l)	8,140-13,520	10,610±1,240
NH_3-N (mg/l)	56.7-179	102±33
TKN (mg/l)	112-296	191±47
NO^-_2 (mg/l)	0.1-1.3	0.4±0.4
NO^-_3 (mg/l)	0.2-3.5	1.2±1.1
TP (mg/l)	4.8-11.6	5.2±2.3

During the treatment, GHG emission was also evaluated using close flux chamber technique. The gas emission was conducted over bare soil and soil with plant for comparison. Methane and carbon dioxide and nitrous oxide was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Treatment performance of the PRB system

Table 2 shows average effluent qualities from the pilot-scale PBR. Moderate organic and nutrient (N,P) removals of about 50-80% were achieved. The removal rates of pollutants were different between the experimental units using different media. The removals were higher in the experimental unit in which ferric sludge were added into clay: sand mixture. On average, BOD, COD and TKN removals were 76.1%, 68.5% and 73.5% respectively meanwhile those of clay: sand mixture alone were 69.5%, 63.3% and 66.9%. Moderate dissolved solids removals in terms of EC (48.4%) and salinity (54.1%) was also observed in PRB system suggesting the removal of salts through precipitation either in media or plant root zone. The enhanced treatment in ferric chloride sludge amended media was possible due to organic adsorption onto sludge particles and Fenton-like chemical reaction between hydrogen peroxide and ferric ions could take place in the ferric chloride amended media and helped improving organic removals. The presence of ferric chloride could yield an improvement of organic (COD) removal organics through the reaction of the iron salt (Fe^{3+}) with H_2O_2 to produces hydroperoxyl radical ($HO_2^{\cdot}$) (Amuda, 2006). Moreover, vegetation could also help improving organic and TKN removal possibly through enhancement of oxygen transfer into the soil by plant root system which subsequently promoted aerobic biodegradation by soil microorganisms.

Table 2. Effluent characteristics and steady state removal efficiencies.

Parameter	system 1 (clay: sand)			system 2 (clay: sludge: sand)			% removal (system 1)	% removal (system 2)
	port 1	port 2	Eff.	port 1	port 2	Eff.		
pH	7.86	7.76	7.71	8.22	8.07	7.79	-	-
EC (ds/m)	13.8	11.5	10.9	13.1	10.9	9.9	43.3	48.4
BOD (mg/l)	577	399	281	544	342	221	69.5	76.1
COD (mg/l)	1,824	1,331	989	1,630	1,196	849	63.3	68.5
SS (mg/l)	-	-	150	-	-	114	73.9	80.2
TDS (mg/l)	-	-	5,475	-	-	4,887	48.4	53.9
NH_3-N (mg/l)	55	52	31	50	45	28	69.5	73.4
TKN (mg/l)	147	112	63	134	92	51	66.9	73.5
NO^-_2 (mg/l)	0.2	0.15	0.05	0.2	0.16	0.04	-	-
NO^-_3 (mg/l)	0.9	0.5	0.24	0.86	0.66	0.21	-	-
TP (mg/l)	3.30	3.03	1.44	3.51	3.17	1.36	71.7	74.4

Growth of plant in the PRB system

During the operation of PRB system, the growth of plant (Guinea grass or *Panicum maximum TD* 58) was also studied. It was found that the growth of plant in system 2 was better than system 1. The provision of ferric chloride sludge in PRB media did not have negative impact on plant growth but on the other hand slightly promoted plant growth. The promotion of plant growth could be due to an improvement on physical properties of media for plant growth or the addition of ferric iron can also help in promoting photosynthesis mechanism of plant chlorophyll. Higher growth of plant in system 2 also promoted water removal through evapotranspiration resulting in lower effluent volume obtained from system 2 compared to system 1.

Greenhouse gas emission from the PRB system

Table 3 compares average methane, carbon dioxide and nitrous oxide emission rates from soil and soil-plant in PRB with different media. For all gases, the emission rates from bare soil were higher than soil-plant location indicating that the plant helped reducing greenhouse gas emission possibly due to improved oxygen transfer into their root system. The system 2 had lower emission rates than system 1 for all gases. These results suggested that an introduction of ferric chloride sludge into the media helped mitigating GHG emission during the treatment. Ferric chloride amended sludge media could promote the activity of Fe^{3+} reducing bacteria, resulting in a switch in electron flow from methanogenesis to Fe^{3+} reduction (Frenzel et al., 1999). Furthermore, plant–microbe interactions could lead to an efficient iron oxidation and reduction reaction in an oxidized rhizosphere environment (Roden and Wetzel, 1996).

Table 3. Emission rate of greenhouse gas from the PRB system.

System	location	Methane		Carbon dioxide		Nitrous oxide	
		range	average	Range	average	range	average
1	bare soil	16.3-52.6	31.2	215.7-570.2	380.7	0.21-0.69	0.42
	soil-plant	14.2-46.8	26.6	155.0-536.0	316.1	0.14-0.53	0.31
2	bare soil	11.3-41.7	22.6	112.5-508.9	293.6	0.07-0.43	0.21
	soil-plant	8.0-37.0	17.8	69.1-373.3	259.6	0.04-0.41	0.19

CONCLUSIONS

Permeable reactive barrier (PRB) with vegetation was successfully applied to remediate leachate from closed landfill site. Moderate removals of organic and nutrients was obtained during which highest removals of BOD, COD and TKN were 76.1%, 68.5% and 73.5%. Introduction of ferric chloride sludge into PRB media slightly improved the treatment performance of PRB while promoting plant growth. It also helped reducing greenhouse gas emission during the treatment. The growth of Guinea grass (*Panicum maximum TD 58*) in PRB system could be sustained in long term operation and it provided positive effect to the treatment and reducing greenhouse gas emission.

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(S6) Effects of Gamma Irradiation on Viability and Infectivity of *Cryptosporidiumspp.*Oocystsin Municipal Wastewater Effluent

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Abstract

The ability of *Cryptosporidiumspp.*oocysts to excyst and inclusion/exlusion of vital dyes DAPI, PI and SYTO-59 were examined after gamma irradiation at various doses (1,5,10,15 and 20kGy). The assays were repeated ten days after thei rradiation for post irradiation effects. The oocysts exposed to 10 kGy were not viable. At 10 kGy the gamma irradiated oocysts were still capable to excyst, however, after ten days they had completely lost the ability to excyst.

Keywords

*Cryptosporidiumspp.,*DAPI,PI, SYTO-59, in vitro excystation, gamma irradiation

INTRODUCTION

Determination of *Cryptosporidium* oocyst in activation following the disinfection procedure has a great importance for the public health as the minimum infectiousdose is low (lessthan 10 oocysts) (3). Theobjectives of thepresentstudywere (i) toexaminetheeffects of gamma irradiation on in vitroexcystation, (ii) todeterminewhetherthepermeability of theoocystswallto DAPI, PI andSYTO-59would be changedbyexposureto gamma irradiationand ten daysafterthegamma irradiation.

MATERIALS and METHODS

WastewaterTreatmentPlant

Treated municipal wastewater samples were collected at the Ankara Central Municipal Wastewater Treatment Plant.

OocystRecoveryandStaining

The oocysts were concentrated and purified by sucrose flotation and Cesium Chloride gradient techniques (4). The viability of oocysts was assessed using the vital-dye assay which relies on inclusion/exclusion of two vital dyes DAPI and PI(2), and SYTO-59 (1). For in vitro excystation the protocol S was carried out as described(2).

Gamma irradiationexperiments

The irradiation were conducted at ^{60}Co Gamma Cell at Sarayköy Nuclear Research and Education Center. A total of five doses of irradiation (1-20kGy) were performed.

RESULTS

Untreated control oocysts maintained 92.2% excystation rates , but oocysts receiving 10 kGydose of irradiationwerecompletelyincapable of excystation 10 daysafterhavingbeentreated (Fig 1and 2,andTable 1). Theviability is reduced at thedose of 5 kGy, andtheoocystsirradiatedwith 10 kGyweremainlynonviable (PI orSYTO-59positive)(Table 1).Inthecontrol, oocystswerehighlyviable (Table 1, Figures 3 and 4).

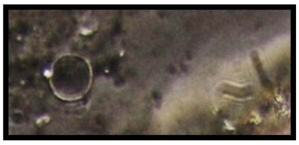

Fig 1. Emptyoocystandfreesporozoites.
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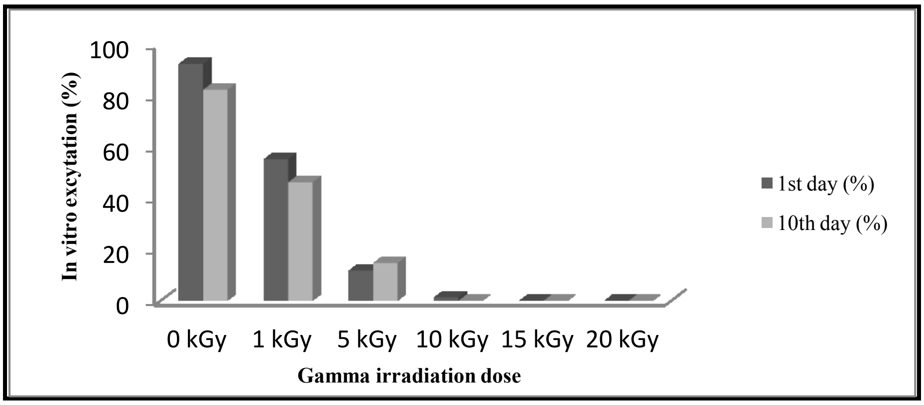

Fig 2. Effects of ionizingradiation on in vitroexcystation of oocysts on firstdayand 10 daysafterirradiation

Table 1. Effects of gamma irradiation on oocystexcystationandpermeabilityto DAPI-PI and SYTO 59 fluorescentdyes

Irradiationdose (kGy)	**Excystedoocysts (%)**		**Viableoocysts (%) DAPI/PI**		**Viableoocysts (%) SYTO-59**	
	1st day	**10th day**	**1st day**	**10th day**	**1st day**	**10th day**
0	92.2	82.2	72.8	67.2	85.2	82.7
1	55.1	46.1	36.7	22.7	36.5	19.9
5	11.8	14.7	8.6	5.6	7.3	5.1
10	1.3	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND	ND

(ND) : Not detected

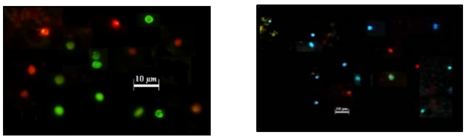

Fig.3 and 4. Viableandnonviableoocystswith DAPI-PI (Left)(40x), andSYTO-59 (right) (60x)

DISCUSSION

10 kGyorhigherdoses of ionizing irradiation prevented the ability of *Cryptosporidium* oocyststoexcystand rendered the contained sporozoites non viable. These results were compatible with the other studies (5,6) Vital dye based assays and in vitro excystation are good indicators of viability to examine the effects of disifection processes.

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(S7) Examination of Selected Alternative Settlement Tests at Small-scale Activated Sludge Plants

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Abstract

The settling behaviour of activated sludge in wastewater treatment plants (WWTPs) is a common operational test used to assess performance and monitor changes in the treatment process. In particular, the sludge volume index (SVI) has long been recognised as a useful index of plant operation. Recent surveys of plant managers and custodians at small and medium-scale activated sludge (WWTPs) in Ireland indicate that, despite being a simple test and providing informative data, the SVI tests are generally not utilised. Similar trends can be found in other countries, particularly, at small facilities without resident staff. At all plants surveyed, a variation of volumetric settleable solids is the only routine operational settlement test being carried out; test frequency varies from daily to weekly. Most commonly, the test comprises a 30-min period of quiescent settling in an Imhoff cone ('cone test'). The resultant volume of sludge settled is the recorded, however, cone test results are not comparable to the standard methods defined stirred settled sludge volume (SSV) test. Furthermore it cannot be used to determine SVI and is thus of limited value. The settleable solids test, on which the cone test is based, is recommended for dilute sludges, which are frequently not representative of activated sludge processes.

This study compared stirred and quiescent 30-min settlement tests carried out in 1.3L and 2L-settleometer vessels, cone tests and quiescent settling in standard 1L-graduated cylinders; activated sludge samples (n = 37) from 8 small-medium scale activated sludge plants were tested. The results show that (i) 30-min quiescent settling in an Imhoff cone generally yields higher settled volumes than quiescent settling in a 1.3L or 2L-settleometer vessel, (ii) equivalent results are derived from an Imhoff cone and a graduated cylinder and (iii) quiescent settling in 1.3L and 2L-settleometers yield higher results than stirred settling in the same vessels. A correlation is observed between the quiescent settling in the 1.3L-settleometer and SSV determined as per Standard Methods. A relationship is also presented to derive SSV from quiescent settling. This may facilitate estimation of SVI using simple apparatus. The results presented indicate that by replacing the vessel used in the 'cone test' with a settleometer, more meaningful information, that could significantly improve facility management, can be derived. Future work is focused on establishing that dilution can significantly reduce settlement test-time while maintaining SVI measurement accuracy.

Keywords

Sludge Volume Index (SVI); Settled Sludge Volume (SSV); Performance and Monitoring Wastewater Treatment Plants; Activated Sludge.

Introduction

The Sludge Volume Index (SVI), was by 1969, considered the standard measure of the physical characteristics of activated sludge.[1,2] Despite reported limitations and the development of alternative settleability indices, the SVI is still widely reported in literature and, along with zone settling rate, is acknowledged as an important measure for quantifying the settling characteristics of activated sludge.[2,3,4] Experience has shown that the SVI is an efficient and useful parameter in routine process control and optimisation.[6,7] SVI, is measured as the volume (ml) occupied by 1g of suspension after 30 min of settling. Thus calculation of SVI requires knowledge of the suspended solids (SS) concentration of a sample and its 30-min Settled Sludge Volume (SSV).[4] The SSV is the volume of sludge occupied by a 1L suspension in a 1L-graduated cylinder at a measured time interval after continuous stirring with 1 or more thin rods at approximately 4rpm (Method 2710C, APHA, 2013). A modified SSV (Method 2710I, APHA, 2013) has been developed that uses a 2L, 120mm diameter cylindrical vessel equipped with 4 stirring rods rotating at approximately 2rpm.[7] The results from standard and modified SSV methods are not considered comparable and only SSV as determined by Method 2710C is used to derive SVI.[7] An alternative, quiescent, settleability test (Method 2540D, APHA 2013) is recommended for dilute sludges; these are not generally a feature of activated sludge processes.[4] This 60-min test is carried out in an Imhoff cone on a 1L sample; the results are not used to derive SVI. In an effort to address the variation of SVI with SS concentration, alternative tests have been proposed, in particular the Stirred Specific Volume Index ($SSVI_{3.5}$) and Diluted SVI (DSVI). In measuring $SSVI_{3.5}$, a bespoke apparatus comprising a 4L-settling column fitted with stirring rods is used to determine the volume of settled sludge at a concentration of 3,500 mg SS/L. DSVI requires recording the settling of alternative sludge dilutions in 1L-graduated cylinders.[3,5] Both alternate methodologies require separate measurement of SS concentration and more manual intervention than that for standard SVI. Thus while there are numerous methodologies for carrying analysing activated sludge it is clear that many are seen as too cumbersome or entail expensive equipment and are thus not widely used. Where simple methods are used (e.g. the cone test) the data may not be suitable to inform good operational practices.

Internationally, the lack of adequate operational practices in smaller and decentralised wastewater treatment plants (WWTPs) is an ongoing challenge.[6,8] Given the operation water and wastewater treatment plants are often the single largest expense for municipal authorities, and these plants are increasingly required to adhere to ever more stringent standards, the need for robust operational control WWTPs is evident. However this must be balanced by practical considerations such as the reliability, operational benefits, cost and ease of implementation of routine testing and monitoring.

This study examines the relationship between results derived from currently practiced settlement testing methods and from Standard Method methodologies and seeks to provide simple relationships to estimate SVI from quiescent tests. Comparative 30-min settlement tests were carried out on sludge samples from 8 small-medium scale activated sludge WWTPs. The results of 1.3L and 2L-settleometer stirred and unstirred tests, cone tests and 1L-graduated cylinder unstirred tests were compared. This simple sludge measurement methodology, similar to current practice, yet yielding more meaningful results could improve WWTP operation and efficiency.

Materials and Methods

Wastewater Treatment Plant (WWTP) Surveys. A comprehensive survey was designed to gather data from activated sludge plants, in particular, in relation to plant operation, monitoring and control testing, size and wastewater composition. Plant managers and/or custodians of 12 municipal activated sludge WWTPs were interviewed.

Automated SSV Rig. A bespoke SSV rig was constructed NUI Galway to test activated sludge samples in accordance with the Standard Methods. The rig comprises 2 independent aluminium frames each with 2 motors and gear boxes. Interchangeable paddle assemblies provide stirring in 2L and 1.3L-settleometer vessels.

Settlement Tests. Stirred settlement tests were carried out in 2 L (183 mm H, 125 mm Dia.) and 1.3L (213mm H, 100mm Dia.) polycarbonate vessels. Quiescent settlement tests were carried out in the 2L and 1.3L-vessels, in 1L-polypropylene (PP) graduated cylinders and 1L-PP Imhoff cones. Testing was carried out on samples collected from 8 municipal WWTPs over a 5-month period. The sludge volume in each vessel was recorded at 5-min intervals for a minimum of 30 min. The SS concentration of each test sample was determined as per Standard Methods 2540D.

Samples. Activated sludge samples were collected and tested on the sampling day or refrigerated to be tested within 36 hours of sampling. All samples were taken at the downstream end of the aeration tanks and where a WWTP had more than one aeration tank, separate samples were taken from each tank and these were treated as independent samples.

Results and Analysis

Survey Results. WWTPs varied in size from 300-25,000 PE with maximum inflows in the range 108–20,000m^3/day. Staffing at the plants varied from 3 full-time personnel to 1 part-time custodian. The surveys established that at all plants, a variation of the Standard Methods Volumetric Settleable Solids is used as the only routine operational settlement test. Most commonly, this 'cone test' is carried out over a 30-min period of quiescent settling in an Imhoff cone. Neither SVI nor SSV tests are carried out routinely at any of the surveyed WWTPs. It is also noted that, suitable equipment to carry out the SSV or modified SSV tests as per Standard Methods is not available in the plants. Equipment to carry out SSVI$_{3.5}$ is available commercially but considered expensive by operators.

Table 1. WWTP Characteristics

Plant Ref	Size Range	Daily Inflow		Average Wastewater Composition		
	(PE)	Min (m^3/d)	Max (m^3/d)	Domestic (%)	Industrial etc. (%)	Other* (%)
01, 09	20,000 – 30,000	3,500	,000	62	28	10
03, 04, 11, 12	3,000 - 6,000	688	1,725	91	7	2
08, 10	1,400 -1500	260	500	98	2	0

* includes imported leachate and/or slurry.

Effect of Stirring Speed on the SSV. Activated sludge samples (n = 12) from 3 WWTPs were subject to unstirred and stirred 30-min settlement in 1.3L and 2L-settlometer vessels varying the stirring speed and paddle arrangement. Sample concentrations ranged from 2,222 to 8,350 mg MLSS/L. The results indicated that for tests carried out in settleometers, the 30 min sludge volume derived from the unstirred tests was significantly higher than those derived from stirred samples. Although the volumes resulting from stirring at 2rpm and 4rpm are similar, T-test analyses indicate a statistical significance between the data sets. Comparing datasets from the 2 and 4rpm stirring speed in each vessel, Pearson correlation coefficients of 0.380 for the 1.3L-vessel and 0.603 for the

2L-vessels were derived indicating a positive linear dependence for the 2L vessel between stirring speed and settled volumes.

Effect of Use of Settleometers on the SSV. 31 activated sludge samples from 8 WWTPs were subject to 30-min unstirred settling in an Imhoff cone, 1L-graduated cylinder, 1.3L-settleometer and 2L-settleometer (Fig. 1). Sample concentrations ranged from 1,036 to 8,350 mg MLSS/L. Statistical analyses do not support a difference in the mean SSV resultant from use of the Imhoff cone and 1L-graduated cylinder. In general, the results derived from the 1.3 and 2L-settleometer were lower than those measured in both the Imhoff cone and 1L graduated cylinder.

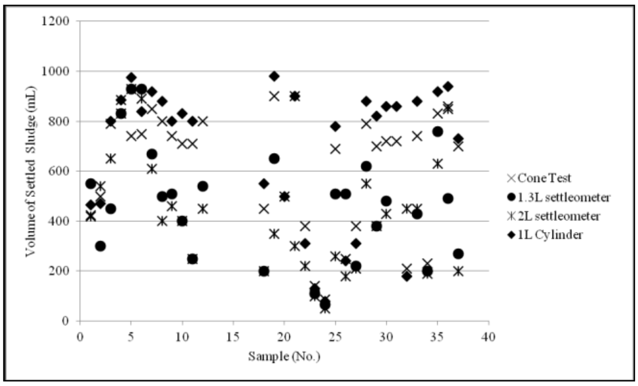

Figure 1. Comparison between unstirred settling tests

Effect of Stirring in Settleometers on the SSV. 26 activated sludge samples were subject to 30-min stirred and unstirred settling in 1.3L-settleometers and 29 samples in 2L-settleometers. Stirred tests in 1.3L-vessels were performed at 4rpm and 2rpm in 2L–vessels; consistent with the Standard Methods.

Sample concentrations ranged from 1,026 to 10,236 mg MLSS/l. The results indicate that the 30-min sludge volume from the unstirred tests is generally higher than that from unstirred test samples (Figs. 2 & 3). Pearson correlation coefficients of 0.816 and 0.642, respectively, were derived for the stirred verses unstirred settlement volumes in the 1.3L and 2L-settleometers, indicating a strong positive linear dependence between the stirred and unstirred SSV values in both vessels and in particular for the 1.3L vessel.

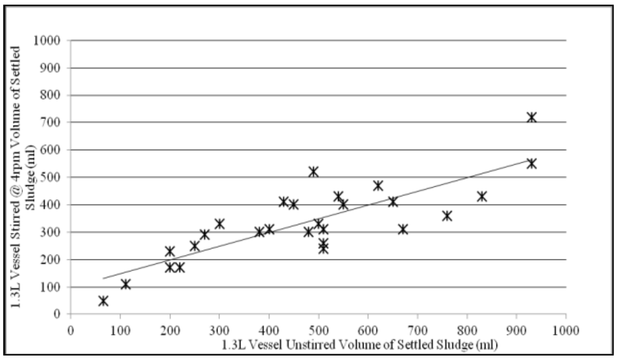

Figure 2. 1.3L Vessel Stirred v Unstirred

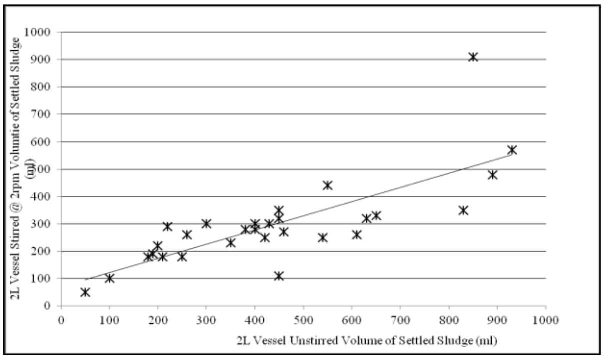

Figure 3. 2L Vessel Stirred v Unstirred

Deriving Stirred SSV and SVI from Quiescent Settled Sludge Volume in 1.3 L Settleometer. Based on the relationship established from the analysis carried out in the 1.3L vessel, stirred SSV values were estimated from measured unstirred sludge volumes. These SSV values were then used to estimate SVI. When compared with measured SVI values, it was found that 85% of the calculated results differed from measured by less than 25 mL/g with 35% differing by less than 10 mL/g. This indicates that calculated SVI values, using an unstirred test, could be used as an alternative to SVI values measured using Standard Methods.

Conclusions

The results of this study indicate the existence of useful correlations between stirred and unstirred SVI tests. On the basis of the results observed, bespoke methodologies could be designed and calibrated for individual plants that would replace current practice using the cone test. Thus more meaningful and applicable results can be derived from operational testing providing operators and management with decision making information to better control and monitor plant operations. Further work to refine this methodology is underway.

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(S8) Treatment of Biomass Gasification Wastewater in a Rotating Biological Contactor

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Abstract

Treatment of biomass gasifier wastewater is attempted with a biofilm developed using activated sludge microbial consortium and *Exiguobacterium aurantiacum*. *E. aurantiacum* had the unique ability of degrade various components in gasifier wastewater as sole substrate. The biomass gasifier wastewater with a chemical oxygen demand (COD) of 1462±11 mg/L contained, phenolics, heterocyclics and polynuclear aromatic hydrocarbons (PAHs). The nutrient supplemented wastewater was treated in a 3-stage rotating biological contactor (RBC, 4 L working volume). Performance of the RBC was evaluated at various flow rates to determine the optimum hydraulic and organic loading rate (HLR and OLR). A flow rate of 2.5 ml/min with HLR and OLR of 0.004 $m^3/m^2/d$ and 6.3 g-COD/m^2/d, respectively, resulted in good reduction in COD and TOC. Biochemical tests on colonies from the biofilm revealed the dominance of *E. aurantiacum* in the biofilm across all the stages.

Keywords

Active biofilm; biomass gasification; *Exiguobacterium aurantiacum*; phenolics; polynucleur aromatic hydrocarbons

INTRODUCTION

There is a great interest in generation of electricity through biomass gasification particularly in rural India where abundant biomass is available. The wet scrubbing method commonly employed in gas cleaning results in generation of wastewater which is characterized by the presence of phenolics, PAHs and heterocyclics. Coal gasification wastewater treatment has been explored extensively, however, only limited studies are available on treatment of biomass gasifier wastewater. An immobilized cell bioreactor with granular activated carbon as the inert material inoculated with two strains of *Pseudomonas* was used to treat a wood based biomass gasifier wastewater. The chemical oxygen demand (COD) in this wastewater was caused by benzene, naphthalene, phenanthrene, pyridine, quinoline, and isoquinoline. For hydraulic retention time (HRT) of 24 hrs, 96% reduction in COD was reported (Tian et al., 2005). Batch studies on degradation of biomass gasifier wastewater using *Pseudomonas, Micrococcus*, *Escherichia coli* and *Staphylococcus* yielded 48% reduction in phenol after 50 hrs and a maximum degradation rate of 15 mg/hr was observed (Lata et al., 2005). Other constituents in the wastewater caused considerable fluctuations in the degradation rate of phenol. Physicochemical treatment of biomass gasifier wastewater using alum, lime and powdered activated carbon (PAC) resulted in 100% removal of phenol with 96% reduction in COD (Mehta and Chavan, 2009).

This work reports the treatment of biomass gasifier wastewater in a rotating biological contactor (RBC). The biofilm is formed using activated sludge microorganisms along with *Exiguobacterium aurantiacum*. In batch culture studies *E. aurantiacum* was found to depict an unique ability for utilizing several phenolic compounds, polynuclear aromatic hydrocarbons (PAHs) and heterocyclics as sole source of carbon and energy. Hence, it was chosen for biofilm formation in attached growth bioreactor for treatment of gasifier wastewater in continuous flow through mode studies. Development of a biological treatment method for economical and effective treatment of biomass gasifier wastewater would facilitate the widespread deployment of biomass gasifiers.

MATERIALS AND METHODS

Chemicals and Bacterial Culture

Various nutrients for mineral media preparation were procured from Merck Ltd., Mumbai, India and were of analytical grade. Osmium tetroxide (10%) and glutraldehyde (25%) used for Scanning electron microscopy (SEM) were obtained from Himedia, Mumbai, India. *E. aurantiacum* (AS1) (Mohanty and Mukherji, 2008) was isolated from oil contaminated soil obtained from a tanker refueling station in an airport using diesel as sole substrate (Mumbai, India).

Maintenance of culture

For the reactor studies involving activated sludge and *E. aurantiacum*, a synthetic wastewater containing phenol (250 mg/l), pyridine (280 mg/L), quinoline (280 mg/l), benzene (200 mg/l), naphthalene(60 mg/l), phenanthrene (0.5 mg/l), fluoranthene (0.2 mg/l) and pyrene (0.12 mg/l) was also supplemented with mineral salts present in the bacteriological nutrient medium (Tian et al., 2005). It had a chemical oxygen demand (COD) of 1462±11 mg/L.

Reactor Start Up and Hydraulic retention time (HRT) studies

After the development of biofilm on the discs, flow through study was initiated and HRT was varied from 17 hrs to 88 hrs in 3 increments. At HRT of 14 hrs severe sloughing was observed hence, lower HRTs were not selected. The reactor was operated at HRT of 88, 44.5, 26.7 and 17.6 hrs, respectively. After every change in flow rate, the reactor was operated for 7 to 8 days before sampling and analysis was initiated so as to avoid the unsteady state. Subsequently, about 7 pair of influent and effluent samples were analysed in duplicate during the steady state condition. After these optimization studies, the reactor was operated at a HRT of 26.67 hrs for the next 40 days and various parameters were analysed for each stage of the RBC. The corresponding hydraulic loading and COD loading were 0.004 $m^{3/}m^2$.d and 6.3g-COD/m^2.d, respectively. The various parameters were analyzed regularly from all the three stages.

Analytical techniques and Microscopy

The performance of the reactor was analyzed by measuring various parameters using analytical techniques recommended in Standard Methods (APHA, 2000). The parameters measured daily were total organic carbon (TOC analyser, Schimadzu, Japan), COD (closed reflux method, HACH, Germany), pH and dissolved oxygen (DO probe, HACH, Germany). For scanning electron microscopy, a (0.5*0.5) cm^2 biofilm was removed from the mid disc of each stage of the reactor. The samples were immediately fixed with 2.5% glutraldehyde for 3 hrs and then washed with Sorenson's phosphate buffer. Secondary fixation was done with 2% osmium tetraoxide and the samples were allowed to stand for 1 hr. After washing with phosphate buffer they were dehydrated in a graded ethanol series (25%, 50%, 75% and 100%) and dried overnight at 50^{o}C. Each specimen coated with gold was viewed on a Fei Quanta 200 HV (Hillsboro, USA) scanning electron microscope.

RESULTS AND DISCUSSION

COD and TOC reduction

After development of the biofilm the RBC was run at 4 different flow rates 0.75, 1.5, 2.5 and 3.5 ml/min resulting in HRT of 88, 44.5, 26.7 and 18.8 hrs, respectively. Only minor changes were observed for average COD removal efficiency for 0.75, 1.5 and 2.5 ml/min, i.e., 91.8, 90.9 and 88.4 respectively. Similarly, TOC removal efficiency did not vary much for 0.75 and 1.5 ml/min which were 94.2 % and 90.3%, respectively. TOC removal efficiency for 2.5 ml/min was 84.1% and for 0.75

ml/min it was 74.4%. Subsequent studies were all conducted at 2.5 ml/min which corresponds to 26.7 hrs HRT. The removal of COD and TOC at various HRTs is depicted in Fig. 1a-b.

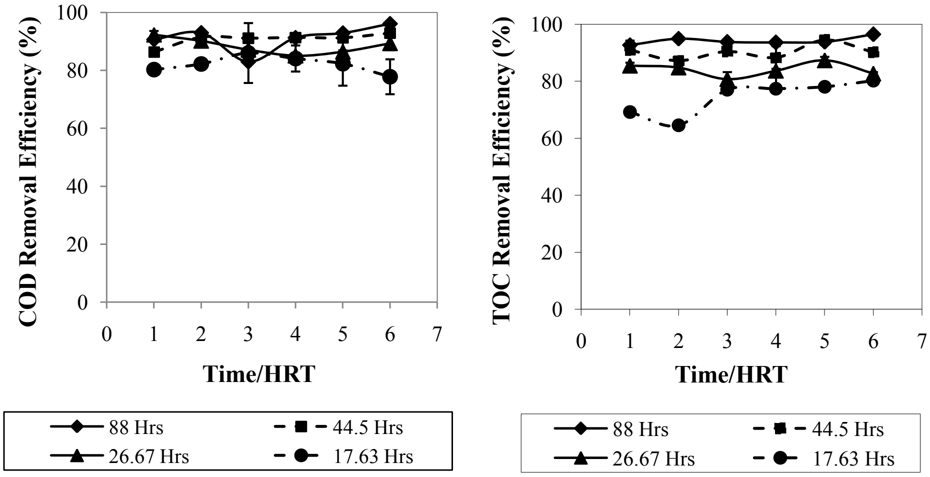

Figure. 1: (a) COD and (b) TOC removal efficiency in the RBC operated at various HRTs

Subsequently, the RBC was run for 40 days at pseudo steady state at a HRT of 26.7 hrs. and a flow rate of 2.5 ml/min. The corresponding hydraulic loading and COD loading were 0.004 m^3/m^2.d and 6.3 g COD/m^2.d, respectively. The COD reduction was checked for each stage. The average COD removal for the first, second and third stage were 53.2%, 27% and 11.3% amounting to an overall reduction of 91.5%. The average TOC reduction for the three stages were 47%, 25.9% and 15.3% amounting to 88.2% TOC removal. The final COD and TOC were 126.9 mg/l and 35.1 mg/l, respectively (Figure2).

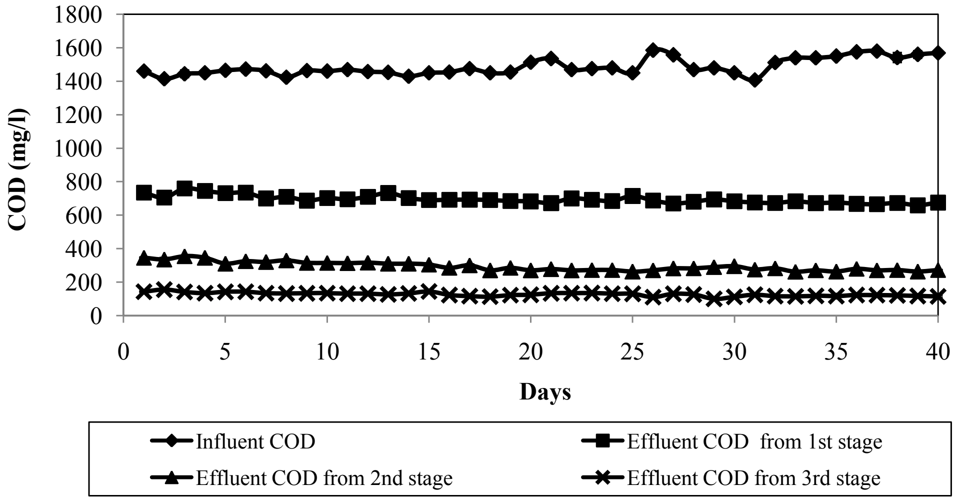

Figure 2: Influent and Effluent COD for the 1st, 2nd and 3rd stage of the RBC at 26.7 hrs HRT

Scanning Electron Microscopy

Scanning electron microscopy was performed on the 10th day during the continuous run of the reactor at a flow rate of 2.5 ml/min by removing (0.5*0.5) cm^2 biofilm from the mid disc of each stage. The first stage had good development of extracellular polymers with chains of bacteria forming a surface whereas the third stage biofilm did not have a well developed network of exopolymeric mesh. The coral reef and meshed network structure which is normally present in a biofilm (Di lorenzo et al., 2005) was observed for the biofilm in each stage although the extent of development varied. Rod shaped bacteria were found in abundance in the biofilm. The coral reef type structures are typically reported for mature biofilms (Di lorenzo et al., 2005).

Characterization of cultures in the biofilm

A smear of the biofilm from each stage was streaked on nutrient agar plates. Three types of colonies were observed in all the three stages with abundance of one type of colony. The most predominant colonies were convex, butyrous, gold coloured and smooth with diameter up to 2.5 mm. When each of the three colonies were added to batch flasks containing pyrene as sole substrate only the gold coloured colonies which were also the most predominant one demonstrated growth on pyrene. Each of the three colonies was also re-streaked on polypetone yeast glucose (PPYG) agar (Collins et al., 1983). Only the most predominant colony grew on PPYG media in butyrous, convex, smooth orange coloured colonies of up to 2.5 mm diameter whereas the other two did not grow on this medium. Growth on PPYG agar giving these colony characteristics established that the most predominant colony is *E. aurantiacum*. A small section of the biofilm (0.5*0.5 cm2) was removed from the mid-disc of each stage and vortex mixed with 5 ml of 2% phosphate buffer (Mohanty and Mukherji, 2008) in presence of beads to obtain a uniform suspension. Various dilutions were plated on nutrient agar plates and the viable counts were observed. Relative abundance of *E. aurantiacum* in the first, second and third stage biofilm was found to be 60%, 68% and 65%, respectively. During reactor start-up its abundance was only 24%. Thus its abundance in the biofilm increased by virtue of its ability to degrade many of the organic contaminants present in the gasifier wastewater.

CONCLUSION

An attached growth bioreactor containing a biofilm composed of activated sludge microorganisms and *E. aurantiacum* could effectively treat gasifier wastewater. HRT of 26.7 hrs, HLR of 0.004 $m^3/m^2/d$ and organic loading rate of 6.3 g-COD/m^2/d was found to be optimum for flow through mode operation of the RBC. The first stage of the RBC accounted for highest COD removal of 53.2%. For the first cumulative COD removal efficiency was 80.2% respectively, while for the overall system the average COD removal efficiency was 91.5%. Abundance of *E. aurantiacum* in the biofilm was established for each of the three stages. Thus, *E. aurantiacum* with mixed microbial consortia can be utilized for the treatment of biomass gasifier wastewater.

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(S9) Stability of aerobic granular sludge under pH stress

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ABSTRACT

pH variation can influence the stability and bioactivity of microbial aggregates. In order to investigate the impact of pH variation on aerobic granular sludge a 9-day pH shock was imposed on three identical sequencing batch reactors (SBR),namely R1, R2 and R3. Mature granular sludge cultivated using sodium acetate as the sole carbon sourcewas used. During the shockthe operating pH was changed to 6 and 9 in R1 and R3, respectively, with R2,as control reactor, operating under pH between 7.8 and 8 as usual. 9 days operation under pH 6 did not have any impact on granule stability and physical properties; while, operating under pH 9 resulted in significant destroying effects on granule structure and stability. After four days of operation under pH 9 almost all granules disintegrated and no recovery observed in the system during the shock. Therefore, high pH has destroying impact on granule stability; however, the pH limit causing disintegration of granule depends on the granule structure, composition and compactness which could be influenced by feed composition and other operating conditions such as aeration intensity.

Keywords

Aerobic granular sludge; sodium acetate; pH shock; stability; SBR

INTRODUCTION

Aerobic granular sludge with distinguishing physical properties is considered to be a paradigm shift in biological suspended growth wastewater treatment (Bathe et al.2005). The two main concerns with this new technology are the rate of formation of granules and their physical stability in the long term operation. The extracellular polymeric substances (EPS) were found to significantly affect the stability of aerobic granules(Seviour et al. 2009a; Tay et al. 2001) .These polymers can affect the physical properties of microbial aggregates and explain the significant difference between the physical characteristics of granular and flocculant sludge, e.g. degree of compaction and the dense structure (Seviour et al. 2009a; Sutherland 2001), therefore, by weakening the polymeric matrix the stability of granules could be threatened. Seviour et al. (2009b) stated that environmental conditions such as temperature, pH and ion strenght could negatively affect the EPS matrix. In this study the impact of long term acidic and alkaline pH shock (which may affect the EPS matrix) on the stability of aerobic granular sludge is investigated.

METHODOLOGY

Three identical SBRs namely R1, R2 and R3 with working volume of 5.7L and HRT of 8h were used in this study. R2 was kept as the control reactor working at pH range of 7.8-8, while the acidic (pH6) and alkaline (pH9) pH shocks were imposed on R1 and R3, respectively; all other operating conditions stayed the same in the three reactors. Mature granular sludge cultivated in the bench-scale SBRs, with more than 95%, 90% and 99% in COD, ammonia and phosphorus removal, respectively, and 1.4mm in diameterwas used as biomass source. Synthetic wastewater, with acetate as only carbonsourcewas used in this study. The influent COD concentration was maintained at about 850±20 mgCOD L^{-1}, imposing

Organic Loading Rate (OLR) of 2.55kgCODm^{-3}d^{-1}.Effluent TSS (ETSS) was measured followingStandard Methods (APHA, 1998).Size distribution of the flocs was measured usingMalvern Mastersizer2000 series.EPS has been extracted according to Adav and Lee (2008). Polysaccharide (PS) concentration was measured followingDubois et al.(1956), using glucose as standard. Protein (PN) content was measured using the Modified Lowry Assay Kit with bovine serum albumin (BSA) as standard solution.

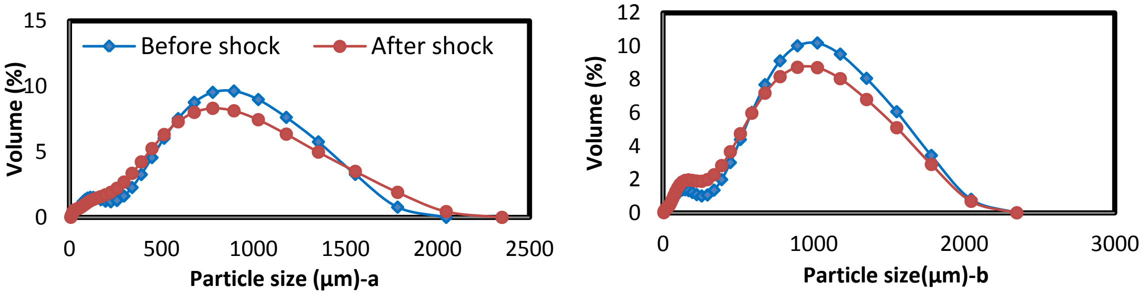
RESULTS AND DISCUSSION

Acidic pH and its impact on granular sludge

The results of this study indicate that long-term (9 days) of acidic pH 6 did not have significant impact on granule stability. Slight changes in the size distribution, protein to polysaccharide ratio (PN/PS) and ETSS show the granule tolerance to pH as low as 6, Figs.1and2. This observation can be explained by the impact of pH on gel-forming EPS. Seviour et al. (2009a) observed that at neutral and acidic pH regions, the EPS extracted from granular sludge stays as a strong gel which is the distinguisherd feature of aerobic granules. The presence of EPS matrix as a strong gel could prove the stability of aerobic granules at acidic pH regions. High PN/PS ratio is considered as one of the characteristics of granular sludge (Adav and Lee 2008; Mcswain et al. 2005), after decreasing the pH value to 6, PN/PS ratio initially decreased from 1.8 to 1.5 and after two days increased to more than 2, indicating the recovery of EPS matrix composition at low pH, Fig.1.

Fig.1 a) PN/PS ratio and b) the effluent TSS concentration during the pH shock.

Size distribution can be considered as one of the parametersfor monitoring the granule disintegration. Fig.2 shows the size distribution in three reactors before shock and 7 days after shock. The size distribution in R1 (pH 6) did not change significantly before and after shock. R1 and R2 (the control) showed the same change in size distribution, indicating that pH 6 did not impact the granules' size and stability in long term.



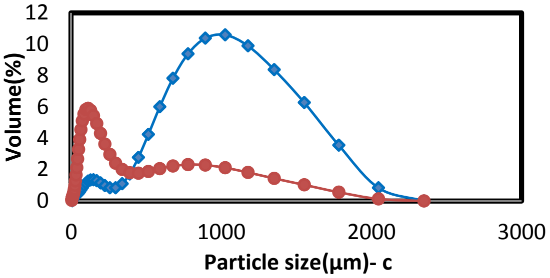


Fig.2 Size distribution before and after shock: a) R1 (pH6) b) R2 (control) and c) R3 (pH9)

Alkaline pH and effects on granular sludge

Unlike the very slight impact of low pH on granule stability, high pH had destroying effects on granules. After increasing pH to 9 the effluent suspended solid increased significantly, up to 450mg/l, indicating the granules disintegration and washout(Fig.1). Moreover, a considerable change observed in particle size distribution, the peak of the size distribution graph changedtoward smaller size ranges(from >1000μm to < 500μm) indicating the granules breakage(Fig.2).Alkali treatment has been used to extract EPS from aerobic granular sludge ((Seviour et al., 2010); Lin et al.2010) which shows the solubility and instability of polymeric matrix at high pH. The PN/PS ratio decreased from 1.6 to almost 1 during the first days after shock (Fig.1). Decrease in PN/PS ratio in R3 could be due to higher concentration of dissolved polysaccharide at high pH.According to Seviour et al. (2009a) polysaccharide plays an important role in the gel forming EPS in granular sludge, under high pH (>9) it colud transferfrom gel to solution.By dissolution of polysaccharide at high pH, the strengthof the EPS matrix and consequently granules' stabilitycould be affected.

CONCLUSION

The results from this study indicate the stability of aerobic granule under long-term low pH (6) shock; while, instability of granular biomass in long termalkaline pH (9) shock was observed. This instability could be due to dissolution of the granule's EPS matrix under high pH (Seviour et al.2009a).Lin et al. (2010) and Lin et al.(2008) stated that the extracted EPS using alkali treatment from acetate fed aerobic granular sludge is more than the municipal wastewater-fed ones. These findings indicate the difference in the EPS matrix of biomass fed with different typesof wastewater causing different stabilities in granules.However, still more research is required to investigate the stability of aerobic granules cultivated using various types of carbon source under variable environmental conditions such as pH and temperature.

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(S10) Design issues for innovative wastewater treatment plants to improve coping with extreme weather events

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Abstract

New innovative technologies for wastewater treatment are continuously developed being driven by technical, environmental and economical challenges; eventually, these technologies are implemented in real-scale wastewater treatment plants (WWTPs). WWTPs are expected to be seriously affected by extreme weather events. Existing WWTPs may cope with these events up to a certain degree via the application of contingency plans; these plans can be taken into account in the design of new WWTPs using innovative technologies. In this work the main aspects and impacts of extreme weather events on WWTPs are presented and general design suggestions that improve coping with these impacts are discussed; these suggestions can be taken into account in the development of innovative technologies and their implementation in real WWTPs to minimise environmental impacts. Integrated mathematical models can be used to assess these impacts and to specify the suggested design actions in WWTPs involving innovative technologies.

Keywords

Innovative technologies, extreme weather events; process design; hydraulic design; wastewater treatment plants; environmental impacts.

INTRODUCTION

In the Mediterranean region the main consequences of climate change are the rise in the average air temperatures, the high variability in precipitation and the extreme weather events (floods and droughts). Extraordinary strong flash rains or long periods of drought are expected to be more frequent and severe as a result of the increase of average temperature, decrease of precipitation amount and its different spread out during the year. In Greece by 2050 and by 2100 sea level is expected to be 15 cm and 34 cm higher than today, respectively; consequently, low lying areas of continental Greece and the Greek islands will be seriously affected. By 2100 it is estimated that about 307 km^2 of land will be lost. The lagoons of Kotyhi, Messologi, Amvrakikos and Porto Lagos will become shallow bays or gulfs, while the island of Kos, Northern Crete and Western Thermaikos Gulf are among the high risk areas. Temperature is also expected to rise significantly and the droughts periods will prolong; during the period 1990-2000 the number of drought periods was already three times more than those recorded during the previous thirty-year period and according to predictions the temperature will increase 2^oC until the end of the 21st century.

Wastewater Treatment Plants (WWTPs) in Greece are expected to be seriously affected by these extreme weather events (http://www.coastalwiki.org/coastalwiki/Main_Page). For existing WWTPs, in order to cope with the consequences of these events it is required to formulate efficient and effective Contingency Plans (SAEPA, 2009). These are plans of actions in extreme weather events of foreseeable emergencies that help preventing and managing these incidents that could result in environmental impacts, such as environmental harm, e.g. soil, surface or groundwater pollution, environmental nuisance, e.g. excessive odour, noise, dust or smoke, and unacceptable risk to public health (DSP, 2004). Moreover, information from such Contingency Plans can be used in the design of new WWTPs that involve innovative technologies.

In this work the main aspects and impacts of extreme weather events on WWTPs are presented and the main design issues that improve coping with these impacts are discussed; these issues may be taken into account in the development of new innovative treatment technologies and their implementation in real WWTPs to avoid or minimise expected environmental impacts.

ASPECTS AND IMPACTS OF EXTREME WEATHER EVENTS

In order to face the expected environmental impacts of extreme weather events on new innovative WWTPs, a list of the expected impacts and the general design issues that can be applied in order to face these environmental impacts can be formulated. This list can be in the form of Table 1 that is very similar to the Table of Aspects and environmental Impacts (TAI), which is often used in the formulation of Contingency Plans (SAEPA, 2009). In Table 1 the following are shown: (1) the aspect, (2) the aspect details, (3) the design suggestions to face the impacts of the aspects, and (4) the subsequent environmental impacts, when these aspects are not faced; these are based on the proposed Contingency Plans for sanitation systems in Greece (Stamou et al., 2011).

Table 1 depicts that storms, heavy rainfall events and flood events may have the following main four aspects: (AR1) increased runoff, (AR2) water level rise of seas and rivers, (AR3) water level rise of seas and rivers (AR3), and (AR4) flooding and storm surges. Moreover, droughts or prolonged periods without any rainfall can be considered to have the following main three aspects: (AD1) decreased water flow rates in rivers and water levels in rivers and reservoirs, (AD2) decreased flow rates in sewers, and (AD3) decreased water flow rates to the WWTPs. Finally, other aspects that are linked to extreme weather events, but not directly related to floods and droughts, are increased air and water temperatures (AT1); these aspects are expected to have various consequences on WWTPs, such as faster biological processes due to higher temperatures of wastewater and higher costs of treatment units, for example for air filtration due to higher dust concentrations in air.

For example, a flood event results in increased runoff (aspect AR1); one series of effects of this aspect includes (1) increased flow rates in the sewers, (2) increased flow rates into the WWTPs and (3) lower hydraulic retention times in the treatment units of the WWTPs. To face the environmental consequences of such an aspect, the process design of units needs to be performed or checked for the expected increased flow rates. If this suggested design action is not followed, then the efficiency of the WWTPs is reduced and the expected environmental impact, which is the increased pollution of water bodies that are used for effluent discharge, occurs.

Table 1. Table of aspects and methods to face their environmental impacts

Aspect	Aspect details	Suggested design actions to face the impacts of the aspect	Environmental impact, when aspects are not faced
Increased runoff (AR1)	Increased pollution load to the WWTPs.	Perform the process design of units for increased process efficiency.	Increased pollution of water bodies that are used for effluent discharge.
Increased runoff (AR1)	Increased flow rates in the sewers and to the WWTPs, and lower hydraulic retention times in treatment units.	Perform the process design of units for increased flow rates.	Increased pollution of water bodies that are used for effluent discharge.
Increased	Increased flow	Perform the	Increased pollution of

runoff (AR1)	rates to the WWTPs, and possible requirement for increased hydraulic energy at the outlet works.	hydraulic design for increased flow rates.	water bodies that are used for effluent discharge. Saltwater intrusion in coastal discharges.
Increased runoff (AR1)	Increased water levels in sewers, possible flow in sewers under pressure, and possible flooding of inlet works.	Perform the hydraulic design for increased hydraulic energy at the inlet. Design to avoid flooding of units.	Pollution in the area of WWTP. Creation of unpleasant conditions with odours etc. Increased pollution of surface and ground water bodies.
Water level rise of seas and rivers (AR2)	Increased water levels of the surface water bodies that are used for effluent discharge.	Perform the hydraulic design for increased hydraulic energy at the outlet.	Increased pollution of water bodies that are used for effluent discharge.
Water level rise of seas and rivers (AR3)	Increased aquifer levels. Possible effect of increased groundwater on the units.	Perform the static design of units taking into account increased levels of aquifers.	Pollution in the area of WWTP. Creation of unpleasant conditions with odours etc. Increased pollution of surface and ground water bodies.
Flooding and storm surges (AR4)	Increased water levels and flooding.	Plan measures to avoid over-flooding of units, disruption of processes, and failure of electricity.	Pollution in the area of WWTP. Creation of unpleasant conditions with odours etc. Increased pollution of surface and ground water bodies.
Decreased water flow rates in rivers and water levels in rivers and reservoirs (AD1).	Increased concentrations of pollutants to the WWTP.	Verify the process design of units for increased concentrations.	Increased pollution of water bodies that are used for effluent discharge.
Decreased flow rates in sewers (AD2).	Lower flow velocities and increased quantities of sediments in sewers. Increased population of	Verify the process design of units that can be possibly affected.	Creation of unpleasant conditions (odours etc.) in the area of WWTP, especially in the pre-treatment units. Increased pollution of water

	rodents.		bodies that are used for effluent discharge.
Decreased water flow rates to the WWTPs (AD3).	Higher concentration of pollutants to the WWTP. Lower hydraulic loads. Higher hydraulic retention times.	Verify the process design of units for increased concentrations.	Increased pollution of water bodies that are used for effluent discharge. Creation of unpleasant conditions (i.e. odours) in the area of WWTP.
Increased air and water temperatures (AT1).	Increased temperatures of wastewater and air.	Perform the process design of units for the increased wastewater and air temperatures.	Increased pollution of water bodies that are used for effluent discharge.

SUGGESTED DESIGN ACTIONS AND MATHEMATICAL MODELS

The information provided in Table 1 is very general; it can more focused for a specific environmental system that contains information on its components; these are (1) the characteristics of the sewerage system, (2) the characteristics of the WWTP including those of the innovative technology, and (3) the characteristics of the natural environment, i.e. the surface water bodies, the aquifers and the atmosphere. Knowing the above-mentioned information, it is possible to determine or estimate when and how an aspect affects environment and the factors and the conditions under which the harm is essential.

To obtain a good knowledge of the environmental system, integrated mathematical models can be used; these models can be considered as consisting of four sub-modules (M1 to M4) that simulate (M1) the hydrodynamics and processes in sewerage systems, (M2) the hydrodynamics and processes (physical, chemical and biological) in the treatment units of the WWTP (Stamou et al., 2009), (M3) the hydrodynamic behaviour and the water quality of the water courses following effluent discharge (Safiolea et al., 2011), and (M4) the effect of the operation of the involved processes in the WWTP on the atmosphere (Gaitanis et al., 2008). Existing various practical and/or theoretical design models are simplified versions of M2, while calculations with the four sub-models can be performed simultaneously or separately. Obviously, the application of the suggested design actions in WWTPS with innovative technologies presupposes the mathematical description of the hydrodynamics and processes of these technologies, even using simplified approaches.

CONCLUSIONS

In this work the main aspects and impacts of extreme weather events on WWTPs are presented and general design suggestions that improve coping with these impacts are discussed; these suggestions can be taken into account in the development of new innovative treatment technologies and their implementation in real WWTPs to avoid or minimise the expected environmental impacts. Integrated mathematical models can be used to assess these environmental impacts and to specify and quantify the suggested design actions in specific WWTPs involving innovative technologies.

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Resource Recovery Technologies

(Tuesday, 24 June 2014, Aula T2, Polo Zanotto)

(K3) Full-scale Phosphorous Recovery As Struvite From Digested Sludge: A Return On Experience

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Abstract

Phosphorous recovery is currently receiving increasing attention from the wastewater sector due to the expected decrease of accessibility to this fundamental resource in the future. To date, phosphorous recovery as struvite in wastewater treatment plants has been mainly implemented on water phases resulting from dewatering processes of the sludge line. However, it is possible to recover struvite directly from sludge phases. Besides minimising the return loads of phosphorous from the sludge line to the water line, placing such a process on the sludge line is claimed to offer advantages such as a higher recovery potential, enhanced dewaterability of the treated sludge and reduced risk of scaling in pipes and dewatering devices. In the sewage plant of Leuven (Belgium), a full-scale struvite recovery process from digested sludge has been tested since March 2013. Several monitoring campaigns and experimental set-ups provided indications on the efficiency of the process for recovery. In the case of Leuven, the load of phosphorous from the sludge line returning to the water line as centrate accounts for about 15-20% of the P-load of the plant. Data indicate that the process reduces this load of about 50%, and thus may positively affect the Enhanced Biological Phosphorous Removal of the plant. An improved dewaterability of 1.5% of dry solids content is achievable with a proper tuning of the installation.

Keywords
dewatering; phosphorous recovery; phosphorous removal; scaling; struvite

INTRODUCTION

So far, struvite ($MgNH_4PO_4,6H_2O$) has been recovered at full-scale mostly from the water resulting from dewatering (Cornel and Schaum, 2009). But this same process can also be implemented directly on sludge phases of the sludge line. High free orthophosphate concentrations are usually met after digestion on plants where Enhanced Biological Phosphorous Removal (EBPR) is used. Compared to implementation on water phases, such alternative is claimed to offer different advantages at full-scale such as a better recovery potential, an enhanced sludge dewaterability, reduced scaling risks and a support of the EBPR. However, very few full-scale pilot experiences have been published to confirm or infirm these expected improvements. A **S**truvite **F**ormation **P**rocess (SFP) has been built and implemented in the municipal WWTP of Leuven (Belgium, 120.000 people equivalents) from March 2013 on. This paper presents the findings of these first months of full-scale operation in terms of modification of phosphorous mass balance in the WWTP and dewatering of the treated sludge.

MATERIALS AND METHODS

Monitoring campaigns

Three monitoring campaigns on the sludge line of the WWTP Leuven were performed in 2013 during spring, summer and autumn. Figure 1 shows a scheme of the sludge line with the 7 locations of the daily sampled flows. Grab samples were taken. The analyses for each sample are described in Table 1. Online flow meters constantly registered the flow at points 2, 3 and 5 and the dry solids content at point 5 and at inlet of the thickening tables. Flows at point 1 and 7 were calculated based on mass balances on dry solids and water, respectively at thickening tables and centrifuge.

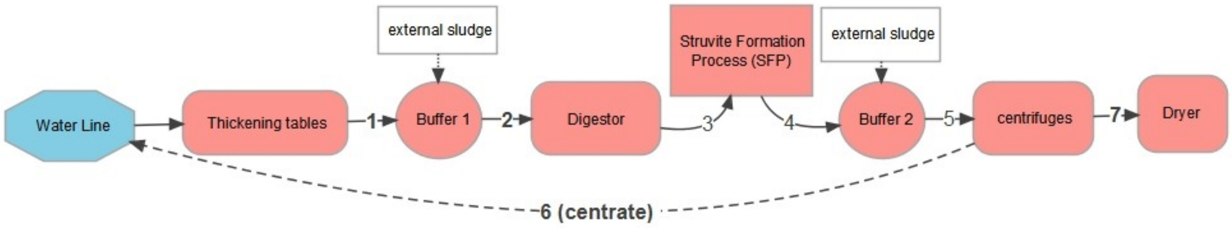

Figure 1. Numbered sampling points on the sludge line of WWTP Leuven

Table 1. Description of the measured physico-chemical parameters for each sampling point.

Sampling points	Measured parameters	Measured parameters after filtration (poresize 0.45µm)	Analyses set 1	Analyses set 2	Analyses set 3
1. Thickened sludge	Analyses set 1	Analyses set 2	pH Dry matter Ash rest on dry matter Nitrogen Kjeldhal Phosphorous total Iron total Magneisum total Calcium total Aluminium total	Nitrogen Kjeldhal Ammonium Phosphorous total Orthophosphate Iron total Magnesium total Calcium total Aluminium total	pH Suspended solids Ash rest on suspended solids Nitrogen Kjeldhal Phosphorous total Iron total Magneisum total Calcium total Aluminium total COD, BOD
2. After buffer 1 before digestor	Analyses set 1	Analyses set 2			
3. Just before SFP	Analyses set 1	Analyses set 2			
4. Just after SFP	Analyses set 1	Analyses set 2			
5. Just before centrifuge (before polyelectrolyte addition)	Analyses set 1	Analyses set 2			
6. Centrate	Analyses set 3	Analyses set 2			
7. Dewatered sludge	Analyses set 1	Analyses set 2			

Dewaterability tests

Three dewatering tests were performed, one at each season during the weeks with the SFP in operation (‘ON’ weeks), by means of a mobile filter press. 1 m^3 of sludge was sampled at the inlet of the SFP (point 3) and dewatered with 3 repetitions in spring and summer and 2 repetitions in autumn and winter. For each dewatering repetition, the obtained %DS of the dewatered sludge was analysed for three different dewatered sludge grab samples. One retention time of the SFP later, the procedure was repeated for the sludge at the outlet of the struvite process (point 4).

Struvite Formation Process (SFP)

The SFP is a two stage reactor consisting of: (1) a CO_2-stripper tank (2) a reactor, mixed by a double propeller, in which $MgCl_2$ and NaOH is dosed and (3) an overflowing settling tank attached to the reactor. The dependency of the installation efficiency on the dosing ratio Mg/P was evaluated on intensive measurement days during which the orthophosphate content before and after the SFP got analysed while changing the dosing of $MgCl_2$. This was done for 3 days at pH=7.3 and for 2 days at pH=7.5.

RESULTS AND DISCUSSION

Process efficiency

For the same magnesium dosing rate, a higher efficiency is obtained at pH=7.5, as the minimum solubility of struvite is located at alkaline pH, which enhances precipitation (Doyle et al., 2002).

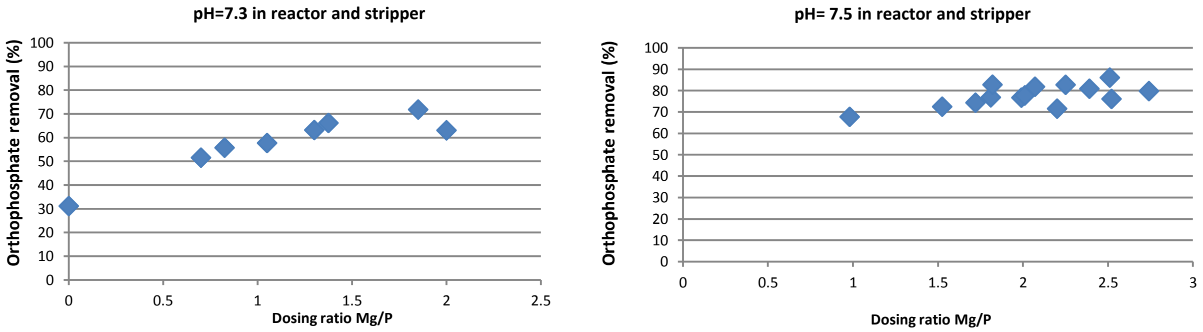

Figure 2. Orthophosphate removal efficiencies of the SFP in function of the magnesium dosing rate at pH=7.3 (left) and at pH=7.5 (right)

Impact of the SFP on the water line

Difference in the phosphorous load in the centrate. P-backloads from the centrate waters to the WWTP are presented in Table 2. The lower summer values compared to spring are explained by the significantly lower population in Leuven city in Summer.

Table 2. Daily P loads of the rejection waters of the centrifuges back to the waterline during monitoring campaigns (in percentage of the P-load on the water line):

	Spring campaign	Summer campaign	Autumn campaign
P-backload WITH Struvite Formation Process	8% (20 from 237 kgP/d)	5% (9 from 156 kgP/d)	8% (17 from 186kgP/d)
P-backload WITHOUT Struvite Formation Process	16% (44 from 237 kgP/d)	16% (30 from 156 kgP/d)	13% (27 from 186kgP/d)

Difference in BOD/P values in the water line. As shown in Figure 3, the averaged daily BOD/P ratio is significantly higher during SFP ON-weeks. This is an element in favor of more substrate availability for the Phosphorous Accumulating Organisms of the water line. However, further surveys are needed to prove that the SFP has a beneficial impact on the overall P-removal and EBPR of the plant.

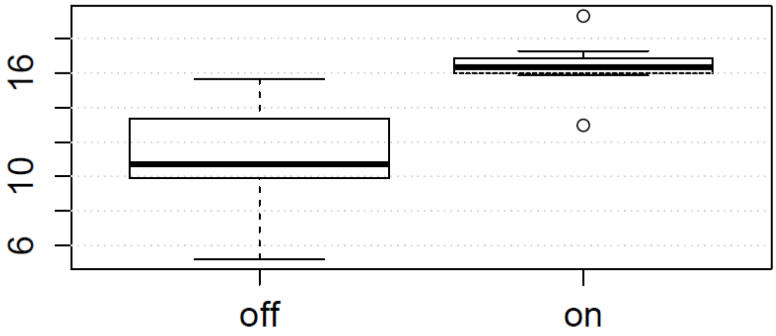

Figure 3. Boxplots of the values of BOD/P (kgBOD/kgP) in the centrate+influent. Y-axis represents the value of BOD/P. 'on' and 'off' cases refer to the average daily value obtained respectively during the ON-weeks and the OFF-weeks. Difference is significant at alfa 0.05.

Advantages of a direct treatment on the digestate

Improved dewaterability. The results of the tests, as shown in Figure 5, need explanations to draw a conclusion. The Divalent Cation Bridging theory states that flocculation, which is strongly linked to dewaterability, is driven by the ratio of monovalent cations (Na^+, K^+, NH_4^+) to divalent cations (Ca^{2+}, Mg^{2+}) concentrations (Sobeck and Higgins, 2002). Divalent cations create bridges between particles whereas monovalent cations tend to deteriorate flocks structures. Therefore an improved dewaterability can be expected if the addition of magnesium divalent cations surpasses the effect of sodium hydroxide dosing. In spring and summer, the average achieved dry solids content is lower after the SFP than before. Worse dewaterability in spring is explained by the use of a type of polymer which was not adapted to the sludge treated by the SFP. Indeed, two different types of polymers are required for the sludge before and after the SFP in the experiment: a more cationic polymer is required for the treated sludge, supposedly due to the dosing of the monovalent chloride ion in the SFP. In summer, proper polymers were used for both sludge before and after the SFP but the NaOH-setpoint was particularly high and lower stripping intensity was used in the SFP. On the contrary, in autumn and winter, the NaOH-dosing could be limited relatively to the dosing of $MgCl_2$ dosing thanks to an enhanced CO_2- stripping for pH-increase. $MgCl_2$ dosing was higher in autumn than in winter, explaining the more pronounced improvement of +2.5%DS in autumn. Due to the few repetitions of the experiments, it cannot be stated that dewaterabilities before and after the pilot SFP are statistically different in any of the seasons.

Prevention of natural scaling.

As shown on Table 3, the SFP operation strongly diminishes orthophosphate and to a small amount the ammonium concentrations. In theory, this should reduce the speed of scaling. In practice, it has been confirmed in the pipe downstream the process (upstream between the digester and the SFP), but it is still early to state if, in the case of WWTP Leuven, it will allow significant economic savings due to less pump and centrifuge maintenance.

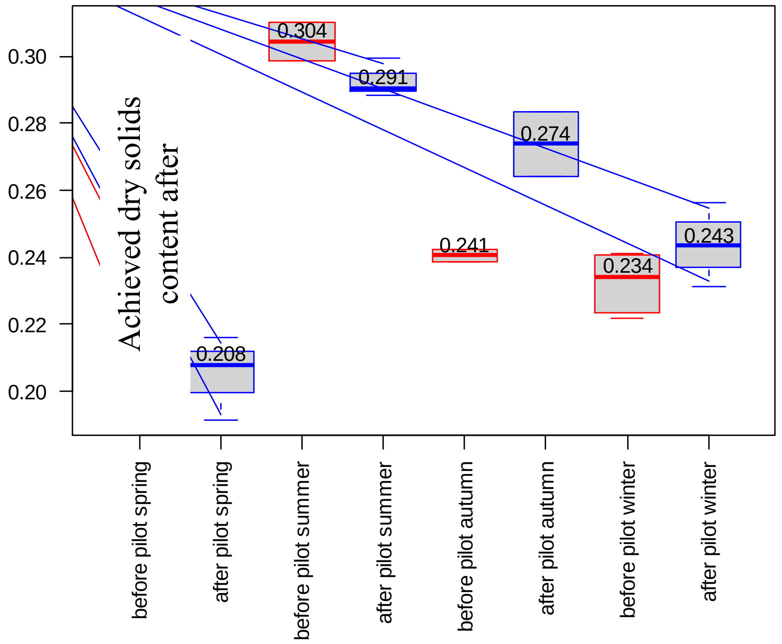

Figure 5. Results of the dewaterability tests in spring, summer, autumn and winter

Table 3. Observed modification of concentrations between inlet (IN) and outlet (OUT) of the SFP

	PO_4^{3-}	PO_4^{3-}	NH_4^+	NH_4^+	Mg^{2+}	Mg^{2+}	Ca^{2+}	Ca^{2+}

	IN (mgP /L)	OUT	IN (mgN /L)	OUT	IN *(mg /L)*	OUT	IN *(mg /L)*	OUT
Average concentration	**179**	**29**	**1036**	**1018**	**5**	**52**	**43**	**68**
Standard deviation	*14*	*16*	*68*	*31*	*8*	*35*	*10*	*13*
Number of daily samples	10	10	9	10	9	10	10	10

CONCLUSION

The full-scale Struvite Formation Process achieved, during the start-up phase, a phosphorous removal from the digested sludge of about 70-80% with a Mg/P dosing ratio around 1.5 and a pH of 7.5. This reduces considerably the backload of phosphorous to the water line, which normally accounts for 15 to 20 % of the P-load of the water line. The extraction of this P-load from the centrate is suspected to support the overall P-removal of the WWTP but further research is necessary. The diminution of scaling speed and beneficial impact on pumps and dewatering devices downstream should be evaluated on a longer term. If the use of NaOH remains limited, the Struvite Formation Process can improve the sludge dewaterability. It is reckoned that +1.5%DS improvement is easily achievable with correct stripping and magnesium dosing setpoints. This phenomenon is attributed to the ‘bridging’ effect of the magnesium divalent cation. The results of this study will be integrated in economic and environmental cost-benefit evaluations, giving elements to determine where to best recover phosphorous from municipal wastewater: on centrate, or on digestate or at end of sludge life cycle from incinerated sludge ashes or by land spreading.

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(P12) Potential for Biopolymers Recovery from Mixed Cultures Coming from Different Wastewater Treatments

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Abstract

New generation of wastewater treatment facilities must include the resource recovery. In this study, we have analysed the potential production of biopolymers within the same reactor used for the biological treatment of wastewater. In this sense, we analysed several mixed cultures in which different industrial wastewater was performed for the removal of organic material (biodegradable or recalcitrant) or nutrients (N and P). It was quantified the amount of biopolymers accumulated as exopolymeric substances (EPS) and poly-β-hydroxyalkanoates (PHA), according to operating conditions of each one of the wastewater treatment performed. The results show a content of biopolymers (EPS +PHA) between 2 and 50 % of the total volatile suspended solids depending on the biomass used in the wastewater treatment. Moreover, in the reactors with the highest accumulation of biopolymers a microbial isolation was performed for evaluating the specific storage capacity of each PHA isolate.

Keywords

poly-β-hydroxyalkanoates; exopolymeric substances; resource recovery; wastewater treatment.

BACKGROUND AND STATE OF THE ART

One of the most promising biodegradable materials to emerge in recent times is the family of poly-β-hydroxyalkanoate (PHA) polymers produced by almost all bacteria as response to environmental stress. Among PHA, the extracellular polymeric substances (EPS), mainly composed of proteins and polysaccharides, are secreted and used by microorganisms as protecting agents against desiccation and predation and as building material in biofilm formation.

The idea of substituting non-degradable synthetic plastics with biodegradable plastics (PHA and EPS) has drawn interest from both academic and commercial world. The prevailing technology for PHA/EPS production is through the use of pure bacterial cultures requiring asepsis and using pure concentrated substrates (Donot et al., 2012). Although currently being produced commercially, the product is more expensive than available synthetic polymers and therefore, is still mostly regarded as a fine rather than a commodity polymer.

Mixed bacterial culture production has recently started to attract a lot of attention. It has the potential to produce large amounts of EPS/PHAs at lower costs due to almost no need of sterility, simple equipment and control requirements and the ability of utilise a wide range of cheap substrates, including industrial and agricultural wastes. The nature of mixed culture EPS/PHA production from waste requires this process to be financially and ecologically competitive compared to other polymer production processes, and also, with other value-adding waste treatment processes that use the same waste resource, such as biogas production.

In this sense, this contribution aims to explore the intrinsic capacity of several mixed cultures performing different wastewater treatment for EPS/PHA recovery. Currently, in our labs several wastewater treatments are being performed, ranging from enhanced biological phosphorous removal (EBPR) to simultaneous removal of recalcitrant compounds and ammonium and autotrophic nitrogen removal.

MATERIAL AND METHODS

Several wastewater treatments are running in our labs for research purposes. From each wastewater treatment 40 mL of sample were taken directly from reactor biomass. 30 mL were used for PHA determination while 10 mL were used for EPS determination. The operating conditions of each of the wastewater treatments screened are described in Table 1.

PHA was extracted from centrifuged samples using hexane and butanol (Werker et al., 2008) and then, it was determined by GC (Agilent Technologies 7820A). EPS was determined as the fractions of proteins and polysaccharides as stated by Adav and Lee (2011).

On the other hand, isolation, counting and identification of predominant microbiota in the reactors with the greatest accumulation of biopolymers were made. The ability of specific PHA accumulation from each of the isolates was also evaluated. Different dilutions of samples were inoculated in tryptone-soy agar plates. Cultures were incubated at 25°C for 72 hours. The isolates were identified by sequencing the 16S rDNA using universal primers. To detect the capacity of PHA production, the isolates were cultured in mineral medium (MM) and LB medium agar plates, supplemented with 2.5 g/L of glucose, 2.5 g/L of fructose and 0.5 mg/L of red Nile. After 72 h of incubation, the plates were observed under UV light. Isolates that accumulate PHA show a high orange fluorescence. Negative controls were done with *E. Coli* and positive controls were done with *Cupriavidus necator*.

RESULTS

Depending on the type of wastewater treatment, the content biopolymers (EPS + PHA) has ranged between 2 and 50% of the total volatile suspended solids (Figure 1). In addition, the composition of EPS varies between 1 and 8 mg of polysaccharides (PS) per mg of proteins (PN), while the composition of the PHA varies between 1 and 27 mg of poly-β-hydroxybutyrate (PHB) per mg of poly-β-hydroxyvalerate (PHV) as shown in Figure 1.

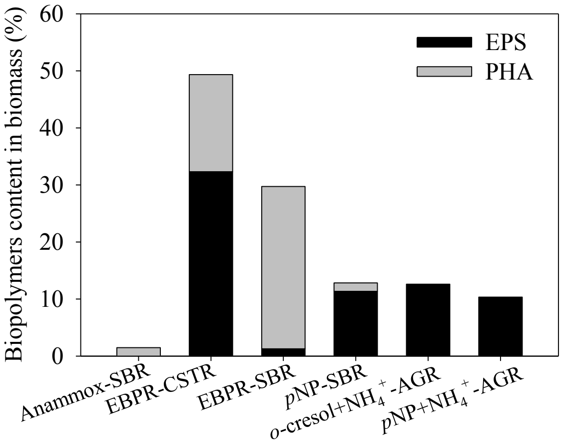

Figure 1. Total content of biopolymers in different wastewater treatment reactors

As expected, the bioreactors with the highest accumulation of PHA/EPS were the ones dedicated to the EBPR treatment, as confirmed by the results. These two bioreactors work with enriched populations of phosphate accumulating organisms, well known accumulators of PHA. The difference in the accumulation of EPS shall be attributed to the different settings of each reactor, since the accumulation of EPS mainly depends of the carbon source (Sheng et al., 2010).

Table 1. Operating conditions of the reactors at the time of biomass sampling

Reactor	Type of biological wastewater treatment	Volatile suspended solids (mg L^{-1})	pH	Solids retention time (d)	Hydraulic retention time (h)	Temp. (°C)	Operation configuration	Type of wastewater	Disolved Oxygen (mg L^{-1})
Anammox-SBR	Autotrophic nitrogen removal with Anammox in a sequencing batch reactor (SBR)	1200	7.5-8.5	40	24	35	6h cycles: 300 min of mixed filling, 30 min only mixing, 20 min of settling and 10 min effluent withdrawal	$N\text{-}NO_2^-$ and $N\text{-}NH_4^+$ at 250 mg L^{-1} each	0.0
EBPR-CSTR	EBPR in continuous stirred-tank reactor (CSTR)	2500	7.3	10	14	25	3 CSTR in series operating in A^2/O configuration	Dairy wastewater COD: 355-455 mg L^{-1} $N\text{-}NH_4^+$: 20 mg L^{-1} $P\text{-}PO_4^{-3}$: 35 mg L^{-1} Total suspended solids: 127 mg L^{-1}	2.0 (aerobic CSTR)
EBPR-SBR	EBPR in SBR	1715	7.5	15	12	25	6h cycles: 120 min of anaerobic phase, 210 min of aerobic phase and 30 min of settling and discharge	275 mg L^{-1} of propionic acid, 20 mg $N\text{-}NH_4^+$ L^{-1} and 10 mg $P\text{-}PO_4^{-3}$ L^{-1}	3.5-4.5 (aerobic phase)

*p*NP-SBR	Biological removal of *p*-nitrophenol in SBR	1600	7.5	20	48	25	24h cycles: 1373 min in aerobic phase + 60 min of settling + 7 min effluent withdrawal	*p*-nitrofenol + glucosa (200 mg TOC L^{-1} cada un) Relació carboni: nitrogen: fòsfor de 40:5:1	8.0
o-cresol +nitritation-AGR	Simultaneous removal of *o*-cresol and NH_4^+ with aerobic granular biomass in a continuous airlift reactor (AGR)	2600	8.0	-	68	30	aerobic granular biomass in a continuous airlift reactor (AGR) 100 % de nitritation	1000 mg N-NH_4^+ L^{-1} + 100 mg *o*-cresol L^{-1}	2.0
*p*NP +partial nitritation-AGR	Simultaneous removal of *p*-nitrophenol and NH_4^+ with aerobic granular biomass in a continuous airlift reactor (AGR)	2200	8.0	-	91	30	aerobic granular biomass in a continuous airlift reactor (AGR) 70% de nitritation	1000 mg N-NH_4^+ L^{-1} + 15 mg *p*NP L^{-1}	4.0

From EBPR-CSTR, EBPR-SBR and *p*NP-SBR, it was possible to identify different species of actinobacteria as *Microbacterium* and *Arthrobacter*, Firmicutes as *Bacillus* and *Enterococcus*, Proteobacteria as *Acinetobacter*, *Aeromonas* and *Comamonas* and Bacteroidetes as *Chryseobacterium* (Table 3). The ability of specific PHA accumulation from each of the isolates was also evaluated (Table 3 and Figure 2).

Table 3. Analysis of species in the reactors with the highest potential for biopolymers recovery.

		Ability of specific PHA accumulation					
Reactor	Counts	PHB-LB	PHB-MM	Identification	Coverage	% similarity	Sequence length
pNP-SBR	5×10^{6}	+	+	*Microbacterium* sp	98	99	930
pNP-SBR	1.1×10^{6}	?	+	*Arthrobacter* sp.	100	99	576
pNP-SBR	1×10^{5}	?	+	*Arthrobacter protophormiae*	100	100	1387
pNP-SBR	1.5×10^{5}	-	-	*Bacillus thuringiensis*	100	100	1485
EBPR-SBR	7×10^{4}	+	-	*Bacillus psichrodurans*	100	99	1466
EBPR-SBR	5×10^{4}	+	+	*Chryseobacterium taeanense*	99	99	1456
EBPR-SBR	4×10^{4}	-	-	*Bacillus thuringiensis*	100	100	1470
EBPR-CSTR	1.5×10^{7}	-	-	*Enterococcus durans*	100	99	876
EBPR-CSTR	1×10^{5}	+	-	*Acinetobacter* sp.	97	99	730

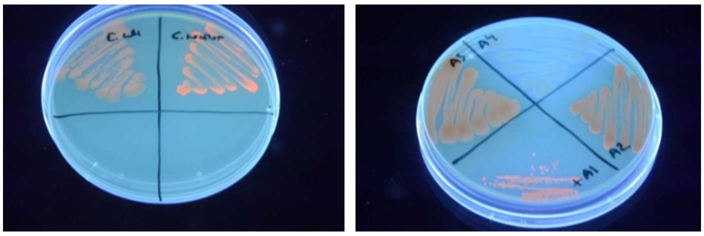

Figure 2. Nile red fluorescence staining from isolates. Left: Negative control of *E. Coli* and positive control of *Cupriavidus necator*. Right: Results for pNP-SBR in LB medium, with positive (+A1) for *Microbacterium* sp.

CONCLUSIONS

The study of the potential recovery of PHA/EPS of some of the wastewater treatment plants of our research group GENOCOV demonstrates, once again, that EBPR systems with PAO microorganisms are the best candidates for PHA recovery, but also for EPS recovery. It should be noted that the biomass of the pNP-SBR (heterotrophic organisms consuming recalcitrant compounds) were found to be also good candidates for PHA recovery.

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(P13) A novel PHA production and nitritation process for treating anaerobic supernatants

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Abstract

Polyhydroxyalkanoates (PHA) are biodegradable polymers, well known for their application in bioplastics. A current challenge is the integration of the PHA production process with wastewater treatment. This study investigates the potential integration of the via nitrite nutrient removal from the anaerobic supernatant of sewage sludge reject water and the selection of PHA storing biomass. Propionic acid (HPr) and sludge fermentation liquid (SFL) were used as external carbon sources in batch reactors. Nitritation was not affected by the type of carbon source, having a rate of 12.7 and 14.6 mgN/gVSS˙h respectively for HPr and SFL. At high F/M ratios (0.12 C-mmol/C-mmol), the nitritation rate dropped to 3.3 mgN/gVSS˙h due to the low dissolved oxygen in the mixed liquor. Initial results show that the use of SFL resulted in a net specific uptake short-chain fatty acids rate (q_{SCFA}) of 0.09 and 0.10 C-mmol/C-mmol·h for F/M ratios of 0.10 and 0.17 C-mmol/C-mmol respectively.

Keywords

Polyhydroxyalkanoates; short chain fatty acids; feast-famine conditions; nitritation; anaerobic supernatant

INTRODUCTION

The application of innovative bioprocesses that will increase the on-site biological valorisation of wastewater and sewage sludge is a major challenge. The occurrence of biopolymers, such as polyhydroxyalkanoates (PHA) in wastewater treatment has been widely recognized (van Loosdrecht and Heijnen, 2002). The growing/enrichment of bacteria with high PHA storing capacity is feasible through the development of feast-famine conditions, thus alternating conditions of carbon availability and unavailability (Dionisi et al. 2004). The common substrate used for the selective growth of the PHA storing biomass is carbon source containing short chain fatty acids (SCFAs), such as acetic acid, propionic acid and butyric acid (Frison et al., 2013). However, the addition of chemically synthesized SCFAs increases the operating cost of the process. The use of non-renewable petrochemicals and the increasing price of oil have renewed the interest in biological routes of SCFA production. Jiang et al. (2009) examined the production of PHA by activated sludge by applying an aerobic sequencing batch reactor (SBR) using alkaline fermentation liquid as carbon source. Recently, Morgan-Sagastume et al. (2013) reported similar results for a pilot SBR treating municipal wastewater that produced biomass with enhanced PHA-storage capacity. The aim of this study was to assess the feasibility towards the application of feast and famine conditions during the ammonium oxidation to nitrite for the treatment of anaerobic supernatant from digested sludge. HPr and real sludge fermentation liquid (SFL) were used as carbon sources at different food to microorganisms (F/M) ratios. This assessment can be useful to evaluate the integration of via the nitrite nutrient removal for the treatment of anaerobic supernatant and the selection of biomass with high PHA storing capacity.

MATERIAL AND METHODS

A pilot SBR (Verona, Italy) was operated was operated at a volumetric nitrogen loading rate varying from 0.45 to 0.53 kgN/m^{3}d for ~100 days. The system was fed with anaerobic supernatant of digested sewage sludge, to accomplishing nutrients removal via-nitrite using fermented sewage sludge liquid as carbon source. The volumetric organic loading rate was 1.12 - 1.32 kgCOD/m^{3}d. The solids retention time (SRT) was kept at 12-15 days. Ex situ experiments were performed using parallel batch reactors with a working volume of 1 L at 20±1°C in order to evaluate the effect of the short cut nitrification on the PHA production/consumption under feast and famine conditions. Propionic acid (HPr) and SFL were applied as carbon sources under different F/M ratios. Two different types of ex-situ activity tests were carried out under aerobic conditions, with and without nitrifying activity. Test with nitrifying activity: 500 mL of biomass was placed in Erlenmeyer flasks under continuous aeration (DO>4 mg/L), the temperature was maintained at 25±2^{o}C and the pH was controlled at 7.4±0.2. The biomass was spiked with ammonium (100 mg NH_4-N/L) as well as with an external carbon source. This initial ammonium concentration is commonly met in SBR influents treating highly nitrogenous streams. The feast conditions were achieved via the addition of the carbon source, while famine conditions prevailed after the depletion of the SCFAs (feast time/famine time = 0.3). The specific ammonium uptake rate (sAUR) was determined. HPr and SFL were spiked in order to achieve an initial COD concentration of 309±39 mg/L (F/M=0.07 C-mmol/C-mmol) and 527±18 mg/L (F/M=0.12 C-mmol/C-mmol). The concentration of SCFAs in the SFL was 12.8 gCOD/L, with the following proportions of acids: acetic acid 57%, propionic acid 7%, butyric acid 33% and valeric acid <3%. The fermentation of the mixed sludge from the Carbonera WWTP (Veneto Region, Northern of Italy) was carried out in an anaerobic batch reactor at 40-45°C of, with a initial suspended solids concentration of ~35 g/L. After six days of fermentation, the fermented sludge was filtered using a membrane filtration unit (MO P13U 1m, Berghof, Germany). Test without nitrifying activity: A similar procedure was followed as the one described above. The only difference was that allylthiourea (50 mg/L) was added to inhibit the oxidation of ammonium.In the activity tests the time profile of nitrite (NO_2-N), nitrate (NO_3-N), phosphate (PO_4-P) and the SCFAs were monitored and analysed by ion chromatography (Dionex ICS -900 and Dionex ICS-1100). The sAUR was monitored both for the ammonium and nitrite oxidizing bacteria activity by measuring NO_2-N and NO_3-N concentration respectively. At the end of the aerobic phase, the biomass was analysed for total and volatile suspended solids (TSS and VSS) and for the PHA content according to the method of Lanham et al. (2013).

RESULTS AND DISCUSSION

The integration of the novel PHA production and nitritation process in a municipal WWTP

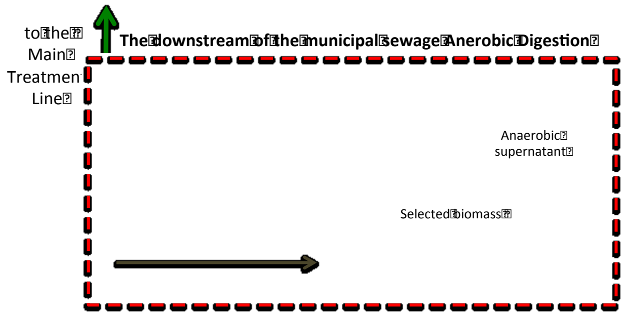

Figure 1. The novel PHA production and nitritation process in a municipal WWTP

The novel scheme of the PHA production and nitritation process and its integration in a municipal WWTP for the treatment of the anaerobic supernatant from digested sludge is presented in Figure 1. Coupling the short-cut nitrification/denitrification in SBR with an adequate feast and famine regime can allow the production of PHA within the WWTP. Nutrients can be removed from the anaerobic supernatant through the nitrite pathway, favouring simultaneously the organisms with a high PHA storage capacity. The feast conditions can be carried out under aerobic environment with the addition of the SCFAs (sludge FL), favouring the nitritation and the PHA accumulation. The famine conditions will be established under anoxic conditions, where the denitritation will be driven using the previously PHA stored as carbon source. The selected biomass from the SBR can be used in a parallel aerobic batch reactor and can be fed with sludge FL, to accomplish the PHA accumulation.

Effect of nitrifying activity and F/M ratio on feast and famine conditions

Table 1 summarizes the effect of the external carbon source and of the nitrifying activity on the PHA production and SCFAs depletion under feast and famine conditions. The oxidation of ammonium was not affected by the type of carbon source. A nitritation rate of 12.7 and 14.6 mgN/gVSS·h was obtained when HPr and SFL were added at F/M of 0.07. When the SFL was dosed at higher concentrations (F/M= 0.12 C-mmol/C-mmol) the nitritation was 3.3 mgN/gVSSh. However, the DO concentration after the addition of the carbon source was less than 1 mg/L and it limited the activity of nitrifying bacteria. Future experiments will be performed at a higher aeration intensity to avoid limiting DO levels and maximise biomass activity. The uptake rate of the SCFA by bacteria depends on the type of the carbon source that is applied. In the current study, HPr showed a lower uptake rate as compared to SFL. Furthermore, in the absence of nitrifying activity, HPr was not completely depleted at the end of the test. As reported by Moralejo-Gàrate et al. (2013), the F/M ratio plays important role during the enrichment of the bacterial community. In this study, the uptake rate of the total SCFAs derived from the SFL was not significantly affected by the F/M ratio or by the presence or absence of nitrifying activity. In both the examined cases (with and without nitritation), the concentration of phosphorus decreased by 7.8±3.3 mg/L at the end of the feast phase from the initial PO_4-P concentration of 15 mg/L; the latter was partly (50%) attributed to the growth of biomass, and partly (50%) to the activity of some organisms with high phosphorus storing capacities. The use of HPr resulted in a low q_{SCFA} and the accumulation of PHA was negligible: only during the nitritation the $Y_{PHA/SCFA}$ was 0.07 C-mmol/C-mmol when a q_{SCFA} was 0.04 C-mmol/Cmmol h. On the other hand, the use of SFL at F/M 0.07 C-mmol/C-mmol resulted in a q_{SCFA} of 0.10 and 0.07 C-mmolC/mmol·h, with and without nitrifying activity, respectively. The increase of F/M to 0.12 C-mmol/C-mmol led to a similar q_{SCFA} of 0.11 C-mmol/C-mmol h (with the presence of nitrifying activity) and 0.08 C-mmol/C-mmol h (without nitritation). The yield of the PHA, PHB and PHV production (calculated on the basis of SCFA uptake) is given in Table 1. The yields obtained are 35% higher when the nitritation is inhibited, but comparable results with other research works were obtained even when nitritation took place (Albuquerque et al., 2010).

Table 1. Effect of carbon source and nitrifying activity on the performance on PHA production and SCFAs depletion during the feast conditions (q_{SCFA}: specific SCFA uptake rate; $Y_{PHA/SCFA}$: observed yield of PHA; $Y_{PHB/SCFA}$ observed yield of PHB; $Y_{PHV/SCFA}$; observed yield of PHV)

Type of carbon source	F/M C-mmol/C-mmol	sAUR mgNO$_x$-N/gVSSh	q_{SCFA} C-mmol/C-mmol·h	$Y_{PHA/SCFA}$ C-mmol/C-mmol	$Y_{PHB/SCFA}$ C-mmol/C-mmol	$Y_{PHV/SCFA}$ C-mmol/C-mmol
HPr	0.09	No nitritation	0.02	-	-	-
SFL	0.10	No nitritation	0.08	0.92	0.71	0.21
SFL	0.18	No nitritation	0.09	0.93	0.64	0.28
HPr	0.10	12.7	0.04	0.07	0.06	0.01
SFL	0.10	14.6	0.09	0.63	0.54	0.08

SFL	0.17	3.3	0.10	0.60	0.39	0.22

Short chain fatty acids uptake monitored by pH during feast and famine conditions

The pH profile is reliable and cost-effective parameter for the real time bioprocess monitoring. When the nitritation did not occur, the consumption of the SCFAs during feast conditions was identified following the pH profile; the pH rapidly increased. Then, the apex in the pH curve indicated the complete depletion of the SCFAs, while in famine conditions the pH stabilized at 8.5. However, as shown in Figure 2, the uptake of HPr was not very effective, since it was not completely depleted. When nitritation took place, the simultaneous oxidation of ammonium provided protons. The apex of pH under feast conditions appeared earlier and did not match with the complete depletion of SCFAs. After that point, the pH decreased steadily along with the presence of famine conditions during the oxidation of ammonium. When the SCFAs were added at higher concentration, the pH followed a similar trend. In that case nitrification was less effective.

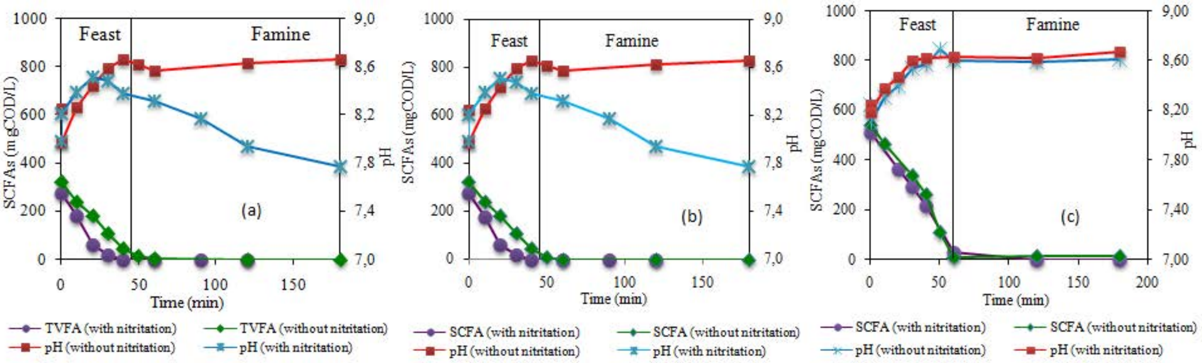

Figure 2. SCFAs depletion monitored by pH under feast and famine conditions; a) Propionic acids, F/M=0.09 and 0.10 C-mmol/C-mmol; b) Sludge FL, F/M=0.10, c) Sludge FL, F/M=0.17 and 0.18 C-mmol/C-mmol

CONCLUSION

In this work, the ammonium oxidation via nitrite exhibited fast kinetics under feast and famine conditions in a batch reactor operating under different F/M and external carbon source. The type of carbon source did not affect the nitritation rate; however high F/M ratio resulted in lower DO concentration that adversely affected the activity of the nitrifying biomass. The use of SFL resulted in a net production of PHA; the F/M that was applied did not influence the PHA production rate.

ACKOWLEDMENTS

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(S11) PHA production from VFAs in microbial mixed culture: bacterial population characterization

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Abstract

Fermented wastewaters can be used as substrate for microbial mixed cultures to store the organic carbon fraction in the form of polyhydroxyalkanoates (PHAs) under transient conditions of presence and absence of carbon source. In the present work a synthetic feeding was used, simulating a pre-acidified wastewater from the washing process of tuna in the boilers of a fish-canning industry, to enrich a PHA accumulating mixed microbial culture. The enrichment stage was performed in a sequencing batch reactor where a feast–famine regime occurred after 6 days of operation. The maximum accumulation capacity of the enriched microbial community was studied in batch assays and a maximum content of 51% PHA in dry weight was reached. In addition, microbial characterization was performed by the FISH technique, indicating that the used inoculum evolved along the time. After the enrichment stage three main genera were identified: *Azoarcus*, *Comamonas* and *Thauera*. They have been recognized as PHA storing bacteria.

Keywords

FISH; Mixed Culture; Polyhydroxyalkanoates; Tuna-processing Wastewater; VFA

INTRODUCTION

It is known that several types of microorganisms react to the stress, produced by transient conditions caused by limitation of some nutrient or electron donor/acceptor, with the production of storage polymers like polyhydroxyalkanoates (PHAs) (Dionisi *et al.*, 2004; Majone *et al.*, 2006). Microorganisms that are able to store high contents of PHA can use them as reserve substance (Castro-Sowinski *et al.*, 2010). PHAs are being deeply studied because they can be good substitutes to conventional oil-based plastics: they have similar properties and are completely biodegradable and biocompatible (Dias *et al.*, 2006; Kleerebezem and van Loosdrecht, 2007; Koller *et al.*, 2010; Serafim *et al.*, 2008). In addition, PHAs have variable properties depending on the type of structure adopted by the compound and on the monomers present and their layout in such a way that over 150 different hydroxyalkanoic acids have been reported (Sudesh *et al.*, 2000).

As naturally occurring organic compounds, they can be produced by microorganisms from different carbon origins as, i. e., waste materials or other renewable sources. Based on these observations, new processes for the production of plastics are under development. However, nowadays all the commercial processes for PHA production use pure cultures together with substrates that rise up the manufacturing costs (Serafim *et al.*, 2008). One interesting way to produce these valuable compounds reducing the operational costs is by using microbial mixed communities instead of pure cultures combined to the use of fermented wastes as substrate. The selection of microorganisms with high storage capacity is one of the main objectives in the PHA production process by microbial mixed communities. This ability has been researched in different bacterial groups, both with different operational conditions (Lemos *et al.*, 2008) and different substrates (Albuquerque *et al.*, 2013). The most abundant microbial populations identified from these works were found to belong to genera *Azoarcus*, *Thauera*, *Paracoccus* and *Amaricoccus*.

The main objective of this work is to study the storage of PHA by mixed microbial cultures using as substrate a mixture of volatile fatty acids (VFAs) simulating a fermented fish-canning wastewater. This process has been studied in terms of the performance of the reactor and identification of the microbial population by the use of the Fluorescence *in situ* Hybridization (FISH).

MATERIALS AND METHODS

The used arrangement is a two-step process: firstly, a PHA producing culture was enriched from activated sludge using VFAs as substrate for PHA production under conditions of excess (feast) and absence (famine) of carbon source; secondly, a batch reactor was used for the PHA content maximization step and it operated under excess of organic matter in order not to limit the storage of biopolymer inside the cells.

The enrichment reactor was a sequencing batch reactor with a useful volume of 1.8 L that operated for 150 days in complete mixing conditions at 30 ºC. This reactor operated in cycles of 12 hours at a hydraulic retention time and solids retention time of 1 day. A synthetic feeding (Table 1) was fed to this reactor mimicking the VFAs composition of the withdrawal of the anaerobic digester treating fish canning effluents. The accumulation step was performed in a batch reactor of a variable useful volume up to 5 L depending on the amount of biomass harvested from the previous stage.

Table 1. Characteristics of the feeding to the enrichment reactor.

VFAs (mL/L)		**Salts (g/L)**	
HAc[1]	1.45	NH_4Cl	0.66
HPr[2]	0.60	KH_2PO_4	0.349
HBu[3]	0.16	$MgSO_4.7H_2O$	0.137
i-HV[4]	0.06	KCl	0.053
n-HV[4]	0.23	Trace Compounds	1.5 mL

[1]Acetic Acid; [2]Propionic Acid; [3]Butiric Acid; [4]Valeric Acid

The pH value was measured with a pH-meter with a glass electrode. VFAs were analysed by gas chromatography, ammonium by ionic chromatography, PHAs by gas chromatography and solids were determined by calculating the difference between the weights before and after freeze-drying.

The characterization of the microbial populations was performed by the FISH technique. Samples were fixed with 4% paraformaldehyde solution (Amann *et al.*, 1995). The hybridization step was performed with the following probes: EUB338$_{mix}$ for *Bacteria*, AZO644 for *Azoarcus*, CTE for *Comamonas*, MZ1 for *Thauera*, GAM42a for *Gammaproteobacteria* and PAR1244 for *Paracoccus.* The abundance of these populations was tested by the Daime software (Daims *et al.*, 2006).

RESULTS AND CONCLUSIONS

Initially the enrichment reactor was operated until steady state conditions were reached. The steady state was identified by means of the several performed cycle measurements that gave concentration profiles of the different measured compounds similar to those observed in Figure 1A. The pH in the enrichment stage was not controlled and it was of 9.2 ± 0.4. Once the stable conditions were achieved, the corresponding accumulation assay was also performed (Figure 1B) using the mixture of VFAs of the feeding but in pulses of 130 Cmmol every time the oxygen rose over 4-5 mg O_2/L. Obtained yields were of 0.47 Cmol PHB/Cmol VFA and 0.46 Cmol PHV/Cmol VFA and the composition of the polymer inside the cells was of 22.9% PHB and 14.6% PHV.

The study of the presence and abundance of microbial populations confirmed the gradual enrichment in PHA accumulating bacteria into the reactor. At the beginning of the experiment the microbial composition was very heterogeneous, consisting of several groups. The genera *Azoarcus* and *Thauera* were the most abundant ones (~40 and ~30% of total bacteria, respectively), followed by *Gammaproteobacteria* (~15%), *Comamonas* (~10%), and finally *Paracoccus* in a percentage of around 5%. However, as a result of the enrichment in PHA storing bacteria, the identification results when the maximum PHA content was achieved, showed that the diversity was reduced to three main populations: *Azoarcus* (~50%), *Comamonas* (~30%) and *Thauera* (~20%) (Figure 3).

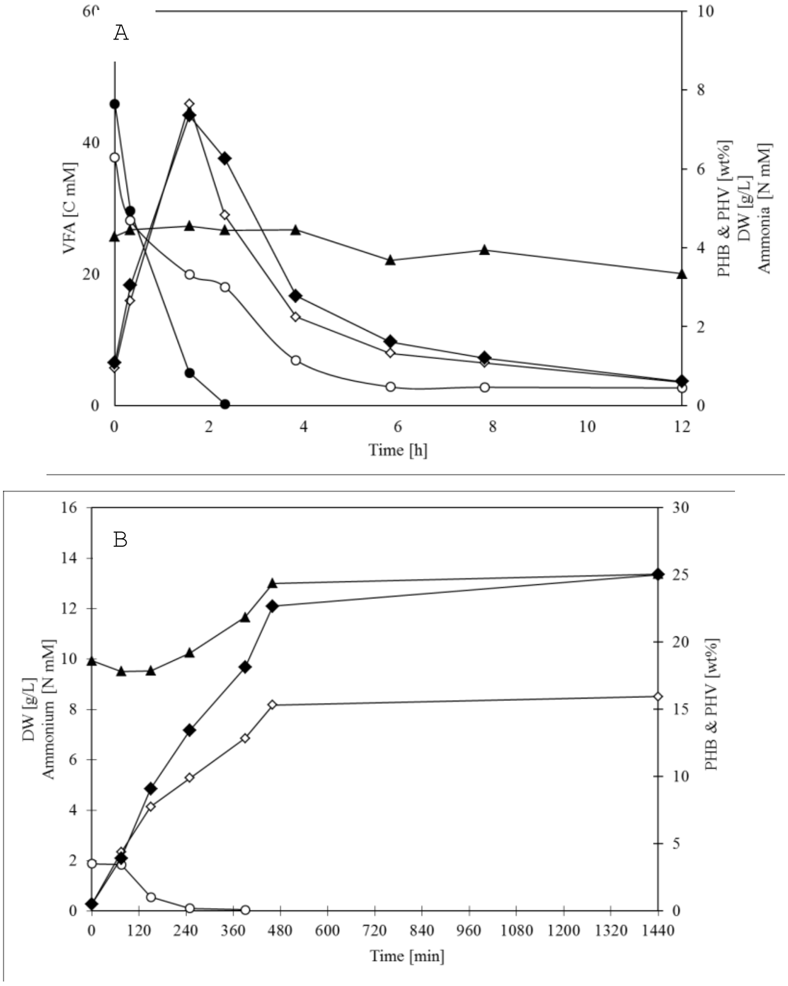

Figure 1. Enrichment cycle (A) and accumulation assay (B). Evolution of the concentrations of VFAs (●); ammonium (○); solids (DW) (▲) and also the percentage of the storage compounds PHB (◆) and PHV (◇), in the biomass sample expressed in dry weight.

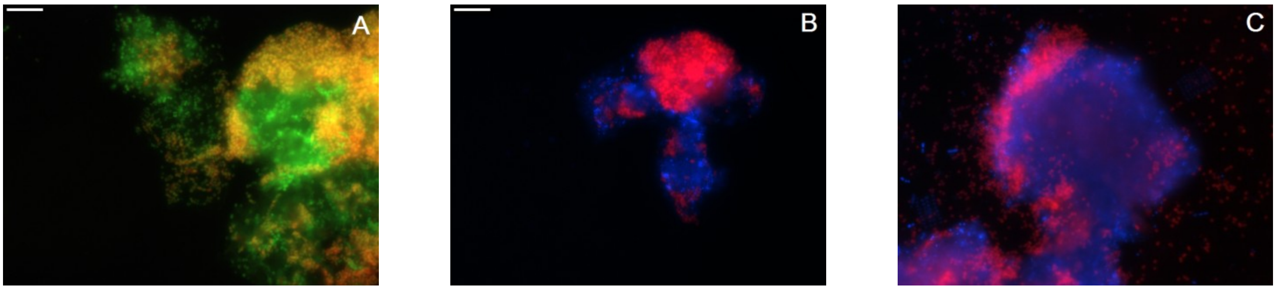

Figure 3. FISH images for microbial community characterization. (A) Specific probe for *Azoarcus* in orange and EUB338$_{mix}$ for other Bacteria in green. (B) Specific probe for *Comamonas* in pink and all DNA with DAPI in blue. (C) Specific probe for *Thauera* in pink and all DNA with DAPI in blue. Bar = 10 µm.

The enrichment of a PHA accumulating microbial mixed culture was achieved by using a mixture of VFAs simulating the effluent from an anaerobic digester of fish canning effluents. Produced PHAs were a mixture of PHB and PHV. The enrichment of the inoculated activated sludge was proved by the identification of the genera *Azoarcus*, *Comamonas* and *Thauera* which accounted for almost 100% of the bacterial populations present in the biomass.

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(S12) Waste to resource: Crude glycerol as substrate for TAGs production by enrichment cultures

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Abstract

Biodiesel production emerged during the last years as an environmental friendly alternative to oil derived fuels. Crude glycerol is generated in large amounts as a by-product during biodiesel manufacturing, and its disposal costs are compromising biodiesel economics. Crude glycerol is polluted and it cannot be used for conventional glycerol applications. Since crude glycerol refining is not economically viable, new uses need to be developed. In this work, a promising valorisation option for crude glycerol is described. Crude glycerol was used as substrate for the production of tryacylglycerols (TAGs) using a low-cost process. Among other uses, TAGs can be converted into biodiesel by transesterification, enhancing the overall yield of the biofuel industry. Open enrichment cultures were used, attaining TAG production capacities of 40wt%. This work demonstrates the promising potential of enrichment cultures-based processes for the production of value-added compounds using wastewaters.

Keywords

Crude glycerol; biopolymer; TAG; feast-famine; enrichment cultures; waste to resource

INTRODUCTION

During the past decades, biodiesel emerged as a potential alternate renewable liquid fuel. Crude glycerol is generated as by product during biodiesel manufacturing. Due to the pollutants derived from the biodiesel production process, crude glycerol cannot be used for conventional glycerol applications (Johnson and Taconi, 2007). Considering that the biodiesel production capacity in Europe during 2012 was 23 10^6 tons (http://www.ebb-eu.org/stats.php), and that on weight basis, per 9 kg of biodiesel 1 kg of crude glycerol is produced, effective and economic utilization of the enormous quantities of crude glycerol needs to be developed in order to enhance the biofuel production process economic and environmental viability (Khanna et al., 2012).

An interesting and innovative treatment is to use the crude glycerol as raw material for the production of triacylglycerol (TAG). TAGs can be converted into biodiesel by transesterification (Cheirsilp and Louhasakul, 2013) with the consequent saving of raw materials. This possibility has been evaluated by several authors using pure culture of eukaryotic microorganisms (funghi or yeast) (Andre et al., 2010; Papanikolaou and Aggelis, 2009). A major drawback associated to this process is the need of sterile operation, which results in high production costs. Scarce information about TAGs production in mixed culture is available in the literature.

In this work, we propose to produce TAG by enrichment cultures using crude glycerol as substrate. An open non-sterile community with the capacity of storing high amounts of TAGs was naturally selected by means of the feast-famine regime.

MATERIALS AND METHODS

Crude glycerol characterization

Crude glycerol was kindly provided by a biodiesel production facility located in Begonte, Lugo, NW Spain. Total organic content (TOC), glycerol, methanol, lipids and sodium cation content were determined (Table 1). In addition, the volatile fraction and density were calculated (American Public Health Association 1995).

Table 1. Crude glycerol characterization

Parameter	Measured concentration
Density (g/L, 20 ºC)	966.9±7.2
Total organic carbon (g C/L)	409.2±30.3
Glycerol (g/L)	696.4±54.0
Methanol (g/L)	225.4±22.9
Lipids (g/L)	60.9±5.8
Sodium (g/L)	14.5±0.3

Enrichment culture establishment

A 2 L jacketed glass reactor was used for the selection of the enrichment culture with lipid production capacity. Crude glycerol was used as substrate and the reactor was operated in a SBR mode which resulted in the occurrence of a feast-famine regime. Cycle length was fixed at 24 h, and HRT and SRT were maintained at 48 h. Temperature in the reactor was kept at 30 ºC and pH value was controlled at 7.

Analytical methods

The following compounds were quantified (analytical method in brackets). Glycerol (HPLC), methanol (GC) and ammonia (spectrophotometrical method by Bower and Holm-Hansen (1980)) TOC (catalytic combustion), total suspended solids (American Public Health Association 1995). For triacylglycerols characterization and identification, the method proposed by Smolders et al. (1994) for PHA was used, using different external standards. A preliminary screen of the long chain fatty acids present in the samples showed that the main components in the TAGs were palmitic, oleic and linoleic acids. Consequently, the following compounds from Sigma-Aldrich were used as external standards: palmitic acid (PO500), oleic acid (O1008) and linoleic acid (L1376).

RESULTS AND DISCUSSION

Enrichment culture with TAG production capacity

Activated sludge was used as inoculum for the establishment of an enrichment culture with the ability to store TAG. Crude glycerol was dosed at the beginning of the SBR cycle resulting in a feast-famine regime which favoured the survival of storing microorganisms. The performance of one representative operational cycle is plotted in Figure 1 A and B. During one operational cycle, substrate was present in the liquid media during 4 hours. A very fast increase in TAG content occurred during the first minutes after substrate dosage, from 4.5 to 21 wt%. Glycerol was consumed faster than methanol. Once glycerol and methanol were depleted, the TOC value remained constant, indicating that slowly biodegradable carbon remained in the liquid media and the community was not capable of using it neither for storage nor for growth.

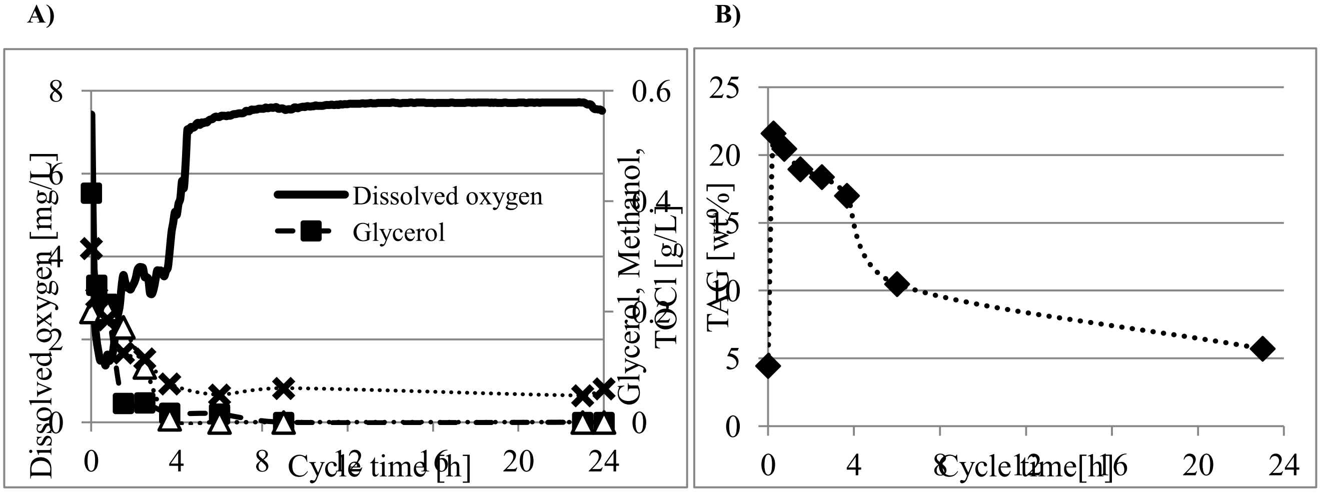

Figure 1. A) Dissolved oxygen (black line), Glycerol (black squares), Methanol (white triangles) and TOC (black crosses) evolution during an operational cycle of the enrichment reactor. B) TAG content inside the biomass expressed in weight percentage [wt%]

To the best of our knowledge, this is the first work that reports the accumulation of TAGs by open enrichment communities using waste as substrate.

Determination of the maximum storage capacity

The maximum lipid accumulation capacity of the enrichment culture was determined in a batch experiment. Biomass collected at the end of one operational cycle of the enrichment reactor was used and a large amount of crude glycerol was dosed. No nitrogen source was dosed in order to force the conversion of the substrate into TAG.

The evolution of the concentrations of the measured compounds during the accumulation experiment is plotted in Figure 2. A rapid TOC consumption was detected from the first minutes after crude glycerol dosage. This fast consumption was accompanied by the production of TAG up to almost 40 wt% after 24 h.

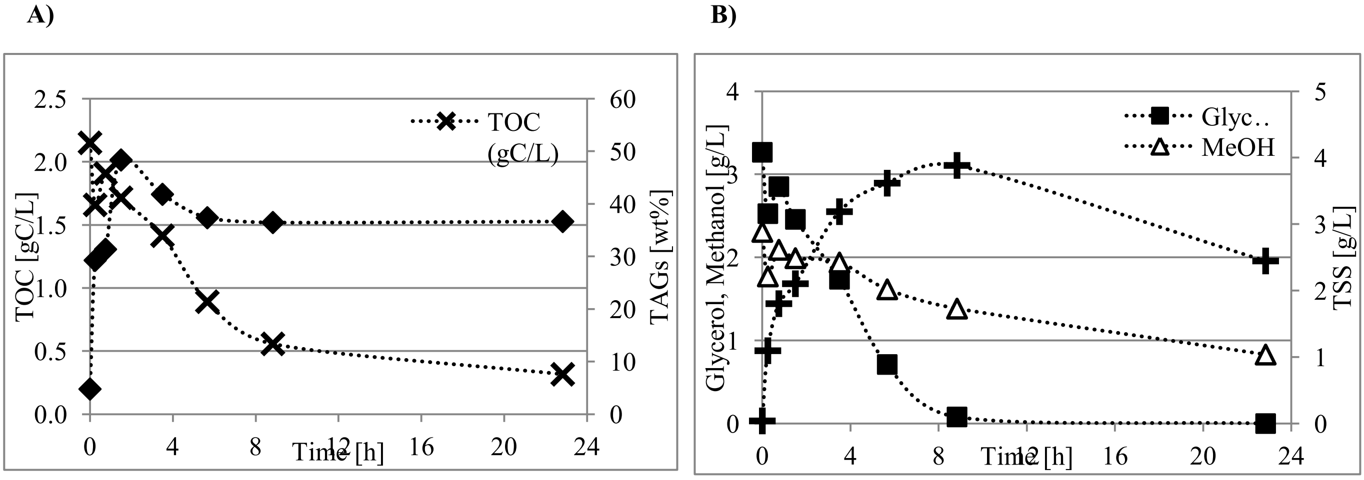

Figure 2. A) TOC (black crosses) and TAG content (black diamonds) B) Glycerol (black squares), Methanol (white triangles) and total suspended solids (black pluses) evolution during the batch accumulation assay.

Glycerol and methanol consumption, figure 2B, showed the same trend as in an enrichment cycle;

glycerol consumption was preferred over methanol. Total suspended solids increased up to 4 g/L, and decreased once glycerol was depleted.

The attained accumulation capacity is comparable to the capacity attained with other studies using crude glycerol as substrate. Cheirsilp et al. (2013) reported up to 61wt% of lipids (TAGs) content using palm oil mill effluent as substrate. André et al. (2010) attained up to 57wt% of lipid accumulation. A clear advantage of the present study is the use of open, non-sterile and non-defined enrichments, which leads to a significant decrease on the production costs due to lower energy requirements and simpler operation, in comparison with the available studies that operated under sterile conditions, using pure and defined cultures.

CONCLUSIONS

This study has proven the feasibility of resource recovery from wastewaters for the production of a value added compound, such as TAG.

Accumulation capacities of 40wt% TAG were achieved using crude glycerol as substrate, proving the viability using of crude glycerol as substrate. A clear advantage, in comparison to the existing literature on the use of waste for TAG production, is presented; the use of open enrichment cultures allows for a low-cost TAG production process since no sterile conditions are needed.

This process not only generates a value-added product, but also enhances the sustainability and economics of the biodiesel industry, since crude glycerol changes its status from waste to resource, and no disposal costs, which negatively affect biofuel economic balance, are needed.

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(P14) Conversion of carbon dioxide from WWTP into valuable products through microbial electrosynthesis

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Abstract

WWTPs are a source of greenhouse gases(GHG) emissions such as carbon dioxide(CO_2) or nitrous oxide(N_2O). Aerobic treatment of organic matter is one of the most contributing processes to carbon footprint of these installations. Microbial electrosynthesis (MES) has been proposedas a technology to convert CO_2 into a valuable product (hydrogen, methane, organic compounds) with electricity as a source of reducing power. In this study, the biocathode of a MES was poised at -600 mV vs SHEto assess different operational strategies to drive biological production of valuable products (methane and acetate) from CO_2.

Electron-driven homoacetogenicmethanogenesis was observed at the beginning of the experimental period, which was inhibited in favour of homoacetogenesis. In both cases, methane and acetate were produced from CO_2 and electrons instead of hydrogen as source of reducing power. The maximum acetate production rate observed was about 1 mmol C-$CH_3COOH \cdot L_{NCC}^{-1} \cdot d^{-1}$. The current demand of the system increased during the experimental period from 1 mA up to values higher than 5 mA, which indicated the growth of electrotroph biofilm. The implementation of a pH control (from 5.5 to 6.0) especially contributed to increase current demand, suggesting that it could be used as the key operational strategy to favour microorganism growth onthe electrode surface.

The feasibility of MES systems to convert CO_2 is demonstrated, and thus carbon footprint of CO_2 emitting installations such as wastewater treatment plants can be reducedwhile producing valuable products that can be used for in-situ or ex-situ application.

Keywords

Added value products; Biocathode; CO_2capture; Microbial electrosynthesis.

INTRODUCTION

Wastewater treatment plants (WWTPs) are a sourceof greenhouse gases (GHG) emissions to the atmosphere,mainly carbon dioxide (CO_2) which contributes to increase the carbon footprint. CO_2 is directly produced as cell excretion product during the degradation of organic matter. Benchmark simulation model 2 (BSM2)(Jeppsson et al., 2007) estimates that CO_2 emissions in WWTPs are of 0.25kg CO_2 eq·$m^{-3}$when considering only the biological treatment and 1.46kg CO_2 eq·m^{-3}if anaerobic digestion of the sludge is also considered. CO_2 is also produced indirectly as a result of fossil fuel combustion to generate the energy required for the operation of the wastewater treatment plant, and as a combustion byproduct during the burning of the biogas produced from anaerobic digester. Bani Shahabadi et al. (2009) estimated that the emissions of $CO_2$from WWTPs treating a wastewater at 2000 kg BOD·d^{-1}were1952, 1992 and 2435 kg CO_2 eq·$d^{-1}$when considering aerobic, anaerobic or hybrid treatment, respectively.These emissions can be duplicated when considering external processes such as electricity consumption, transport of chemicals, etc.

In the recent years, the biocatalytic transformation of CO_2 into valuable productsby microbial electrosynthesis (MES) has been investigated (Rabaey and Rozendal, 2010), which could be used as a carbon capture technology. Among these valuable products are found gases such as hydrogen and methane which can be used in-situ for energy generation (electricity or thermal energy). On the other hand, organic compounds such as alcohols and volatile fatty acids (VFA) can be also produced, which are easier to transport and in consequence, suitable for other ex-situ applications. The MES describes the biological reduction of CO_2 to valuable products (hydrogen, methane, organic compoundsand biofuels) with electricity as energy source. MES offers the possibility of storing renewable-harvested electricity into chemically-stable products (Lovley and Nevin, 2013).

The potential electrotrophic activity of methanogenic microorganismsto drive the production of valuable products through MES have been recently proposed by different studies(Lovley and Nevin, 2013). Microbial routes for methane and acetate production in anaerobic digestionare shown on Fig.1. Methane production in a MES system has been studied byEerten-jansen et al., (2012), whodemonstrated the potential of MES to drive hydrogenotrophicmethanogenesis by providing CO_2 and electrons instead of hydrogen as a source of reducing power.Hence it might be possible to drive homoacetogenesis by changing the operational conditions of the system.

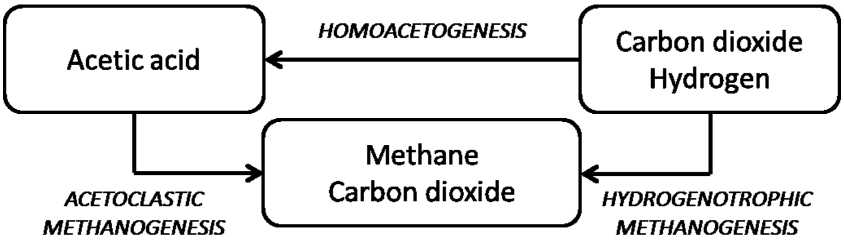

Figure 3. Schematic representation of methanogenesis, the final step in the anaerobic digestion process.

Further research in this novel technology is still necessary to understand the mechanisms and microorganisms involved in carbon transformation processes through MES with the objective of increasing CO_2capture andbiofuels production rates. This study evaluatesthe feasibility of a MES system for the conversion of CO_2 into valuable products and the dynamics of the system in the selection of a target product depending on operational conditions.Thus, the potential adaptabilityof microorganisms coming from anaerobic digestersto drive the production of different target products in MES systems has also been studied.

MATERIAL AND METHODS

A MES wasset-up and operated to convert $CO_2$to valuable products. Granular graphite was used as anode and cathode electrodes. The anode was not inoculated. The cathode was inoculated in closed circuit voltage mode (CCV) with a mixture of sludge from two different sources: i) the effluent of an anaerobic digester, and ii) fresh cow manure. Both chambers were fed with a mineral solution bubbled with CO_2 as the only carbon source. The biocathode mineral solution also contained vitamins and trace metals for biomass growth. The net cathodic camber (NCC) was 0.45 L and the hydraulic retention time (HRT) 19.5 h. MES system was operated in three-electrode configuration using a potentiostat (BioLogic, Model SP-50). To drive the biocatalytic reduction of CO_2, cathode potential was poised at -600 mV vs Standard Hydrogen Electrode (SHE). A gas chromatograph (Agilent Technologies, 7890A) equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionisation Detector (FID) was used to analyse hydrogen, methane and CO_2 concentration in the gas phase and organic compounds in the liquid phase, respectively.

RESULTS AND CONCLUSIONS

The MES was continuously operated feeding carbon dioxide for 88 days.Fig. 1 shows methane and acetate production coupled to the current demand and the pH evolutionduring the experimentalperiod. Gas production was observed after 10 operational days. Analysis showed that the gas contained methane (26 - 36%), CO_2(7 – 22 %) and nitrogen gas (52 - 56 %).Methane was being produced at a maximum rate of 0.66 mmol $C\text{-}CH_4 \cdot L_{NCC}^{-1} \cdot d^{-1}$. Previous studies demonstrated that methane production cannot take place abiotically at such cathode potentials (Batlle-Vilanova et al., 2014). Therefore, hydrogenotrophicmethanogenesis was likely taking place by using electrons instead of hydrogen as source of reducing power.These results are alike to other studies (Eerten-jansen et al., 2012; Lovley and Nevin, 2013). Cyclic voltammetry analysis demonstrated thatmethanogenic microorganisms coming from anaerobic digestion processeswereelectrotrophically active.Despise theachieved methane production rate, the production of other products with higher value (such as acetate) was also assessed. For this reason, an inhibitor of methanogenesis (10 mM of 2-bromoethanosulfonate) was added to the system at day 16 under the assumption that homoacetogenic microorganisms were present in the inoculum and they could grow on the electrode surface (Fig. 1).

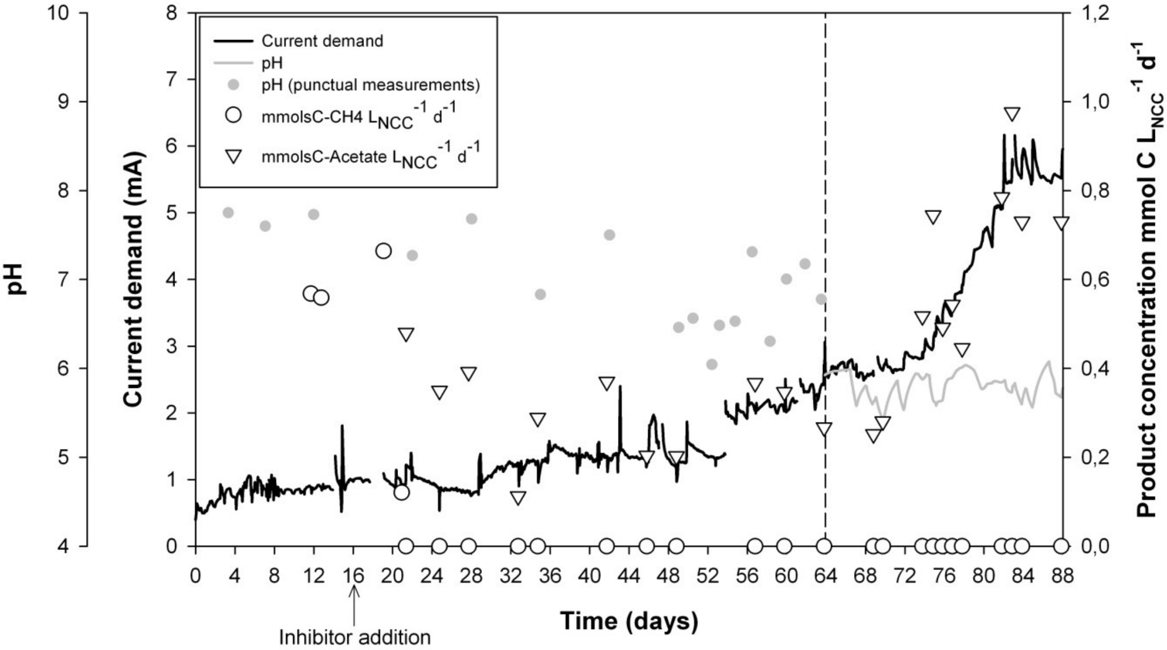

Figure 4. Evolution of current, pH and product concentration in MES system during the experimental period.

After 7 days of inhibitor addition, methane production almost disappeared and acetate was detected in the liquid phase. Production rate of acetate at day 21 was 0.48mmol $C\text{-}CH_3COOH \cdot L_{NCC}^{-1} \cdot d^{-1}$. Homoacetogens produced acetate from carbon dioxide and electrons instead of hydrogen as electron donor. During the experimentalperiod acetate production increased following a similar trend ofthe current demand. The highest acetateproduction rate observed was 0.97 mmol $C\text{-}CH_3COOH \cdot L_{NCC}^{-1} \cdot d^{-1}$, with an energy recovery of 43.7% (i.e. electrons recovered as product versus electrons consumed).

Although the current demand of the system was relatively low at the beginning (values lower than 1 mA), it was gradually increased along the experimental period. During the firsts 64 days, the pH of the cathode was not controlled. The pH average value was 6.99 ± 0.49. A pH control between 5.5 and 6.0 was implemented on day 64, which contributed to increase the current demand of the system up to values higher than 5 mA (Fig. 2). This current demand increase suggests the growth of theelectrotroph biofilm on the electrode surface and demonstrated that pH must be considered as one of the key parameters.

The results obtained demonstrate thefeasibility of MES to convert CO_2 into a valuable product using electrons as a source of reducing power. Production of methane or acetate can be selected by changing operational parameters of the system (i.e. pH control) or by cutting off metabolic routes of microorganisms. It is stated that current demand had a direct relationship with biofilm development and also had a clear effect on product formation rate. The development of this technology and its implementation could lead to reduce the carbon footprint of WWTPs and other CO_2 emitting installations or industries.

ACKNOWLEDGEMENTS

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(P15) Integration of algal production in WWTP sludge line

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Abstract

The integration of a photobioreactor for algal culture in the process scheme of WWTPs could have positive effects on mass and energy balances. The algal biomass could grow on N rich liquids, such as centrates from sludge dewatering, improving N removal and reducing the overall energy consumption, andthen undergo anaerobic digestion generating biogas. The preliminary balance shows thatthe energy cost of the activated sludge process could be reduced by 21%. Expected drawbacks are an increase in the land request and in the soluble N in the AD, thatshould be considered for its possible inhibitory effect on the methanogenesis. To validate computation and optimize a scale-up, a pilot plant research was started, whose first results are in agreement with the previously obtained lab-scale results. N removal was 73% (monthly average), specific growth rate 0.07 d^{-1} and algal biomass concentration in the photobioreactor effluent 2.03 g SS/L (max 4.7 g SS/L at 10 days HRT).

Keywords

Energy production,Integration, Microalgae, Wastewater Treatment Plants

INTRODUCTION

Actual sewage treatment relies on conventional activated sludge, which reaches sufficiently low carbon and nutrients effluent levels, but is not cost-effective, requires electricity equivalent to a fossil fuel consumption of 85 kWh per inhabitant equivalent (IE) per year and has an operationalfootprint of 80 kg CO_2 IE^{-1} $year^{-1}$ (Verstraete and Vlaeminck, 2010). This is mainly due to the high electrical energy that is needed in long sludge-age biological processes, designed to comply with nutrient discharge limits.Moreover, when working with long sludge ages, the biogas production rate of anaerobic digestion is poor and digesters have potential spare capacity to be used for co-digesting extra organic matter (Bolzonella et al., 2006).Nowadays, modifying the conventional wastewater treatment scheme in order to improve the energy efficiency thus reducing the carbon footprint is an important target. The feasibility to improve the energy balance of a conventional WWTP by integrating a photobioreactor (PBR) for microalgae cultivation is considered as already suggested previously (Ficara et al., 2013). This paper is focused on the mass and energy balances, computed to quantify the impact of the proposed treatment scheme on the nitrogen (N) and suspended solid(SS) fluxes and on the amount of biogas that can be produced by their anaerobic digestion.The first experimental data (September 2013) obtained at lab-scale are also presented.

MATERIAL AND METHODS

Mass and energy balances

Some preliminary mass balances were set across the sludge line in order to evaluate the effect that the integration of a PBR would have in mass (N, and SS) and energy balances. In Figure 1, the main sections and units included into this evaluation are reported. Calculations were based on the following typical data:

- typical daily loads per inhabitants equivalent (IE): N: 12 g $IE^{-1}d^{-1}$; per-capita sludge production (primary+secondary): 70 g $IE^{-1}d^{-1}$(Metcalf and Eddy, 2003), corresponding to 30 gCOD $IE^{-1}d^{-1}$of primary sludge, and 36 gCOD $IE^{-1}d^{-1}$of secondary sludge(Fdz Polanco et al., 2009).
- Fraction of the influent nitrogen that is sent to the sludge line: 15% (van Kempen et al., 2001).
- Anaerobic degradability of primary and secondary sludge of: 60% and 20%, respectively.
- Fraction of nitrogen in microalgal cells: 11% w/w of dry matter.
- Specific energy request for nitrification: 4.3 kWh/kgN (Metcalf and Eddy, 2003).

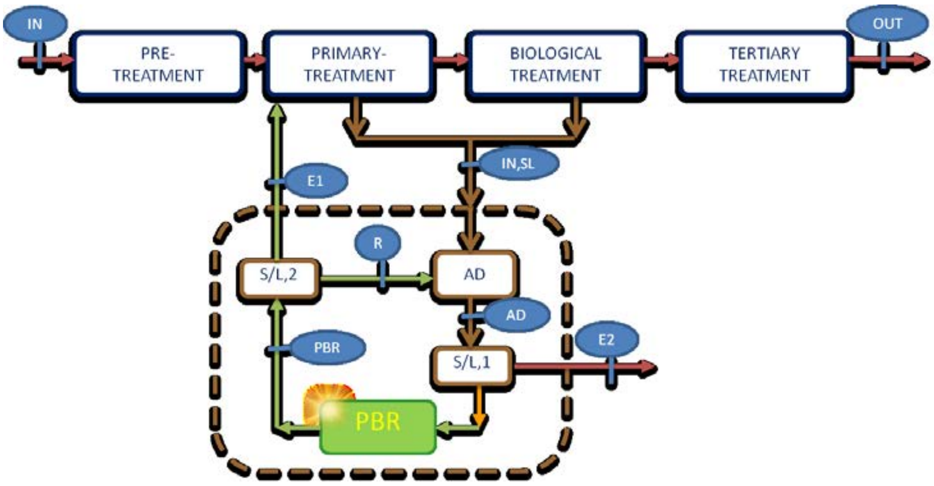

Figure 1. Simplified scheme of the sludge treatment train used (in the dashed box) to set energy and mass balances. AD = anaerobic digester, PBR = photobioreactor, S/L = Solid/Liquid separation.

Moreover, the following assumptions were made:

- N uptake efficiency in the PBR= 80% (Ficara et al., 2013).
- Hydrolysis has been considered as the limiting process in the anaerobic digestion of microalgae; the hydrolysis efficiency has been assumed to be around 60% (this value needs to be confirmed by experimental data).The fraction of N in the microalgae biomass that is released in solution during anaerobic digestion has been assumed to equate the hydrolysis efficiency (i.e. 60%)
- For simplicity, the separation efficiency of all solid/liquid (S/L) separation units hasbeen assumed to be 100%.
- The algal biomass has been assumed to be basically made of proteins, corresponding to a COD content of algal biomass of 1.42 $gCODgSS^{-1}$.

The pilot plant

At Bresso (MI) wastewater treatment plant (WWTP) a pilot plant (Figure 2) has been installed including a storage tank for feeding and one for the discharge of the effluent and a column photobioreactor in plexiglas. CO_2 is supplied using the off-gas from the turbine of the WWTP, fed on the biogas produced by the anaerobic digestion of sewage sludge.

Monitoring was carried out by regular sampling and analyses at the inlet and at the outlet of the photobioreactor. The development of algal biomass was determined by the measurement of Total Suspended Solids (g/L) and of the absorbance (at 665 nm wavelength) of the algal suspension. Total, ammonia and nitrate nitrogen were determined according to Standard Methods; Temperature (°C), pH and P.A.R. (Photosynthetically Active Radiation, µmolphotons $m^{-2}s^{-1}$, measured by a DeltaHom HD21 specific instrument) were monitored.

The plant was operated without any modification in environmental conditions, i.e. at natural temperature and solar radiation.

Figure 2. The pilot plant installed at Bresso (MI) WWTP.

RESULTS

Mass and Energy balances

Mass balances were based on the assumptions listed in Materials and Methods and by imposing the mass conservation principle. Results are summarized in Table 1 and indicate that the amount of solids that are produced by microalgal growth account for the 18% of the SS that are normally fed (primary and secondary sludge). As for the N load, the presence of the PBR modifies the apportioning of N among the two fluxes exiting the sludge line (E1 and E2) increasing the fraction of N leaving as biosolids (E2) which increase from 0.7 (obtained by assuming the efficiency of the PBR = 0) to 1.4 gN $IE^{-1}d^{-1}$; this reduces the N load returned to the water line from 1.1 to 0.4 gN $IE^{-1}d^{-1}$. On the other hand, the load of soluble N that leaves the anaerobic digester increases from 1.1 to 2.1 $IE^{-1}d^{-1}$, therefore free ammonia inhibition on methanogenesis should be monitored.

As for the energy balance, the energy produced by anaerobic digestion in the absence of the PBR is computed in 31 Wh IE^{-1} d^{-1}, while the extra energy produced from the microalgal biomass results to be 15 Wh IE^{-1} d^{-1} (+48% of energy production from anaerobic digestion). Moreover, the reduction of the nitrogen loads that has to be nitrified in the water line results in an further energy saving of 3 Wh IE^{-1} d^{-1}. On the overall, the PBR allows for an extra net energy production of 18 Wh IE^{-1} d^{-1}, which corresponds to the 21% of the average energy cost of the activated sludge process (assumed as 86 kWh IE^{-1} d^{-1}, after Müller and Kobel, 2004). However, the increase in the footprint of the WWTP has to be taken into account as a major drawback of this new treatment scheme. By assuming a specific microalgal productivity of25gSSm^{-2}d^{-1} (Lardon et al. 2009), the land request for the PBR would be of 0.6 m^2IE^{-1} d^{-1} in comparison to an average of 0.25 0.6 m^2IE^{-1} d^{-1} of Italian WWTPs.

Table 1. Main results of mass balances. Section nomenclature refer toFigure 1

	Nitrogen load (g $IE^{-1}d^{-1}$)			SS load(gSS $IE^{-1}d^{-1}$)
Section	total	Soluble	particulate	
IN	12	0	0	
IN,SL	1.8	0	1.8	70
AD	3.5	2.1	1.4	85
IN PBR	2.1	2.1	0	0
OUT PBR	2.1	0.4	1.7	15
E1	1.4	1.4	0	0
E2	0.4	0	0.4	34

Pilot plant performance

The results obtained at pilot scale are in substantial agreement with those obtained in the previous lab-scale experiments (Ficara et al., 2013). Percent N removal and biomass production were a little lower (73% vs. 77-82% and 0.123 g SS/L/d, respectively, on undiluted centrate), and specific growth rate (μ) a little higher (0.07 vs. 0.04÷ 0.06 d^{-1}). The algal biomass concentration in the photobioreactor effluent (2.03 g SS/L) was higher than observed before, with a peak of 4.7 g SS/L at 10 days HRT and made of *Scenedesmusquadricauda* and *Chlorella vulgaris*

CONCLUSIONS

Mass and energy balances suggest that the presence of the PBR allows to increase the SS load to the AD section and therefore the energy produced by the combined heat and power (CHP) unit, while reducing the nitrogen load that is returned to the water line, resulting in reducing the energy cost of the activated sludge process by the 21%. On the other hand, expected drawbacks are an increase in the land request and an increase of the soluble nitrogen in the AD should be considered for its possible inhibitory effect on the methanogenesis. Of course, more experimental data are needed to confirm the values assumed for computing. On the other hand, experimental work is needed to optimize the process performance and to provide the basis for a scale-up.

Till now, the results obtained at pilot scale confirm the ones obtained at lab-scale. It will be important to observe the seasonal influence and to eventually define the thresholds for solar radiation and temperature below which artificial interventions (lightning, heating) could be cost-effective in the light of energy and mass balance.

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(P16) WWTP primary sludge pre-concentration with membrane and biosorption to increase biogas production

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Abstract

In the present work the pre-concentration of primary sludge from WWTP was studied with membranes and biosorption. The best working conditions in terms of technical feasibility and economics aspects where fulfilled with biosorption technology with a cost of 12 €/IE in front of 40 €/IE when using membranes. The efficiency of COD, TSS and N recovery was 80%, 95% and 40% respectively using Fe as a coagulant. The energetic balance confirmed that with this configuration 110% of the theory energy of the WWTP could de recovered with the biogas production that increased to 0.25-0.36 L CH_4/g VS.
The results and knowledge obtained from this work is the basis of on-going LIFE NECOVERY project which is focused on demonstrate, by means of a prototype, the feasibility of an innovative wastewater treatment plant (WWTP) flowsheet based on an up-concentration step at the inlet of the WWTP and the recovery of nutrients and energy.

Keywords
Biogas; Biosorption; Pre-Concentration.

INTRODUCTION

In the current economic and environmental context, the increase of energy prices and consumption lead to look for newer alternatives to increase energy and resource recovery of wastewater treatment plants (WWTP). The most common treatment system for domestic wastewater, currently in use, is presented in Figure 1. This process reaches sufficient low pollutant effluent levels but has a high energy consumption of 20-35 kWh_{el}/PE-y and does not recover most of the valuable resources that are present in the wastewater, such as energy and nutrients (Verstraete and Vlaeminck 2011). The feasibility of a new sustainable and resource-efficient WWTP with the purpose of recovering more solids than in a primary settler (pre-concentration), as alternative to conventional systems, has been considered (Figure 2) with membrane concentration or biosorption. The latter would allow producing more biogas as well as reducing energy required. (Wett et al. 2007, Verstraete et al 2009).

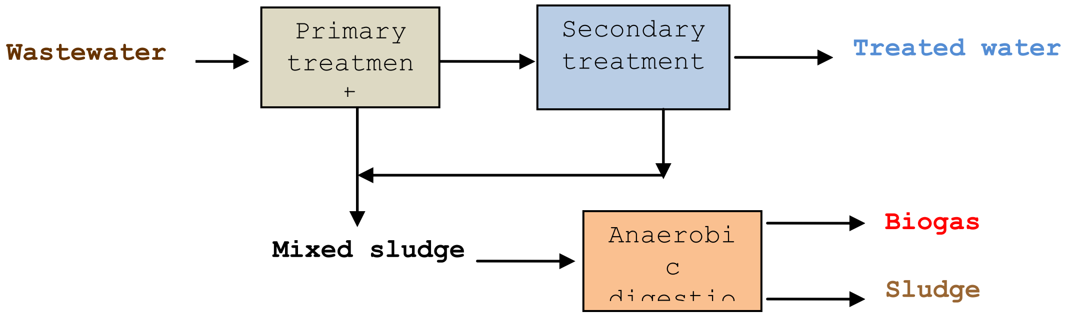

Figure 1: Conventional configuration of a wastewater treatment plant.

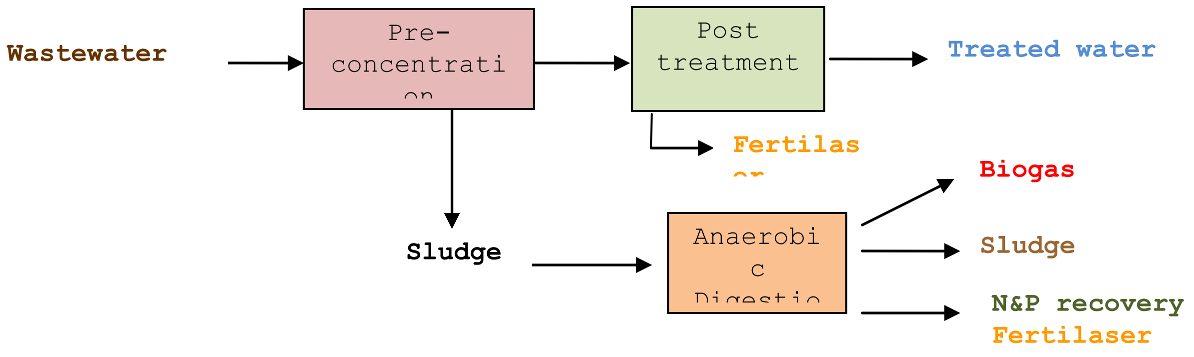

Figure 2: New concept of a wastewater treatment plant.

MATERIAL AND METHODS

A wide range of influent composition of sewage wastewater was tested for up-concentration tests (CODt: 300 -1,500 mg/L; CODs: 150-500 mg/L; VSS: 70-400 mg/L; NH_4-N: 25-85 mg/l).

Membrane device: The first feasibility studies consisted of the up-concentration of the sewage influent by membrane filtration (tests with a specific Filmax unit with vortex generator to reduce membrane fouling). Batch experiments were carried out using 200 L of sewage wastewater and have been followed up until the maximal achievable up-concentration (Figure 3). Four different types of membranes were tested (Enanics, FU-N50, FU-N10, FM-N005).

Biosorption device: The AB-Boehnke system consists of a biological system comprising a highly loaded first stage (A-stage) followed by a lowly loaded second stage (B-stage). Both stages have a separate settling tank and sludge recycle system. The first small reactor (A) is the biosorption one used that has high sludge loading rate (3-15 kg biodegradable COD/kg MLVSS·day). Moreover, it has a high rate of sludge withdrawal (SRT of 0.1-0.5 days) which allows to remove from 45 % to 65 % of BOD by biosorption. During the total test period the lab biosorption reactor (4.5 L) of Figure 4 was operated in a continuous way with different operating conditions (HRT and SRT). Additionally, some experiments by means of Chemical Enhanced Primary Treatment (CEPT) with $FeCl_3$ and $FeSO_4$ addition were also done.

Figure 3. FMX-set-up used

Figure 4. Aerobic biocontactor.

- Anaerobic digestion device

A 5 L reactor was operated with biomass from the A process of Breda WWTP (The Netherlands) to provide inoculum for the tests in a temperature-controlled room (33°C). The reactor worked as an anaerobic contactor (AC) instead of as a continuous stirred tank reactor (CSTR) to avoid that HRT = SRT and be able to obtain more biogas production. The feeding of fresh substrate and the withdrawal of digested effluent was done manually three times a week (batch wise).

RESULTS AND CONCLUSIONS

In general, it can be concluded that membrane filtration with the different types of membranes mainly retained the COD fraction that was present under suspended form in the wastewater and almost no soluble COD, N and PO_4^{3-}-P were retained. Enanics membrane presented the best results of removal and are the one presented in Table 1.

The results of the biosorption tests revealed that this process is suitable for up-concentration of urban wastewater. TSS was removed in the lab-scale test, but also an important part of the COD, present under dissolved/colloidal form. However, the N and P removal efficiencies strongly fluctuated.

From the economic point of view, CAPEX of the membrane up-concentration solution is estimated to cost around **40 €/IE**, while the biosorption with Fe would have a cost of **12 €/IE**. Moreover, the CEPT-bioflocculation treatment with low addition of Fe (extra 0.3-0.6 €/Kg) seems to be the most suitable option from the N&P recovery point of view.

The theoretical maximum biogas production rate of a sludge is 0.45 L CH_4/g VS_{added} and with the experiments carried out, a range of 0.26-0.37 L CH_4/g VS was obtained for the up-concentration with membrane and a range of 0.25-0.36 L CH_4/g VS was obtained for the biosorption sludge. In a normal plant with an AD of mixed primary and secondary sludge the latter value is placed around 0.25-0.30 L CH_4/g VS (or 0.9 L biogas/VS destroyed) which means that in overall the ratio is equal or improved using the up-concentrated sludge obtained.

Considering the research done, it can be concluded that the biosorption process is the most appropriate process for pre-concentration of urban wastewater taking into account technical feasibility (COD and N recovery) and economic aspects (Table 1).

Table 1. Comparative of alternatives with conventional primary settler

	Conventional primary settler	**Concentrates Membrane**	**Bioflocculation no additives**	**Bioflocculation + $FeCl_3/FeSO_4$**
COD recovery	20-25	60 - 70	80	80
CODs removal	No	No	Partial	Partial
N recovery %	10	10 – 20	40	40
TSS removal %	50-60	100	90	95
WWTP Energy Balance	40% Recovery of Energy Used	20% Recovery of Energy Used	110% Recovery of Energy Used	110% Recovery of Energy Used
Bulking	No	No	No	Yes

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(S13) Comparison of different reactor configurations for struvite crystallization by using a low cost magnesium product

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Abstract

The crystallization of struvite (magnesium ammonium phosphate, $NH_4MgPO_4 \cdot 6H_2O$) could be an economical alternative to recover phosphorus from wastewaters. In this sense, development of cost-effective processes requires the selection of appropriate alkalinity and magnesium sources, and suitable reactor configuration.

This study presents a comparative approach to investigate the potentials of two different reactor configurations for the struvite crystallization. Struvite crystallization was promoted by using an industrial grade magnesium hydroxide suspension. The reactors were fed with a wastewater with a phosphate concentration range between 62 and 280 mg P/L. Struvite crystallization was observed with a phosphate removal being above 76%. pH of the operation ranged from 8.0 to 9.0. Magnesium hydroxide consumption was estimated to be around 3.8 and 2.2 t-magnesium product/t-P precipitated for the two-phase fluidised bed reactor and for stirred tank reactor, respectively.

Keywords

continuous stirred tank reactor; fluidized bed reactor; magnesium hydroxide; phosphate recovery; struvite crystallization

INTRODUCTION

Phosphate recovery in wastewater treatment plants only will be viable, if there is an economic incentive to implement phosphate recovery technologies. The crystallization of struvite (magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$) could be a sustainable alternative to recover phosphate from wastewater, especially at high phosphate concentrations. Struvite may be used in agriculture as a slow release fertilizer (de-Bashan and Bashan, 2004).

In this sense, struvite crystallization costs should be compared with those used conventionally for phosphorus removal processes. The costs for the phosphorus removal from wastewater can be set at 2-3 €/kg P at minimum and may amount to more than 10 €/kg P under specific conditions. On the other hand, the recovery of phosphorus are in wide range of 2.2-8.8 €/kg P depending on the process (Dockhorn 2009). On the other hand, the main cost factors that affect the economy of the struvite crystallization process are magnesium and alkali sources (Dockhorn 2009). Development of cost effective struvite precipitation processes requires the selection of appropriate alkali and magnesium sources.

In recent years, several studies based on struvite crystallization have used mainly $MgCl_2$, $Mg(OH)_2$, MgO, seawater and NaOH, as magnesium and alkalinity sources. These studies have been developed using different reactor configurations, such as airlift, fluidized bed or continuously stirred tank reactors (Morse et al, 1998). The aim of this study was to compare the use of a low cost magnesium product for struvite crystallization by using a two-phase fluidised bed reactor (FBR) and a continuous stirred tank reactor (CSTR).

MATERIALS AND METHODS

This study was carried out using two different reactor configurations to promote the struvite crystallization: a FBR and a CSTR coupled to an external settler to separate and recycle precipitates to the reactor. The reactors were fed with a synthetic solution with a similar composition to centrate wastewater. The phosphate concentration of the FBR was fixed at 62 mg P/L and 280 mg P/L during stages 1 and 2, respectively. Phosphate concentration of the CSTR was 62 mg P/L and 112 mg P/L during stages 1 and 2, respectively. Magnesium hydroxide suspension was fed as both magnesium and alkali source. The magnesium hydroxide suspension was prepared by hydrating powdered industrial grade magnesium oxide in water. pH was controlled by using magnesium hydroxide suspension. Most of the analyses performed in the liquid phase were done accordingly to standard methods (APHA, 1998). The nature of the precipitates was determined by X-Ray Diffraction (XRD) Siemens D505 and the appearance of the precipitates were analyzed by Scanning Electron Microscopy (SEM; ZEISS EVO®LS).

RESULTS AND DISCUSSION

Phosphate recovery percentage in the FBR and CSTR were around 92% and 76%, respectively. For FBR the pH ranged from 8.0 to 8.5, whilst that for CSTR the operation pH ranged between 8.0 and 9.0. The precipitates obtained in each reactor operation were observed and analyzed using SEM (Figure 1). The SEM observations for these precipitates showed that most of precipitates were monocrystals. According to XRD results these crystals were mostly composed of struvite. XRD analyses also indicated the presence of a small fraction of brucite ($Mg(OH)_2$). The content of $Mg(OH)_2$ in the precipitates of FBR and CSTR was 4% and 1% by weight, respectively.

During the operation of FBR the magnesium product requirements were around 3.8 t-magnesium product/t-P precipitated, whilst that for STR operation was 2.2 t-magnesium product /t-P precipitate. The molar ratio of $Mg(OH)_2$ added/P precipitated were 1.6 and 1.0 for the FBR and CSTR, respectively. This indicated that CSTR was more efficient for recovering phosphate as struvite using the magnesium hydroxide suspension. Moreover, costs due to magnesium hydroxide requirements were estimated to be around 1,330 €/t-P precipitated and 770 €/t-P precipitated by using the FBR and the CSTR, respectively. These costs are much lower than those estimated by other authors (Dockhorn 2009).

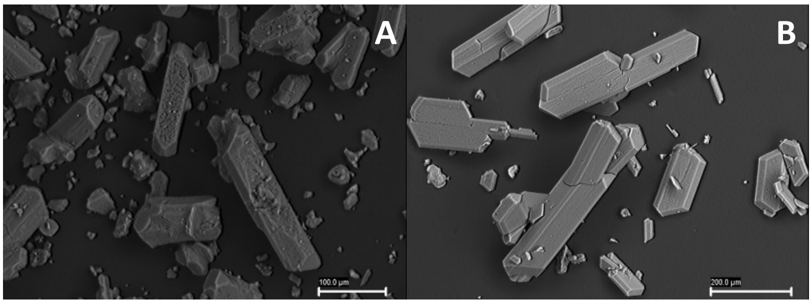

Figure 1. SEM microphotographs of the precipitates formed during the operation of (A) fluidized bed reactor and (B) continuous stirred tank reactor.

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(S14) Recovering salts from industrial brines by NF-MD: Case studies on IEX regeneration wastewater and chloride rich wash water from a zinc ore refinery

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Abstract

The possibilities for salt recovery from industrial brines by a coupled nanofiltration - membrane distillation (NF-MD) process are illustrated in this paper by two case studies i.e. the recovery of water and chloride salts from Ion Exchange (IEX) regenerate and from zinc ore refinery wastewater. Ion exchange based demineralization of tap water for the preparation of process water results in a saline regeneration wastewater. Techno-economical evaluation shows that NF-MD on this wastewater is economically feasible for midsized and larger scale demineralization plants (200 to 2000 m^3/day demineralized water) but only when discharge is prohibitively expensive or not allowed. Scaling is found to be a main bottleneck for NF-MD. It is therefore concluded that further physicochemical pretreatment is required to improve the process. The cost benefits of water reuse (1.5% to 3.2%) and salt recuperation (0.16% to 0.36%) are small when compared to the overall treatment cost. The main benefits are reduced discharge of chlorides and cost reduction for middle sized (43%) and larger installations (47%) in comparison to the cost of external wastewater disposal. An important step in the production of secondary zinc oxides is the washing of zinc oxide to remove chlorides and fluorides. During this washing step, a chloride rich waste stream is generated. A valorisation of this chloride rich waste stream is desired both to improve local environmental conditions and to allow increased zinc production capacity currently limited by chloride load based discharge limitations. Nanofiltration is able to remove the major part of the metals present in the feed stream. During membrane distillation of the NF permeate no scaling issues were experienced. The final brine can be evaporated to a salt containing 45.9 % NaCl and 54 % KCl.

Keywords

Resource recovery; membrane distillation; nanofiltration; NF-MD; brine; chloride, regenerate, IEX, ore refinery

INTRODUCTION

Chloride rich wastewaters are found in many industrial sectors e.g. chemical, petroleum, textile and leather industries and where ion exchange (IEX) processes for softening and demineralisation of water are applied (Levebre and Moletta, 2006). The discharge of these brines is continuously becoming more problematic due to increasingly stringent discharge limits. The growing application of industrial wastewater reuse moreover results in an increased effluent salinity. Production facilities discharging to small inland rivers are more affected than sites located near the sea or a brackish water body where discharge of brine may be environmentally acceptable. In specific cases the inability to discharge a wastewater due to high salt content can become a real bottleneck for a plant and limit industrial production. An increasing interest in new technologies and concepts for the recovery of inorganic salts from industrial brines is therefore observed (Kim, 2011). Depending on the flow and composition of the brine there are several possible concepts on how to deal with this: e.g. purification of the brine for internal reuse in the production site (Tang and Chen, 2002) and purification-concentration-crystallization for internal reuse or external valorisation. The Flemish innovation and cooperation project “The Blue Circle” (IWT VIS-traject De Blauwe Cirkel) focuses on these concepts for recovery of water and resources from inorganic concentrates. The application of a coupled nanofiltration - membrane distillation process (Hassan et al., 1998, Gryta et al., 2006) is evaluated during this project among other technologies and is illustrated in this paper by two case studies. Membrane distillation (MD) is combined with nanofiltration (NF) to create an integrated separation system in which NF functions as the purification stage and MD as the concentration stage. NF retains multivalent ions like calcium, magnesium or sulphates and metal ions resulting in a sodium chloride rich and purified permeate stream. Partial desalination using NF also softens the MD feed and is therefore expected to reduce MD scaling issues (Gryta et al., 2006). Membrane distillation is an emerging evaporation technology that allows strong volume reductions of brines, depending on salt solubility while using cheap waste heat. Recent research shows the possibilities of recovering crystalline products directly from an integrated MD - crystallization process (Curcio et al., 2010). The process scheme envisaged in this work incorporates MD only for brine concentration until saturation followed by conventional crystallization. The main objective of this work is to evaluate the performance of NF-MD (Figure 1) for the recovery of distilled water and chloride salts from IEX demineralization regenerate and zinc ore refinery wastewater.

[redacted]

Figure 1. Process scheme for NF-MD on brine

MATERIALS AND METHODS

Wastewater samples were obtained from a large demineralisation plant in the port of Antwerp and from a local zinc ore refinery. Following NF membrane screening both wastewater samples were filtrated using a 2.4 inch spiral-wound NF module. The zinc ore wastewater was first pretreated with UF. DOW-Filmtec NF270-2540 was used for the IEX regenerate, Osmonics Desal 5DK was used for the zinc ore refinery wastewater. NF permeates were further concentrated on a labscale MD unit using 80°C influent temperature and 10°C transmembrane temperature. A polypropylene membrane was used for the zinc refinery wastewater and a PTFE membrane for the IEX regenerate. Chemical analysis was performed on raw wastewater and NF-MD fractions. Cost estimation for the treatment train was done based on technology supplier's information.

RESULTS AND DISCUSSION

Case study 1: IEX regeneration wastewater

Ion exchange based demineralization of tap water is frequently used to prepare process water for industrial activities. The wastewater from the regeneration of ion exchange resins consists of an aqueous mixture of salts, organic matter and metals and has a considerable salinity typically ranging from 20 to 100 mS/cm (Gryta et al., 2005). Sodium chloride is the major component in ion exchange regeneration wastewater (Table 1). Nanofiltration on the regenerate wastewater was done at 7 bar and resulted in a 15 $l.m^{-2}.h^{-1}$ flux; only 60% water recovery could be obtained due to scaling. MD on the NF permeate of the mixed regeneration wastewater resulted in a constant flux of 17 $l.m^{-2}.h^{-1}$ and no flux decline was observed until a 26-fold volumetric concentration was obtained. Signs of scaling were observed on the MD membrane. The resulting salt composition (calculated) is not sufficiently pure for reuse in chemical industry but is expected to qualify as a road de-icing salt.

	regenerate	NF concentrate	MD distillate	MD concentrate		salt composition	
Q	300	120	173	7.2	m^3/day	1.45	ton/day
Cl-	5460	9260	80	123000	ppm	61	%
NO3-	256	370	< 0.89	5590	ppm	2.7	%
SO4 2-	920	3624	< 3.0	220	ppm	0.11	%
Ca2+	1270	3765	< 10.0	12300	ppm	6.1	%
K+	81.8	95	8.8	2160	ppm	1.1	%
Mg2+	142	519	< 0.50	422	ppm	0.21	%
Na+	2410	2785	51.8	57600	ppm	28.5	%

Table 1. Chemical composition of IEX regenerate and NF-MD resulting fractions

Techno-economical evaluation shows that the NF-MD process is economically feasible for midsized and larger scale demineralization plants (200 to 2000 m^3/day demineralized water) but only when discharge is prohibitively expensive or not allowed. Scaling is found to be a main bottleneck for the process both for NF and MD stage. It is therefore concluded that further physical chemical pretreatment is required to improve the process. The cost benefits of water reuse (1.5% to 3.2%) and salt recuperation (0.16% to 0.36%) are small when compared to the overall treatment cost. The main benefits of the process for this case study are the reduced discharge of chlorides to the environment and cost reduction for middle sized (43%) and large installations (47%) in comparison with the costs of external wastewater disposal.

Case study 2: Ore refinery wash water

An important step in the production of secondary zinc oxides is the washing of zinc oxide to remove chlorides and fluorides. During this washing step, a chloride rich waste stream is generated. This wastewater contains high amounts of sulphates and metal ions such as cadmium, strontium, lead and zinc (table 2). Sodium chloride and potassium chloride are the main constituents of the wash water. Preliminary experiments show that when permeate recovery was further increased, flux declined strongly and the retention of Cd, Zn, Pb, and sulfates declined. A permeate recovery of 50% was determined to be optimal for NF on this wastewater. When applying NF in the wastewater, a flux of 46 l.m^{-2}.h^{-1} was obtained at 50% permeate recovery (12 to 14 bar TMP). The NF concentrate fraction can be reused in the washing process. MD on the NF permeate resulted in a constant flux of 14 l/m^{-2}.h^{-1}, flux declined to 10 l/m^{-2}.h^{-1} during the last part of the experiment. A 25-fold volumetric concentration was obtained. No signs of scaling were found on the MD membrane. The final brine can be evaporated to a salt containing 45.9 % NaCl and 54 % KCl. The salt could qualify as a road de-icing salt and can also be reused by industry in the aluminium recycling process given the specific KCl/NaCl ratio. When NF-MD is applied, the recovery of chlorides from the zinc refinery wastewater reduces the discharge of chlorides below the imposed discharge limit. This is beneficial for the local environment and also allows an increased zinc production capacity, currently limited by a mass load based discharge limit for chlorides.

Table 2. Chemical composition of zinc ore refinery wash water and NF-MD resulting fractions. n.m. = not measured

	wastewater	NF permeate	MD distillate	MD concentrate		salt composition	
Q	480	210	201.5	8.5	m^3/day		ton/day
Cl^-	6310	4880	32.8	120000	ppm	49.9	%
SO_4^{2-}	1790	7.5	<3	138	ppm	0.057	%
K^+	3760	2790	n.m.	69750	ppm	29.0	%
Na^+	2610	2010	n.m.	50250	ppm	20.9	%
Cd (tot.)	1.26	0.461	<0.0020	6.42	ppm	0.0027	%
Zn (tot.)	27.2	5.19	<0.025	82.6	ppm	0.034	%
Sr (tot.)	1.65	0.071	<0.050	1.6	ppm	0.00067	%
Pb (tot.)	0.032	0.017	<0.010	0.342	ppm	0.00014	%

CONCLUSION

The recovery of salts from the presented saline wastewaters by NF-MD is technically feasible but not economically interesting as long as discharge is allowed. The main and current driver for implementation of NF-MD like resource recovery processes is discharge regulation. In the IEX regeneration wastewater case study, NF-MD was found to result in improved techno-economical feasibility when compared to external treatment of the wastewater. For the zinc ore refinery case, brine recuperation by NF-MD may results in a significant reduction of the chloride emission to surface water. However the investment and operational costs are high. Only under the conditions that the zinc production capacity of the site can be increased due to the lower environmental impact, an economical feasible business case is possible.

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(S15) Effects of sodium on the PHA accumulation by a microbial mixed community

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Abstract

Polyhydroxyalkanoates (PHAs) are a group of biopolyesters that can be produced by bacteria. Their production has been extensively studied during the last decades due to their potential to replace the conventional oil-based plastics and to their characteristic of being fully biobased and biodegradable. Furthermore, they can be produced from different kinds of wastewater.

The present work studies the feasibility of the production of PHA by the use of microbial mixed cultures fed with a mixture of volatile fatty acids and a concentration of 1 g Na^+ L^{-1}, mimicking the effluent from anaerobic digesters treating fish canning effluents. Alternating conditions of presence (feast) and absence (famine) of substrate were used to enrich a PHA accumulating community. For this purpose, a sequencing batch reactor was used.

The maximum PHA accumulating capacity of the microbial community was studied in fed-batch experiments. The feeding was a synthetic medium with the same composition in volatile fatty acids as the one previously used in the enrichment stage but with addition of different sodium concentrations (6 and 10 g Na^+ L^{-1}). These different sodium concentrations were used to study its effect over the accumulation capacity of the culture. The microbial enrichment obtained in the presence of 1 g Na^+ L^{-1} was able to accumulate, after 24 hours, a maximum of 41% PHA in dry weight with a HB:HV ratio of 1.57 g/g. Results obtained from the batch assays performed with 6 and 10 g Na^+ L^{-1} indicated that 5.7% and 1.2% of PHA were accumulated after 24 hours with HB:HV ratios of 2.14 and 3.83, respectively.

Obtained results indicate that the concentration of Na^+ affected the PHA accumulation in two ways: it influenced, firstly, the total amount of polymer stored inside the cells and, secondly, the HB:HV ratio.

Keywords

Fish-canning Wastewater; HB:HV ratio; Mixed Culture; Polyhydroxyalkanoates; SBR

INTRODUCTION

Polyhydroxyalkanoates (PHAs) are a group of polyesters from biological origin that can be synthesized under stress conditions by several microorganisms and stored inside the cells as carbon and energy source. Since the discovery of polyhydroxybutirate (PHB) production in *Bacillus megaterium* by Lemoigne in 1926, hundreds of different types of microorganisms have been reported as natural PHA producers (Steinbüchel and Valentin, 1995) and over 150 different hydroxyalkanoic acids have been identified as products (Sudesh *et al.*, 2000). Due to their properties, they could be good candidates to replace the conventional plastics and also their production system.

The key factor in PHA production with mixed microbial communities is the enrichment process. This is achieved by applying a selective pressure based on the ecological role of PHA as a microbial storage material (van Loosdrecht *et al.*, 1997). The strategy is based on alternating conditions of substrate in order to enhance PHA storage capacity. For this purpose, conditions of excess and limitation of carbon source (feast-famine regime) are applied. The enhanced capacity of the microbial communities to store PHA under these conditions was confirmed in previous works (Dionisi *et al.*, 2005; Moralejo-Gárate *et al.*, 2011; Reis *et al.*, 2003).

As naturally occurring organic compounds, microorganisms can produce them from different carbon origins as, i. e., waste materials or other renewable sources. This allows the development of sustainable new processes for the production of plastics. In Galicia, one important waste stream is produced from the fish-canning industry which is usually rich in salts like those containing sodium.

In the light of the above, the main objective of this work is to study the influence of sodium in the accumulation stage of a mixed culture enriched using a mixture of volatile fatty acids.

MATERIALS AND METHODS

A sequencing batch reactor (SBR) of 1.8 L was used for the enrichment of the PHA accumulating culture. It was operated in cycles of 12 hours at a hydraulic retention time and solids retention time of 1 day. A PHA producing culture was enriched, under conditions of feast-famine regime, from activated sludge using a synthetic mixture of volatile fatty acids (VFAs) as substrate (Table 1). Allylthiourea was added to inhibit the nitrification process.

A second reactor, inoculated with the biomass harvested from the previous unit, was operated discontinuously under excess of organic matter to evaluate the maximal PHA accumulation capacity of the mixed culture. It had a variable useful volume up to 5 L which depended on the amount of biomass harvested from the enrichment reactor. The same feeding was used in terms of nutrients and VFAs composition (Table 1) but with different concentrations of Na^+ in order to check its influence over the accumulation of polymer in the cells.

Both reactors were operated under fully aerobic and mixing conditions at 30 ºC and without pH control.

Table 1. Characteristics of the feeding of the enrichment reactor.

VFAs (mL/L)		**Salts (g/L)**	
HAc[1]	1.45	NH_4Cl	0.66
HPr[2]	0.60	KH_2PO_4	0.349
HBu[3]	0.16	$MgSO_4.7H_2O$	0.137
i-HV[4]	0.06	KCl	0.053
n-HV[4]	0.23	Trace Compounds	1.5 mL

[1]Acetic Acid; [2]Propionic Acid; [3]Butiric Acid; [4]Valeric Acid

Respirometric assays (Mosquera-Corral *et al.*, 2005) were performed in vials of 10 mL to evaluate the effects of different concentrations of sodium (1, 3, 5 and 7 g $Na^+ L^{-1}$) on the respiration capacity of the enriched sludge. Biomass concentration in the vials was of 1 g VSS/L.

The pH value was measured with a pH-meter with a glass electrode. VFAs were analysed by gas chromatography, cations by ionic chromatography., PHAs by gas chromatography and solids according to the *Standard Methods* (APHA-AWWA-WPCF, 2005).

RESULTS AND CONCLUSIONS

The enrichment reactor was operated at 0.91 ± 0.16 g Na^+ L^{-1} and the pH value was of 9.2 ± 0.4 without control. The length of the feast phase was of 2.5 h when steady state conditions were achieved. The HB:HV ratio was close to 1 g/g during the enrichment.

Respirometric batch experiments, performed with different concentrations of sodium, indicated that the presence of 1 g Na^+/L provoked a decrease of the oxygen uptake rate of the enriched culture of 50% (Figure 1). For higher sodium concentrations the effect over the respiration activity is even more severe. These results suggest that the respiration capacity of the enriched mixed culture could be affected by this compound. It might be the case that the accumulation capacity could experience a similar effect.

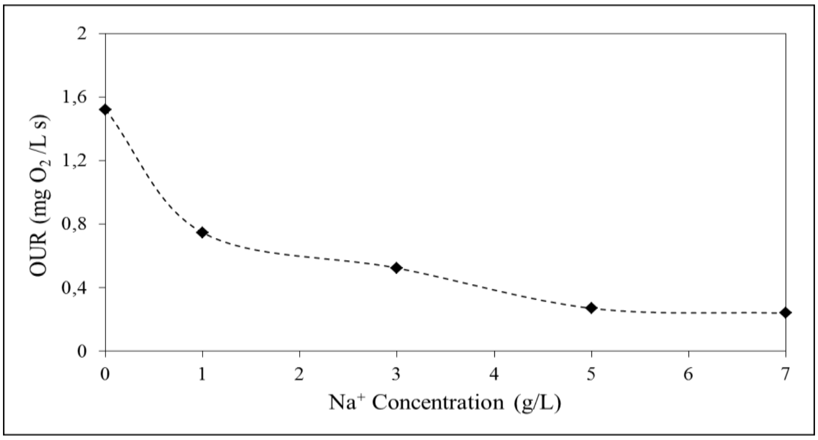

Figure 1. Effect of the Na^+ concentration on the oxygen uptake rate of the enriched mixed culture.

To evaluate this possible effect of the Na^+ concentration on the accumulation capacity of the enriched mixed culture experiments were performed at different concentrations (1, 6 and 10 g Na^+ L^{-1}). Fed-batch assays of 24 h length were performed using the same VFA composition of the feeding but added in pulses every time the oxygen rose up over 4-5 mg O_2/L. The concentration of sodium was constant along the batch experiment for each concentration tested. The evolution of the concentrations corresponding to the different compounds present in the liquid phase and in the biomass where measured along the experiment and the polymer accumulation along the time was measured (Figure 2). Maximum PHA contents inside the biomass at the end of the experiments were 41wt%, 5.7wt% and 1.2wt% and HB:HV ratios of 1.57, 2.14 and 3.83 for experiments performed with 1, 6 and 10 g Na^+ L^{-1}, respectively.

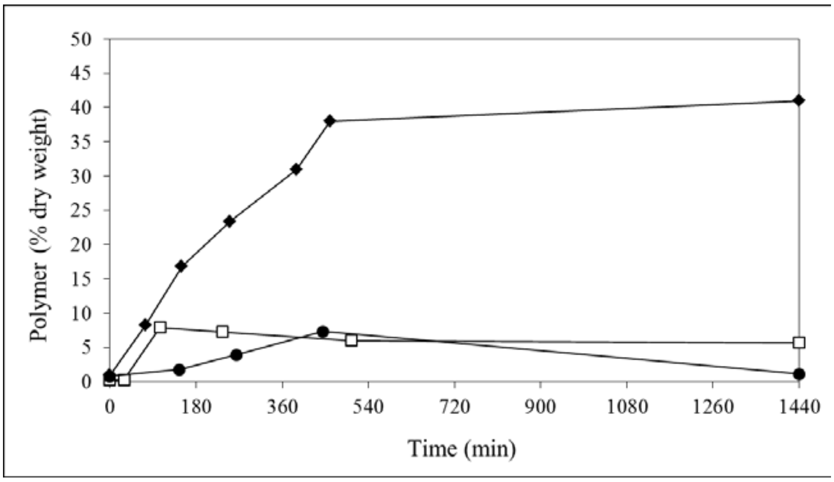

Figure 2. Results of the accumulation assays under different sodium concentrations: 1 g Na^+ L^{-1} (◆), 6 g Na^+ L^{-1} (□) and 10 g Na^+ L^{-1} (●).

The maximum polymer production rates estimated from the obtained results were of 6.34, 6.24 and 1.12 g PHA g^{-1} biomass h^{-1} for the concentrations of 1, 6 and 10 g Na^+ L^{-1}, respectively. The PHA production rates were similar for the assays with 1 and 6 g Na^+ L^{-1}. A lag phase at the beginning of the assay at 6 g Na^+ L^{-1} can be observed and after that the subsequent consumption of polymer began. In the assay with 1 g Na^+ L^{-1} no consumption was observed after reaching the maximal accumulation capacity and the curve followed the shape of a normal accumulation curve. Another useful indicator of the performance of the batch assay is the evolution of the ammonium concentration. It was totally consumed after 460 minutes and 1440 minutes for the experiments with 1 g Na^+ L^{-1} and 6 g Na^+ L^{-1}, respectively. However, it was not fully consumed when the concentration of sodium inside the reactor was of 10 g Na^+ L^{-1}.

At the sight of the previous results, it is possible to assess that the concentration of Na^+ affected the PHA accumulation of an enriched mixed culture in two ways: firstly, the total amount of polymer stored inside the cells decreases when the sodium concentration increases and, secondly, the HB:HV ratios change. These findings are of interest when a certain composition of the polymer in HB and HV is desired for application purposes.

ACKNOWLEDGEMENTS

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Efficient Technologies - Membrane technology

(Tuesday, 24 June 2014, Aula T2, Polo Zanotto)

(K4) Energy Production Potential of a Pilot-Scale Staged Anaerobic Fluidized Membrane Bioreactor (SAF-MBR)

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Abstract

Performance of a staged anaerobic fluidized membrane bioreactor (SAF-MBR) including energy balance was studied with pilot scale SAF-MBR treating primary clarifier effluent from domestic wastewater treatment plant. It operated more than a year with 4.6 to 5.5 h of total hydraulic retention time (HRT), and the COD and BOD_5 removals were 81% to 94% and 85% to 98%, respectively. Biosolids production was 0.03 to 0.05 g VSS/g $COD_{removed}$. Also, the membrane was continuously operated without any chemical cleaning or back-flushing by scouring effect of granular activated carbon (GAC) on the membrane surface. Estimated energy requirement for the system operation could be reduced to 0.079 kWh/m^3 with optimal design, which is smaller than that could be produced from methane of 0.14 kWh/m^3.

Keywords

Anaerobic; fluidized-bed; membrane bioreactor; domestic wastewater; energy

INTRODUCTION

Low energy consuming and less sludge producing wastewater treatment processes (WWTP) are drawing more concern recent years. In this regards, anaerobic processes would be an alternative to aerobic processes. Kim et al. (2011) proposed a staged anaerobic fluidized membrane bioreactor (SAF-MBR) as a high-efficiency and energy-producing process for the treatment of low strength wastewater. Later, Yoo et al. (2013) reported that COD and BOD_5 removal efficiency were higher than 90% and 94%, respectively, for a lab-scale SAF-MBR operated at temperature between 10 ^{o}C to 25^{o}C and a total hydraulic retention time (HRT) of 2.3 h treating 2 mm screened domestic wastewater. The lab-scale SAF-MBR was operated for 301 days without chemical cleaning.

Although the lab scale SAF-MBR showed good organic removal, energy requirement was calculated just based on that required for GAC fluidization. In this paper, detailed analysis on energy balance including biogas production and reactor optimization together with general performance of the pilot-scale SAF-MBR system are provided.

METHODS AND MATERILAS

Description of pilot plant

The pilot scale SAF–MBR system installed at the Bucheon WWTP, Republic of Korea, was used to treat 2 mm screened primary effluent, and consisted of two reactors, as illustrated in Figure 1. The 3 m tall by 0.65 m diameter AFBR was fabricated with stainless steel. The AFBR packed 139 kg of GAC (Calgon F300, USA), representing packing ratio was 25%. The GAC expended to about 40% of the reactor height by recycling bulk at a flow rate 0.15 m^3/min. The rectangular shaped AFMBR was 0.9 m by 0.4 m in area, and with a 2 m depth had a working volume of 0.77 m^3. Hollow fiber Polyvinylidene fluoride (PVDF) hollow fiber membranes with pore size of 0.03 µm and 1.85 m long (provided by Cheil Industries, Republic of Korea) were submerged in the AFMBR. The total membrane surface area of the membranes was 39.5 m^2. The AFMBR contained 206 kg of GAC, which occupied 50% of the reactor volume when settled. The recycle flow rate was of 0.53 m^3/min expanded the GAC to 100% of the membrane surfaces came into contact with the fluidized GAC particles.

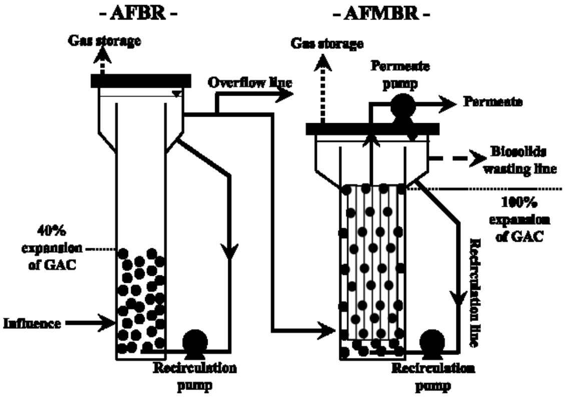

Figure 1. Schematic diagram of the pilot scale SAF-MBR system (After Shin et al, 2014)

Operating conditions

The AFBR, seeded 100 L of digested sludge obtained from a Bucheon WWTP digester, had 94 days for start-up period with step reducing HRT condition with 11.1 hr to 2.0 hr. The AFBR was then operated at HRT of 2.0 h with corresponding flow rate of 12 m^3/d for the remainder of the study. The membrane flux of the AFMBR was set at 6.7 to 7.5 L/m^2/h, and corresponding HRT of AFMBR was 2.6 to 3.5 hr. On 95 d of operation of the AFBR, the AFMBR was started. This is termed day 0 of system operation. On day 101, biosolids wasting from the AFMBR was begun through the withdrawal of bulk liquid from the AFMBR settling tank. The bulk wasting ratio, was maintained at 5% for days 101 to 340, and then was gradually decreased to 1% over a 10 d period. In order to prevent an excessive trans-membrane pressure (TMP) drop from occurring, a membrane relaxation approach was used after day 107.

Analytical methods

Chemical oxygen demand (COD), total and volatile suspended solids (TSS and VSS), 5-d biochemical oxygen demand (BOD_5) and alkalinity were determined according to Standard Methods (APHA, 1998). To eliminate the effect of hydrogen and dissolved methane on COD and BOD_5 measurements, samples were purged with air for 10 min except influent sample. Details of chemical analyses for gas composition and dissolved methane are as described by Yoo et al (2012).

Energy estimation

The energy requirements of the SAF-MBR system were estimated with headloss measurements and considered energy transfer efficiency of 65% in conversion of electronic energy to pump energy. The energy requirement is mainly associated with GAC fluidization by recirculation of bulk liquid; energy loss associated with the fluidization of GAC and friction loss along the recycle pipe. Minor energy requirements are for permeate pump, diffuser, etc.

The energy production of SAF-MBR system was estimated with methane energy. Methane was produced both gaseous and dissolved form. Energy content of one mole of methane is 800 kJ/mol, which is equivalent to 0.222 kWh/mol. The energy potential was calculated considering 33% of conversion efficiency for methane to electricity.

RESULTS

General performance of the SAF-MBR

General performances of the pilot-scale SAF-MBR in terms of membrane fouling control, organic removal, and biosolids production are as follows. The SAF-MBR system was operated continuously for more than 400 days at the AFMBR flux of 6.7 to 7.5 L/m^2/h, without chemical cleaning of the membranes. The TMP generally increased with time, and reached 0.4 bar at day 400. After the system was fully accumulated, BOD_5 removal efficiency was higher than 94%, leaving effluent BOD_5 value of 7 mg/L. From this, the almost portion of biodegradable organic was removed by the SAF-MBR system. Biosolids production of the SAF-MBR was 0.03 to 0.05 g VSS/g $COD_{removed}$, which is significantly lower than that of aerobic processes.

COD mass balance indicated that the methane portion was 53% of COD removed, which was 121 mg/L as COD concentration. Of the produced methane, 73% existed in gaseous and the remaining was dissolved in the AFMBR effluent.

Net energy estimation and improvements

The energy requirement for the SAF-MBR was estimated to be 0.256 kWh/m^3. The energy requirement for the AFBR was only 0.016 kWh/m^3 representing 6% of total energy requirements. Table 1 compares the energy requirement before and after the optimization of the AFMBR. As the headloss in a recycle line is inversely proportional to the cube of pipe diameter, the headloss could be reduced 20 to 2.5 cm by increasing the diameter from 10 to 20 cm. Another way to decrease the energy requirement is to increase the membrane density in the pilot AFMBR. By doubling the pilot scale AFMBR membrane density of 50.5 to 100 m/m^2, which was used in the lab-scale AFMBR, about 50% of energy requirements could be reduced. By implementing two options, the energy requirement for the AFMBR could be reduced from 0.240 kWh/m^3 to 0.079 kWh/m^3.

Table 1 AFMBR energy requirements of origin reactor and optimized design reactor

AFMBR Energy requirements	Origin reactor Recirculation line D = 100 mm Membrane density = 50.5 m/m^2				Optimized reactor Recirculation line D = 200 mm Membrane density = 100 m/m^2			
	E (kWh/m^3)	Portion (%)	H (cm)	Q_{in} (m^3/d)	E (kWh/m^3)	Portion (%)	H (m)	Q_{in} (m^3/d)
Column	0.006	2	1	5.4	0.003	4	1	10.4
Diffuser	0.006	2	1	5.4	0.003	4	1	10.4
Membrane module	0.006	2	1	5.4	0.003	4	1	10.4
GAC	0.101	42	18	5.4	0.053	67	18	10.4
Recirculation line	0.112	47	20	5.4	0.007	9	2.5	10.4
Permeate pump	0.010	5	0.35 (bar)	5.4	0.010	12	0.35 (bar)	10.4
Total	0.240	100.0			0.079	100		

Energy can be obtained by converting the methane produced to electricity through cogeneration. The theoretical energy available from the methane produced and its concentration was 121 mg/L as COD equivalent, which represents 0.42 kWh/ m^3 (1 mole of CH_4 or 64 g COD equivalent = 0.222 kWh). Considering an energy transfer efficiency of 33% in conversion of methane to electricity, the potential electrical energy production from the pilot SAF-MBR is 0.14 kWh/ m^3. This is sufficient to satisfy an energy requirement of 0.079 kWh/ m^3 obtained through a modification of the AFMBR recycle line and membrane density. Although there would be an additional energy required for the recovery of dissolved methane, its energy requirement is known as relatively low value of 0.05 kWh/m^3 to remove higher than 99% of dissolved methane by a simple air stripping process (McCarty et al., 2011). In sum, the SAF-MBR could be a net energy positive system, even with a domestic wastewater.

CONCLUSIONS

The pilot-scale SAF-MBR treated primary clarifier effluent of WWTP at HRT of 4.6 to 5.5 h for more than a year. After fully accumulated, BOD_5 removal efficiency was 94% with corresponding effluent BOD_5 concentration was 7 mg/L. Low biosolids production rate was obtained with 0.03 to 0.05 g VSS/g $COD_{removed}$. Membrane flux was continuously maintained 6.7 to 7.5 L/m^2/hr for more than a year without chemical cleaning due to scouring effect from fluidizing GAC. The energy balance indicated that the SAF-MBR could become an energy positive system with high organic removal efficiency and low biosolids production.

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(P17) Membrane bioreactor (MBR) process using commercial and novel low-fouling membranes for treatment of textile dye wastewater

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Abstract

A novel antifouling coating based on PolymerisableBicontinuousMicroemulsion (PBM) technique for membranes in Membrane Bioreactors (MBR) was developed and tested within a small-scale pilot and compared with a commercial UF membrane. The MBR process with novel PBM coated membrane using an artificial model textile wastewater was run stable and smooth without cleaning with high COD removal rate. However, water permeability is significantly lower than for the commercial membrane. After 6 month of operation the novel membrane still showed antimicrobial effect.

Keywords:

Wastewater treatment, textile industry, membrane bioreactor (MBR), low-fouling membrane, polymerisablebicontinousmicroemulsion (PBM)

1. Introduction

Since water scarcity isa growingproblem particularly in the Middle East and Northern African countries(MENA) the useof alternative water resources will be more important in near future.In this context reuse of treated wastewater offers a viable option to reduce freshwater consumption. The textile industry which plays an increasingly important role in MENAcountries is long regarded as a water intensive sector due to its high demand of water for all parts of its processes. Membrane bioreactor (MBR) systems are very attractive for industrial wastewater treatment as the implementation of membrane micro/ultra-filtration for solids retention into biological treatment system leads to several substantial improvements compared to conventional biological processes (Brik et al., 2006). However, membrane fouling is regarded as the most important bottleneck for further development of MBR technology. It is the main limitation for faster development of this process, particularly when it leads to flux losses that cleaning cannot restore (Howell et al., 2004)

This paper presents findings of an EU funded project “Development of the next generation membrane bioreactor system (BioNexGen, 2013) which aims at developing novel functionalized low-fouling membranes for membrane bioreactors (MBRs) in wastewater treatment.

2. Materials and methods

The results were obtained in a small pilot-scale submerged membrane bioreactor treating model textile dye wastewater (MTDW). The MBR was equipped with adequate sensors as well asLabVIEW (National Instruments) data acquisition system in order to monitor performance (Fig.1). The hydraulic volume of the employed MBR reactor was 57 L. The mode of operation was as follows: 8.5 min suction - 0.5 min relaxation - 0.5 min backflush - 0.5 min reaxtion - 8.5 min suction. A novel hydrophilic nanostructured membrane layer has been developed as special coating on a commercial membrane. For this purpose the layer has been casted on an UF membrane (PES) using polymerisablebicontinuousmicroemulsion (PBM) method. The commercial as well as the novel module consisted of 3 sheets, with 25 cm × 25 cm dimensions of each sheet covering total active membrane area of 0.33 m^2.

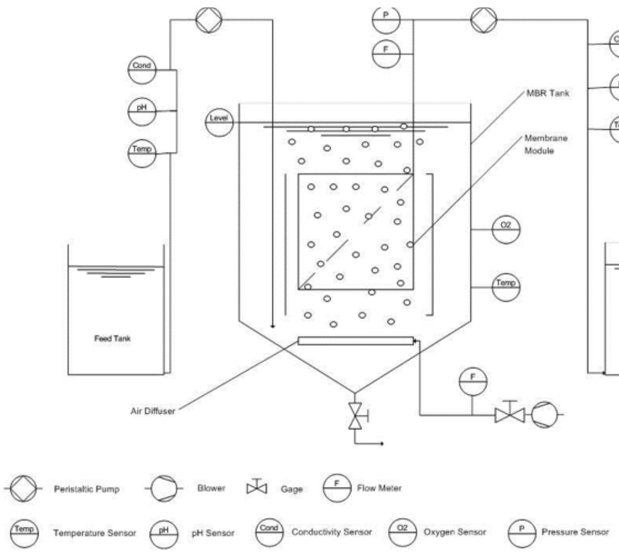

Fig.1 Schematic of pilot-scale membrane bioreactor

For benchmarking submerged commercial and novel MBR modules were tested in the same MBR tank to compare the performances of both modules. To keep the operating process conditions constant, MTDW has been used as test media (Tab.1) because the composition of real textile dye wastewater change over the time and season of the year. The MTDW is mainly based ona red reactive dye (Acid Red 4)and on a blue anthrachinone dye (Remazol Brilliant Blue R) which represent typical industrial dyes being widely applied in textile industry. Besides a typical industrial detergent (Albatex DBC) glucose was added as C-source as well as the following salts:NaCl, Na_2CO_3/$NaHCO_3$ and NH_4Cl (N-source). The tests with the novel PBM coated membrane were carried out over a period of 6 months.

Tab.1 Composition of Model Textile Dye Wastewater (MTDW)

No.	Dyestuffs&chemicals	oncentration (mg/L)
1	RemazolBrilliant Blue R	50
2	AcidRed 4	50
3	NaCl	2500
4	Na_2CO_3/$NaHCO_3$	1000
5	Glucose	2000
6	Albatex DBC (Detergent)	50
7	NH_4Cl	300

3. Results and discussion

Within the pilot-scale trials different process parameters such as COD, BOD, TOC, pH, conductivity, flux, TMP, MLSS, dye concentration, air supply, O_2 consumption, HRT, SRT,drying residue, N-balance have been investigated. The experiments have been conducted with the commercial and novel membrane under similar operating conditions and the same process parameters have been investigated.

Water permeability of the novel coated membrane averaged 35 L/(m^2 h bar) and was lower than for the commercial membrane (ca. 60 L/(m^2 h bar), however, showed a relative smooth and stable trend without any cleaning procedure.

The COD removal efficiency with the novel modulewas very stable at around 96% (2450 mg/L inlet COD fed to the membrane bioreactor) at a hydraulic retention time (HRT) in the range of 50-200 days and a Mixed Liquor Suspended Solids (MLSS) of 8-12 g/L. The COD removal efficiency of the commercial modules showed higher fluctuations at the beginning due to acclimation and technical failure (Com1) and during period with feed pH 10.5 (Fig. 2). However, a commercial modulewhich was run directly after trials with PBM module at pH 7.5 (Com2) showed similar COD removal efficiency as for the novel module.

Both dyes applied have low molecular weight (Acid red 4: 380.4 g/mol, Remazol Brilliant Blue R: 626.5 g/mol) and hence removal mechanismbasically depends on biodegradability in the activated sludge system.The removal efficiency of the Acid red 4 was very much fluctuating 20 – 70% (Fig. 3) for the commercial and the novel module respectively. Only a commercial module directly tested after PBM trials showed lower fluctuation. As for theblue dyeremoval efficiency for the novel module increased to more than 60% whereas for the commercial modules fluctuated around below 40%.

After end of pilot trials the commercial and novel PBM membrane were investigated by anti-microbial test, SEM and AFM (Fig. 4). In contrast to the commercial membrane the PBM coated novel membrane still shows antimicrobial properties. In addition SEM and AFM showed a smoother surface.

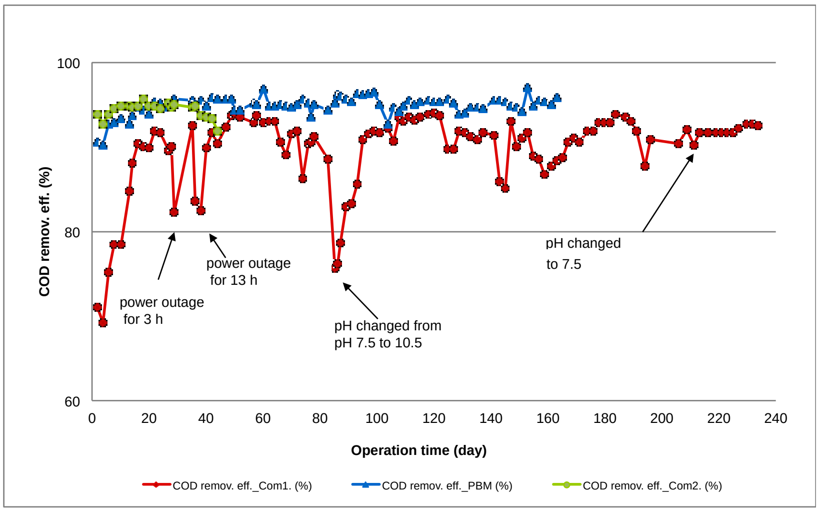

Fig.2 COD removal efficiency of the novel PBM and commercial modules

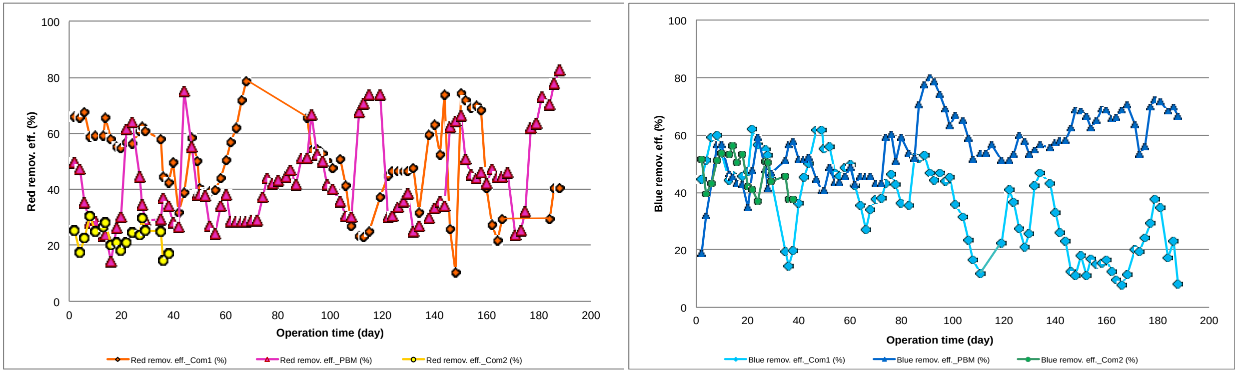

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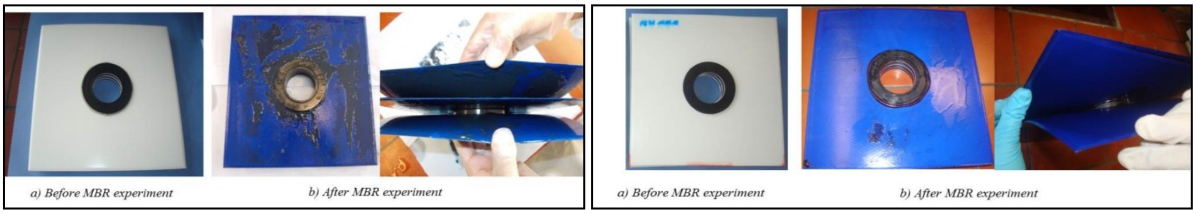
Fig. 3 Removal efficiency of a) Acid red 4 and b) Remazol Brilliant Blue R



a b

Fig. 4 a) Commercial and b) novel PBM membrane modules before and after pilot trials

4. Conclusions

These results indicate that the MBR process with novel PBM membranewas run stable and smooth without cleaning with high COD removal rate. However, water permeability is significantly lower than for the commercial membrane. After 6 month of operation the novel membrane still showed antimicrobial effect and AFM indicated higher surface smoothness than for the commercial membrane. Red dye removal efficiency fluctuated markedly and no difference was observed between the commercial and novel membrane. Whereas blue dye removal efficiency showed 20 percent points higher removal efficiency for the PBM module. Pilot tests with real textile wastewater are currently ongoing at the Centre of Biotechnology, Sfax, Tunisia within the BioNexGen project.

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(P18) MBR – AD pilot system for the co-treatment of municipal wastewater and biodegradable solid waste

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Abstract

This study focuses on the performance of an integrated MBR – AD pilot plant for the co-treatment of municipal wastewater and biodegradable solid waste. The wastewater system consists of a membrane bioreactor (MBR) obtaining treated effluent that is examined for its physical and chemical characteristics in order to be used for irrigation purposes. The produced sludge is used as feedstock material to an anaerobic digestion along with various types of biodegradable solid waste. The experimental results indicate that the MBR effluent is of good quality obtaining the necessary standards for its reuse while the biogas yield and quality is comparable to existing and commercially available AD systems.

Keywords

Municipal wastewater; biodegradable waste; membrane bioreactor; anaerobic digestion

INTRODUCTION

The European Union calls for mandatory pre-treatment and decreasing of disposal of biodegradable materials in landfills through Directives 1999/31 and 2008/98. This has led to relatively high landfill tipping fees, which, in combination with the establishment of bio-waste source separation schemes in many EU countries, has created an active commercial market for anaerobic digestion (AD). The number of AD plants treating the organic fraction of household waste in Europe is constantly growing and represents 20%–30% of the biological treatment capacity for organics derived from household waste (Baere et al., 2008). Co-digestion of biowaste with municipal sludge provides a feasible solution to the utilization of two waste streams. Numerous reports on successful digestion of biowaste and primary and/or excess activated sludge (Zupančič et al., 2008), livestock waste (Callaghan et al., 2001; Hartmann and Ahring, 2005) as well as industrial organic waste (Fernández et al., 2005), confirm the feasibility of co-digestion.

Wastewater treatment is of critical importance in the EU. The stringent rules currently applied concerning the effluent quality are met utilizing both old and proven technologies, such as activated sludge with extended aeration, and new approaches such as membrane bioreactors (MBR). By using micron or ultra filtration membrane technology, MBR systems allow the complete physical retention of bacterial flocs and suspended solids (SS) within the bioreactor (Le-Clech, 2006). This compact configuration produces high quality effluent, suitable for reuse applications leading to wider use of MBR technology for municipal and industrial wastewater treatment.

Both of the above mentioned technologies produce by-products, which, if not treated properly, may cause secondary pollution. In the case of MBR, the by-product is the excess activated sludge and in the case of the AD, the liquid digestate. Furthermore, both of these systems require electrical energy. To this end this study aims to present a sustainable stand alone system which integrates MBR and AD technologies for the co-treatment of municipal wastewater and biodegradable solid waste. Through the operation of this pilot system, critical design and operational parameters for each component are tested in order to maximize the biogas yield, so as to obtain as much energy as possible while providing high quality irrigation water.

EXPERIMENTAL STUDY

Apparatus – The integrated MBR-AD system

A simplified flow diagram of the integrated MBR-AD system for wastewater treatment and biogas for electricity production is presented in Figure 1. Primary treated wastewater was fed from the equalization tank to the MBR unit. The treated effluent was collected in the collection tank, prior to irrigation. The organic wastes, together with the excess sludge produced in the MBR unit were fed to the AD unit. The produced biogas passed through the clenching line to be used as fuel in the CHP unit. The digestate was dehydrated and the leachates were recycled to the MBR unit to be treated as wastewater. The dehydrated digestate was sent to a small scale composting unit.

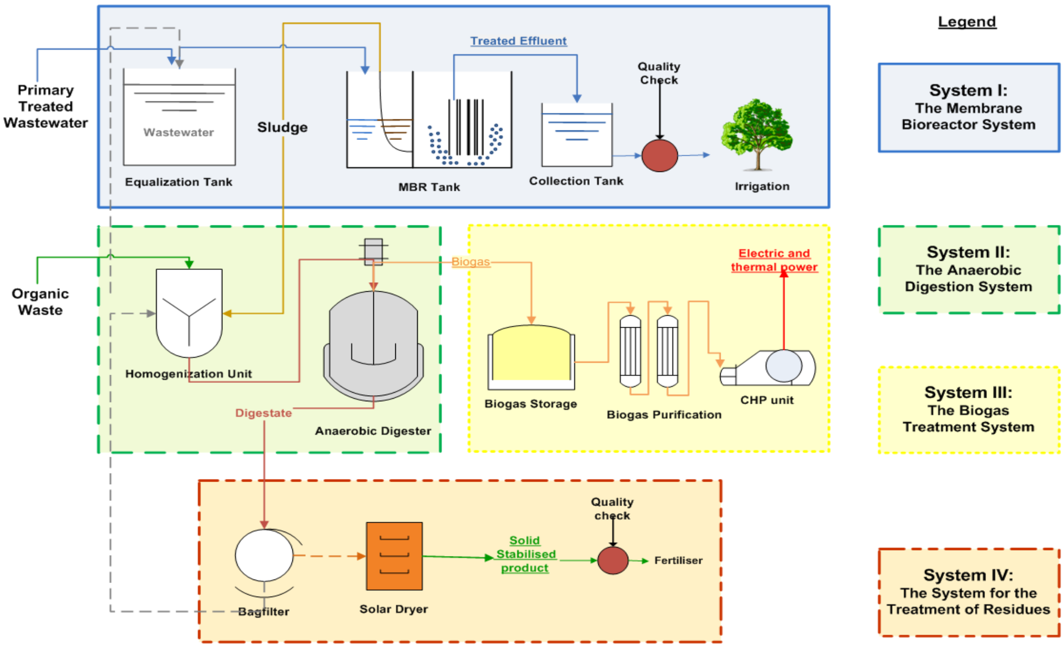

Figure 1. Simplified flow sheet diagram of the integrated MBR – AD system

Waste and wastewater

Primary wastewater was supplied by a Wastewater Treatment Plant in Anthoupoli, Cyprus, which treated mainly municipal wastewater, facilitating a population of 300.000 habitants. Pet food, dough, fruit & tomato pulp and milk waste was used as feedstock to the AD unit.

Experimental procedure

This study presents the start–up period and the early steady state conditions of the integrated MBR-AD unit (80 days continuous operation) using municipal sludge and various biodegradable organic waste. Initially, the MBR unit was tested with water in order to examine its performance and possible failures. In a second stage, the MBR system operated with diluted primary treated wastewater (1:2) in order to avoid shock and damage of the membranes. During this period the system was maintained in aeration mode aiming at the development and growth of sludge as well as at achieving steady state conditions for a pre-selected SRT of 20 days and a steady HRT of 1 day, thus processing 1.5 m^3 of wastewater per day. The selected SRT is commonly used in MBR system for the treatment of municipal wastewater. Samples were collected from three (3) different points namely influent wastewater, sludge (MBR tank) and treated effluent from the MBR system. After the period of steady state operation of the AD unit, the produced leachates from the treatment of digestate (bagfilter), were redirected to the MBR unit for treatment. Daily measurements of the transmembrane pressure (TMP) in the MBR membrane module, pH and temperature were performed.

In order to accelerate the biological growth, the digester was inoculated with 3.5 m^3 of active anaerobic sludge. In the beginning of the operation, a first stage of acclimatization took place and expired pet food along with sludge produced from the MBR were selected as the first organic raw material for the acclimatization and the buildup of sludge in the AD. Since after the acclimatization expired food waste was introduced into the AD plant constituted by mixed dough pastries and starchy food waste such as unbaked cheese pies, chocolate croissant, bread, pasta, and expired condensed fruit juices and pulps. Daily preparation of the feedstock was performed. Apart from weighting, dilution, mixing, homogenization, in order to achieve the desirable TS (less than 10%) and VS content, the starchy food waste was hydrolyzed using sulphuric acid. The mixture of the organic raw materials was diluted to 150 L, keeping the HRT of the AD constant at 20 days. Biogas production and composition was monitored daily.

RESULTS AND DISCUSSION

During the start up and operation of the MBR some operational difficulties concerning blockage and steady state flow of the inlet and outlet were encountered. The problems were overcome by placing a filter in the line of the feedstock and a level controller for the inlet pump. During the early stages of biomass buildup, partial blockage of the membranes was detected as foaming bacteria thrived which was resolved by applying extended aeration through the core of the membrane module. When the first SRT=20d was achieved the performance of the MBR was tested. The biomass accumulation is presented at Figure 2. The reduction of COD, TN, and NH_4 was constant regardless of the fluctuations of the wastewater (Table 1). Limited membrane fouling was observed with the rate of the transmembrane pressure (TMP) reduction being less than 0.4 kPa/d.

The potential for biogas production from expired dry pet food mixed with sludge produced from the MBR was investigated by measuring biogas yield and composition. The produced biogas was 10.2 m^3/d with an average composition of 56% CH_4. The passage to the second experimental conditions was very smooth by introducing gradually dough and pulp waste and replacing dry pet food, to a point where the latter was only 10% w/w. The initial lag of the system was overcome in short time and the biogas yield increased, so was the methane content of the biogas. The biogas yield, expressed as L/kgVS, is shown in Figure 2. The methane content of the biogas was approximately 59% throughout the second experimental phase.

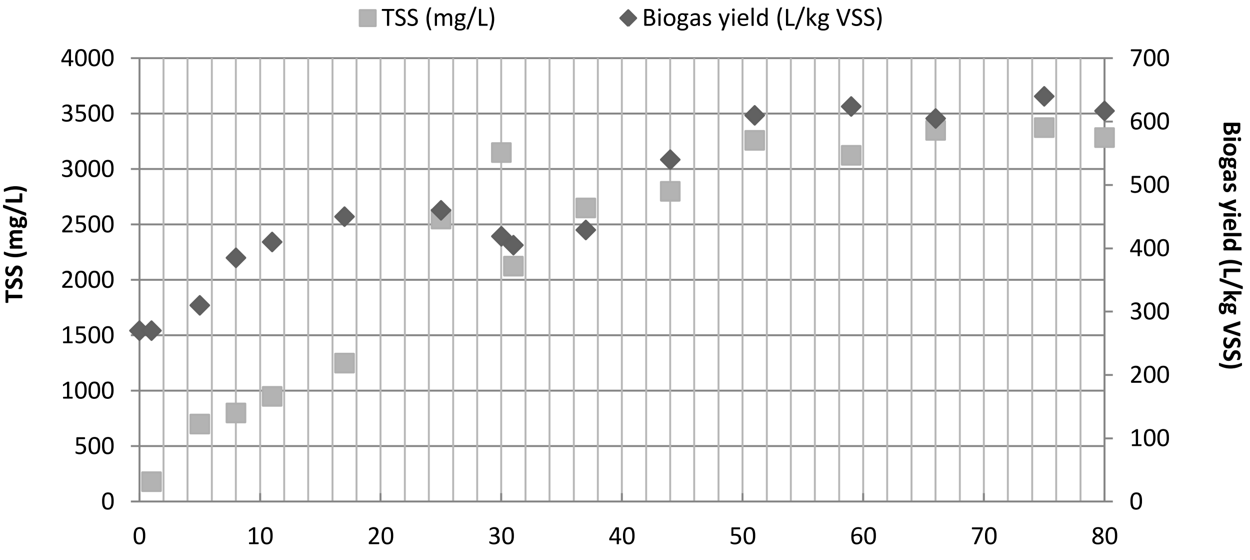

Figure 2. Biomass buildup and biogas yield in MBR and AD units respectively

Table 1. COD, TN and NH4 of the wastewater (in) and the treated effluent (out)

Days	COD (mg/L)		Reduction	TN (mg/L)		Reduction	NH4 (mg/L)		Reduction
	in	out	%	in	out	%	in	out	%
1	325	69.7	78.6%	70.3	8.31	88.2%	62.4	6.370	89.8%
5	336	70.9	78.9%	81.6	8.75	89.3%	60.3	6.150	89.8%
8	290	70.5	75.7%	87.8	10.9	87.6%	74.3	6.870	90.8%
11	428	69.5	83.8%	87.9	9.96	88.7%	65.1	7.640	88.3%
17	350	72.3	79.3%	88.6	8.78	90.1%	74.8	6.400	91.4%
25	571	68.2	88.1%	96.2	8.60	91.1%	69.5	0.676	99.0%
30	912	65.4	92.8%	105.0	8.76	91.7%	89.4	0.638	99.3%
31	666	73.1	89.0%	98.0	8.72	91.1%	84.0	0.686	99.2%
37	647	80.7	87.5%	91.0	8.67	90.5%	78.6	0.734	99.1%
44	857	77.5	91.0%	101.3	6.07	94.0%	92.2	0.324	99.6%
51	559	56.2	89.9%	84.7	7.03	91.7%	69.2	0.373	99.5%
59	1064	68.7	93.5%	99.0	7.77	92.2%	91.6	0.374	99.6%
66	1080	84.7	92.2%	99.1	6.02	93.9%	96.4	0.785	99.2%
75	1074	73.5	93.2%	96.2	5.64	94.1%	92.8	0.768	99.2%
80	1098	88.8	91.9%	98.7	5.56	94.4%	95.0	0.789	99.2%

CONCLUSIONS

An integrated MBR-AD system was developed by combining two well known and proven technologies for the effective co-treatment of municipal wastewater and biodegradable organic waste. It has been shown that the MBR unit operates under steady conditions with a relative low SRT, achieving above 92% removal of COD and almost complete reduction of nitrogen compounds which is indicative of good quality characteristics of the effluent. The AD unit operated at relative low organic loading rate, as the system is yet to be pushed to its limits. The variation in the composition of the raw material has a direct affect on the biogas yield while the hydrolysis of the starchy raw material leads to an increase in biogas yield. The biogas produced by the AD unit had the necessary qualitative and quantitative to be used as a renewable energy source for electricity and thermal energy production.

Overall the primary results of the MBR-AD system are very encouraging indicating that the combinations of these technologies have the potential to effectively and sustainable manage municipal wastewater and biodegradable organic waste without any secondary pollution issues.

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(P19) Simultaneous nitrogen and methane removal in an MBR after a methanogenic pre-treatment

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Abstract

In the anaerobic treatment, especially at low temperatures, two different concerns are commonly extended; nitrogen depletion and dissolved methane removal need to be accomplished to fulfil legal and environmental requirements. Using methane as external carbon source to denitrify could be a solution. Until now, two different microbiological pathways are known to be involved in this process: aerobic, including oxidation of methane coupled with conventional denitrification; and anaerobic, where methane is used as both carbon and energy source for denitrification. This processes have been reported at laboratory scale, however, little information is available at pilot scale. This investigation focuses on studying the feasibility of simultaneous nitrogen and methane removal at pilot scale. On the other hand, two different support carriers and four recirculation ratios were tested to improve the conditions for the development of the process.

Keywords

Anaerobic digestion; denitrification; greenhouse gas; membrane bioreactor; methane

INTRODUCTION

In the last decades, anaerobic treatment has been extended all over the world because of its positive aspects such as energy recovery and low sludge production. Recent studies were focused on operating at ambient temperatures (McKeown et al. 2012). Nevertheless, in these conditions, a high fraction of the produced methane gets out the digestor dissolved in the effluent, accounting even up to 50% of the produced methane (Noyola et al. 2006). Apart from the energetic loss, methane is a strong greenhouse gas (GHG) with a warming potential 25 times higher than carbon dioxide. When released to the environment, it can be a potential contributor of global warming. Additional strategies as biofilters or biological methane oxidation need to be applied to counteract these concerning emissions (Cakir and Stenstrom 2005).

In terms of nitrogen, in anaerobic treatment no depletion is usually observed. To fulfil legal and environmental requirements nitrogen elimination is needed. Conventional nitrification-denitrification systems require an external carbon source.

Previous studies have proved the feasibility of simultaneous removal of methane and nitrogen, following two different pathways of methane oxidation: aerobic and anaerobic. Aerobic methane oxidation coupled to denitrification is the most known process (Modin 2007). Very recently, a more efficient anaerobic oxidation of methane mediated by a complex consortium of archaeon and bacteria has been discovered (Raghoebarsing 2006). In reference to both pathways, most available information was obtained in discontinuous assays.

In the present work, a membrane bioreactor (MBR) was proposed as UASB post-treatment in such a way, that methane present in the anaerobic effluent was used as an inexpensive electron donor to denitrify. The proposed system was operated in continuous mode, to evaluate the feasibility of simultaneous nitrogen and methane elimination at pilot scale. Moreover, two different support carriers and four recirculation ratios were tested to improve the conditions for the development of the microbiological processes before mentioned.

MATERIALS AND METHODS

A scheme of the operated system is depicted in Figure 1. A 120 L volume UASB system was used for the first methanogenic stage. The effluent of the UASB was led to an MBR reactor (56 L) composed by two compartments: a first anoxic compartment, with biomass growing onto support and in suspension, where both methane and nitrate removal was performed; a second aerobic compartment, where ammonium was oxidised and biomass/effluent separation was carried out with an ultrafiltration membrane module (Zenon ZW-10). An internal recirculation from the aerobic to the anoxic compartment was used to return suspended solids and nitrate.

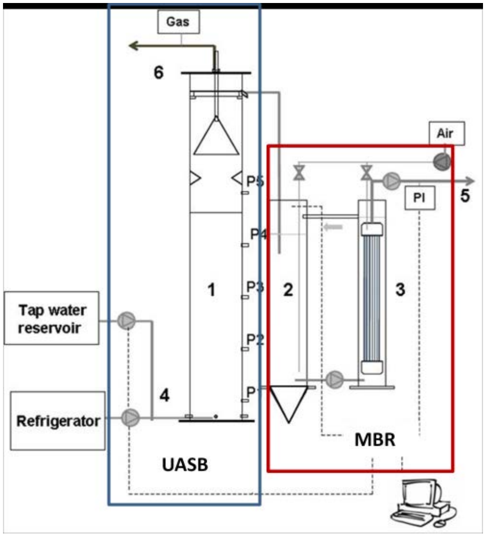

Figure 1. Flow diagram of the pilot plant. (1) UASB reactor to methanogenic pre-treatment. (2) Anoxic compartment. (3) Filtration aerobic compartment. (4) Feeding point. (5) Effluent. (6) Biogas outlet

In terms of operational strategy, six different stages were established. The aim of the first two stages was to assess the efficiency of simultaneous nitrogen and methane removal using two types of commercially available biomass support carriers: plastic (stage I) and foam (stage II). Stages III to VI were used to evaluate the impact of the recycling ratio (R) between aerobic and anoxic compartments. R of 0.8, 2.0, 3.0 and 4.0 were used in stages III, IV, V and VI, respectively.

RESULTS AND DISCUSSION

The current results are related with 280 days of operation. Concerning the membrane operation, flux was maintained at 10-15 $L·m^{-2}·h^{-1}$, with permeability values between 100-250 $L·m^{-2}·h^{-1}·bar^{-1}$ during the whole experimental period. The system was fed with a synthetic wastewater with 400-600 $mgCOD·L^{-1}$ and 30-40 $mgTN·L^{-1}$, with a flow in between 225-300 $L·d^{-1}$. The operation was performed at ambient temperature (17-23 ºC).

Biomass carrier impact – stages I and II

Biomass carriers have been extended as a common strategy of biomass attachment. Plastic and foam supports were tested to find a suitable type for the proposed system. During stage I plastic support was present in the anoxic compartment, being substituted for foam carriers in stage II. In both stages the recycling ratio was maintained constant at R = 0.8. Experimental results are shown in Figure 2.

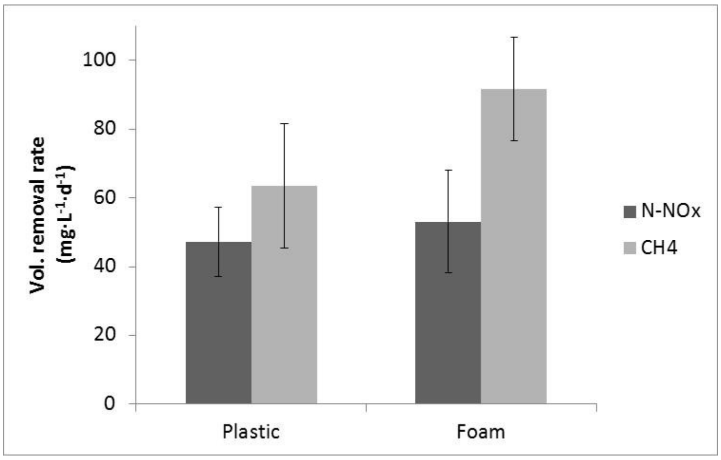

Figure 2. Volumetric removal rates of methane and nitrite/nitrate in presence of plastic or foam carriers

In terms of nitrogen removal, no difference between plastic and foam carriers was observed. Nevertheless, methane elimination was significantly improved in presence of the foam support. One of the reasons could be the properties of this kind of carriers (water binding, adsorbing, porous biocarrier) which promote a proper environment and the growth of the population able to denitrify with methane as electron donor. Based on these results, foam support was maintained in the anoxic compartment during the next stages of the operation of the pilot plant.

Recycling ratio effect

During stages III, IV, V and VI the system was operated with four different R values, from R = 0.8 to 4.0. Figure 3 summarizes the experimental results in terms of nitrogen and methane elimination. As can be observed, recycling ratio (R) was a key parameter in the simultaneous methane and nitrogen removal efficiency. On the one hand, nitrogen species and dissolved oxygen concentration in the anoxic compartment strongly depended on recycling ratio. On the other hand, residence time in the MBR was set by R.

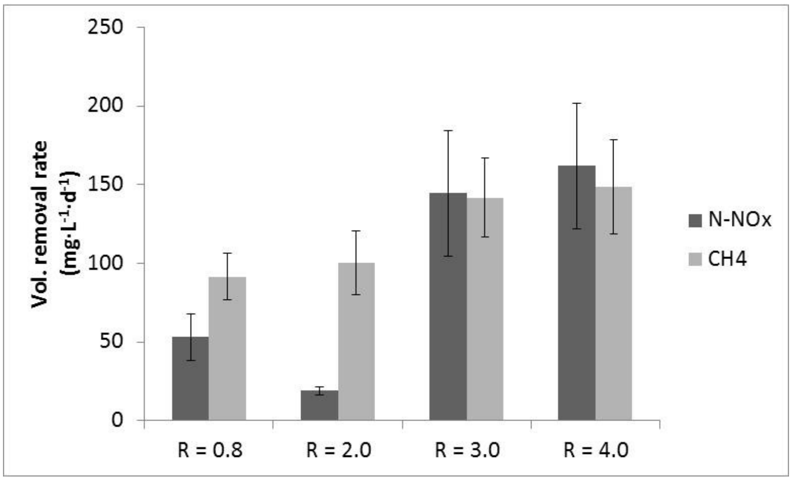

Figure 3. Volumetric removal rates of methane and nitrate as a function of the recycling rate in presence of foam carriers in the anoxic compartment

Lower nitrogen removal was observed at the lowest recycling ratios (R = 0.8 and 2.0). It seems that in presence of low nitrate concentrations (4-8 mgN-NO_3^-·L^{-1}) the system was not able to use methane to denitrify.

A significant enhancement of nitrogen removal was observed when recycling ratio was set at higher values (R = 3.0 and 4.0). The achieved values of nitrate removal rates were lower comparing with previous studies. Nevertheless, activity of 295 mg N-NO_3^-·L^{-1}·d^{-1}, reported previously by Islas-Lima et al. (2004), was measured in batch assays, where optimal operational conditions could be established. In terms of methane elimination, a similar behaviour was observed. At the highest recycling ratios, volumetric removal rates were higher than in stages I and II. Nevertheless, the increase in methane removal with recycling ratio R=3.0 and R=4.0 was not as remarkable as in the case of nitrogen. When operating with the highest recycling ratios it was observed that, suposedly, the increase of methane transformation could promote the process of denitrification because of methane electron donor capacity.

Regarding overall removal rates, eliminations up to 40% of nitrogen and above 90% of methane were achieved at the highest R. Since the remaining fraction of COD in the UASB effluent was insufficient for the stoichiometric requirements to carry out a conventional denitrification (less than 34 $mg \cdot L^{-1}$), it seems that the role of methane as a carbon source in nitrogen removal was important to achieve these rates.

Microbial population analysis (FISH) revealed the presence of different microorganisms responsible for either aerobic or anaerobic methane oxidation. High abundance of Methanotrophs type I was observed during the whole operational period. These bacteria can oxidize methane to methanol or acetate at low oxygen concentrations, which can be subsequently utilized by heterotrophs as carbon source for denitrification. Moreover, increasing amount of bacteria belonging to newly discovered NC10 phylum and able to carry out nitrite-driven methane oxidation was detected within the 280 days of operation. Finally, some microorganisms closely related to and *Methanosaeta* and archaea belonging to ANME group were found. These archaeal species use reverse methanogenesis and electron shuttling to the denitrifying partner and therefore also play an important role in simultaneous methane oxidation and denitrification. However, what fraction of dissolved methane was oxidized via the aerobic or anaerobic pathway remains unclear.

CONCLUSIONS

The feasibility of denitrification coupled to methane oxidation in continuous pilot plant operation was demonstrated. Up to 40% of nitrogen and 90% of methane removal were achieved, with the recirculation ratios of R=3.0 and 4.0. Foam carriers were the most suitable for this application among two different support materials tested. In terms of operation, high recycling ratios showed better behaviour in terms of simultaneous nitrogen and methane removal.

ACKNOWLEDGEMENTS

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Efficient technologies - Novel processes

(Tuesday, 24 June 2014, Aula T2, Polo Zanotto)

(P20) Modelling of microbial population and metabolism in full-scale EBPR plants

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The microbial communities of enhanced biological phosphorus removal (EBPR) systems are complex and diverse in terms of phylogenetic composition and metabolic function. Itis still not well understood the way these metabolic traits are expressed in real systems, neither is the microbial community dynamics in full-scale wastewater treatment plants (WWTPs) with different design, and operational and environmental conditions. Detailed knowledge on the potential and adaptability of full-scale EBPR communities is needed, and will likely have a direct impact on the operation of the plant and its efficiency, where WWTP optimisation can be achieved through the application of metabolic modelling techniques (Oehmen et al. 2010).

This study compared the EBPR microbial community and metabolic behaviour of three Danish and three Portuguese WWTPs (DK_1 to DK_3 and PT_1 to PT_3, respectively),through fluorescence *in situ* hybridisation (FISH) combined with laboratory batch tests fed with acetate as carbon source under anaerobic-aerobic conditions. Several tests were done in each plant and over different periods of the year to assess variations of the microbial community and metabolism between different plants but also within the same plant over time. FISH analysis targeted mainly the organisms known to be part of the EBPR community, namely polyphosphate accumulating organisms (PAOs) such as *Accumulibacterphosphatis*(both Types I and II), as well as glycogen accumulating organisms (GAOs) such as *Competibacterphosphatis* and *Defluviicoccus*related-GAOs. This information was combined in a metabolic model describing the activity and microbial competition between *Accumulibacter*PAOs and *Competibacter*and *Defluviicoccus* GAOs, but also to describe different metabolic pathways observed in each microbial community.

According to Figure 1, the PAO populations in both the Danish and Portuguese plants were stable and showed little variability between each plant (2.5-6.5% *Accumulibacter*). GAOs (either *Competibacter* and/or *Defluviicoccus*) presented a greater variability, from absent to high values of up to 8% of the biovolume. Also, GAOs were present in one WWTP from each country, suggesting that the higher wastewater temperatures in the Portuguese climate did not necessarily lead to the development of more frequent GAO problems, unlike previous reports.

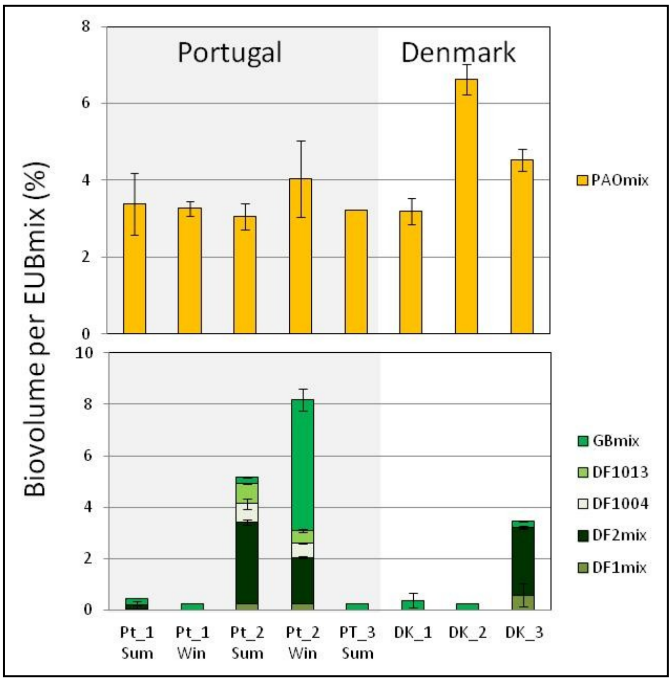

Figure 1: Microbial composition of the EBPR-related organisms in the sampled WWTPs in Portugal and in Denmark; error bars represent the standard deviation between different sampling dates. Win-Winter; Sum - Summer

The metabolic activity of each sludge showed the frequent involvement of the anaerobic tricarboxylic acid cycle (TCA) in PAO metabolism for the generation of reducing equivalents, in addition to the frequently reported glycolysis pathway. This was determined through analysing the glycogen and polyhydroxyalkanoate (PHA) yields per acetate in the anaerobic phase (Figure 2), and comparing to the known stoichiometric coefficients established previously in metabolic models. These metabolic differences were observed not only between different plants, but also within the same plant at different time points.

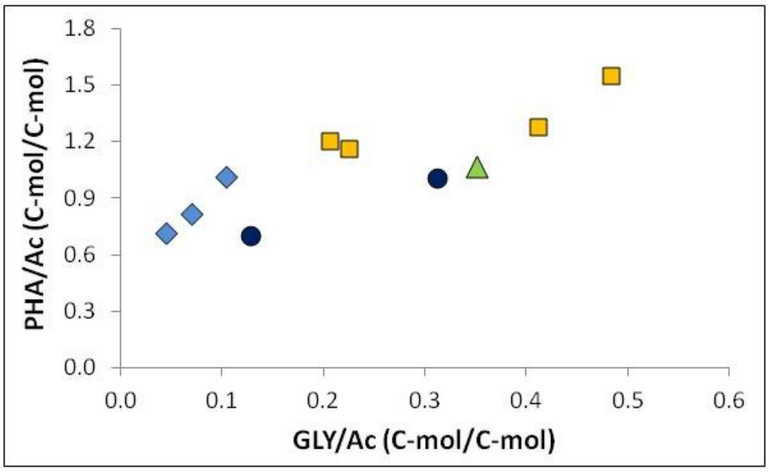

Figure 2: Correlation between the glycogen and the PHA yield per acetate consumed in anaerobic conditions for the different WWTPs tested – PT_1 (diamonds), DK_1 (squares), DK_2 (triangles), DK_3 (circles).

Thus, a metabolic model was implemented incorporating both pathways, and was shown to describe well the phosphorus, acetate, polyhydroxyalkanoate and glycogen transformations (Figure 3) occurring in the sludge, with minimal calibration required. The model was then used to simulate the role of operational factors on the prevalence of a TCA-like metabolism over a glycolysis-like metabolism in EBPR systems. This approach indicated that the key factors included the influent organic carbon to phosphorus ratio and the length of the aerobic phase (Figure 4). Both parameters had an impact on glycogen availability in the anaerobic phase, and hence, it becomes more advantageous for PAOs to use a TCA-like metabolism in situations with longer aerobic periodsand lower available carbon, such as those normally present in full-scale plants.

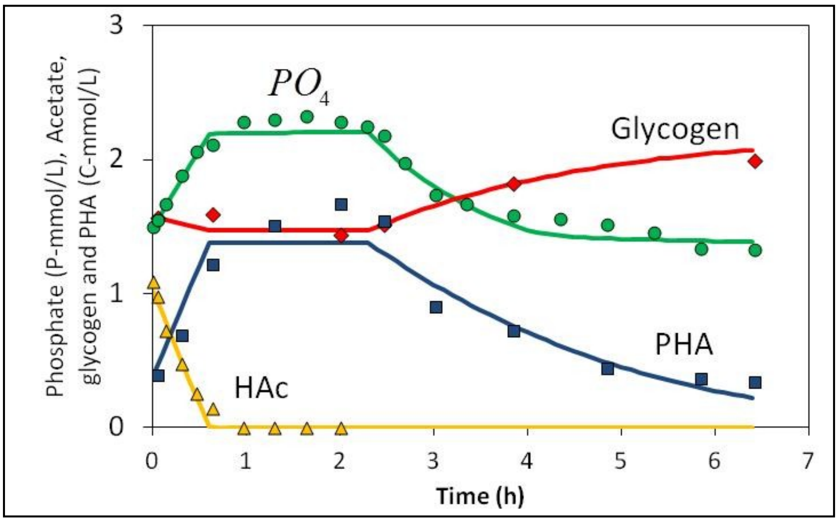

Figure 3: Model validation for PAO model in PT_1by fitting experimental data for phosphate (circles), PHA (squares), acetate (triangles) and glycogen (diamonds)

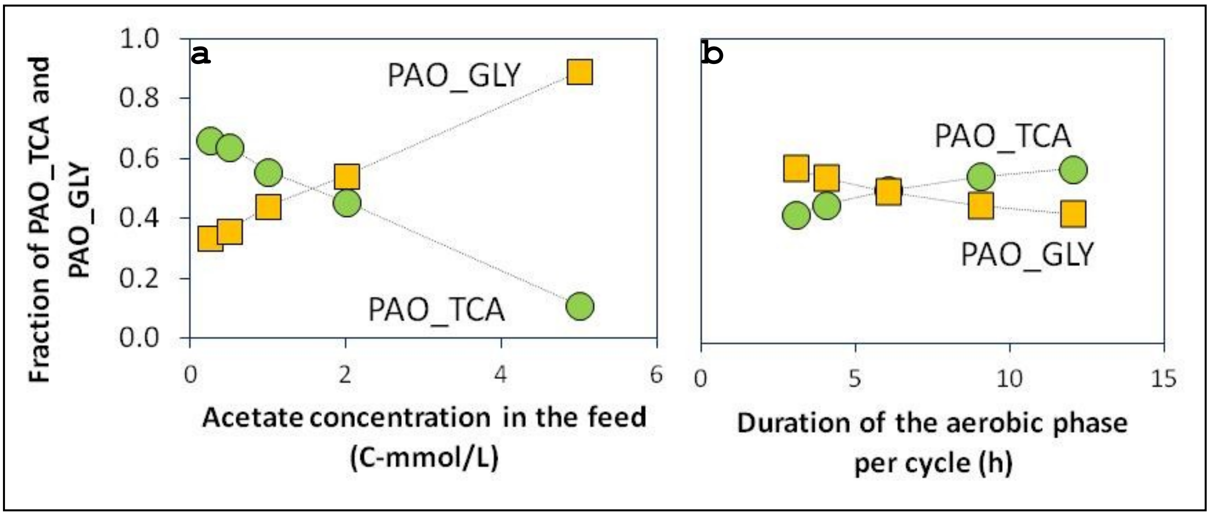

Figure 4: Effect of acetate concentration in the feed (with a constant influent P concentration of 0.16 P-mmol/L) (a) and duration of the aerobic phase (b) on the competition between the two anaerobic metabolisms of PAOs: TCA cycle (circles) vs. glycolysis (squares). Simulations were run for 40 d using the model fitted to the experimental data of plant PT_1 during summertime; simulations in (a) were conducted with an aeration period of 4 h and simulations in (b) were performed at an acetate initial concentration of 2 C-mM.

This assessment of the microbial community in different plants showed for the first time that operational factors may have a strong role in selecting not only for a certain microbial community but also to influence the metabolic behaviour of that community. Modelling this metabolic versatility, in order to predict the experimental results and to link these with the effect of certain operational parameters reinforced the fact that metabolic models are advantageous towards describing and optimising enhanced biological phosphorus removal processes.

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(P21) N and COD removal of leachate enhancing the COD biodegradability combining Panammox® and photo-Fenton

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Abstract

Autotrophic N removal by anammox implies a marginal NO_3^- production (about 10% of the influent total N), which can exceed the N discharge limits when treating N-rich streams, such as landfill leachates. Mature leachates present high chemical oxygen demand (COD), mainly composed by refractory organic matter. The aim of this study was to improve the N removal efficiency of a combined Panammox®/Photo-Fenton process by enhancing the production of biodegradable COD (bCOD) during advanced oxidation and take advantage of it for denitrifying purposes. Thus, a biological denitrification process could be subsequently applied to remove the remaining NO_3^- after the anammox process. High removal efficiencies were obtained in terms of total N and COD removal, 93 and 80% respectively. The optimal Fenton reagents dosage to enhance bCOD production was assessed, increasing the BOD_5/COD_t ratio from 0.03 to 0.14 in photo-Fenton. Therefore, optimal COD and N removal could be achieved without external C source dosage.

Keywords: Landfill leachate; anammox; high N load; biodegradability; photo-Fenton.

INTRODUCTION

The application of combined Panammox® process followed by a photo-Fenton process has been proved effective to treat mature landfill leachates, achieving efficient N and chemical oxygen demand (COD) removal, up to 87 and 98%, respectively (Anfruns *et al.*2013). Anammox process is able to remove about 90% of the incoming N. However, the fixation of CO_2 by anammox cells is associated to NO_3^- generation, which represents about 10% of the initial N. Therefore, as the total nitrogen (TN) in leachate can often be above 2 g N L^{-1}, the presence of NO_3^- in the effluent of the process can compromise the commitment of the TN discharge limits. The aim of this study was to improve the N removal efficiency of a combined Panammox® - Photo-Fenton process by enhancing the production of biodegradable COD (bCOD) after photo-Fenton treatment. In this sense, the produced bCOD would serve as electron donor in a subsequent denitrification tank for NO_3^- removal.

METHODOLOGY

The raw leachate used in this study was collected in municipal solid waste landfill site, located in Reus, Catalonia, Spain. The landfill leachate was first treated with the Panammox® process for autotrophic N removal, which consisted in two sequencing batch reactors of 250 L each for partial-nitritation (PN) and anammox, respectively. PN was operated under anoxic/aerobic configuration to promote bCOD removal and an effluent $NO_2^-:NH_4^+$ ratio of 1.32 to feed the subsequent anammox reactor (Ganigué *et al.* 2009). The Panammox® effluent was acidified down to pH 3 using H_2SO_4 prior to feeding photo-Fenton. Photo-oxidation experiments were carried out in a 1 L photo-reactor equipped with a low pressure mercury UV lamp. $FeSO_47H_2O$ was added to achieve the required amount of Fe^{2+}. The H_2O_2 was stepwise added every 60 min.

RESULTS

The main characteristics of the raw leachate, together with the main characteristics of the Panammox® and photo-Fenton (after 180 min of treatment) effluents are presented in Table 1. The Panammox® process was operated during more than 3 months treating leachate. The average N-removal efficiency was 92 ± 2% and the soluble COD (COD_s) was reduced by 52%. Due to the extreme leachate's NH_4^+ and COD concentrations, the effluent still contained 125 ± 34.5 $mgN\text{-}NO_3^-\ L^{-1}$ and 1775 ± 64 mgCOD L^{-1}, while alkalinity was reduced to only 924 ± 246 $mgCaCO_3\ L^{-1}$. Thus, the effluent presented optimal characteristics to be treated by advanced oxidation processes, i.e. photo-Fenton.

Table 1. Main characteristics of the raw leachate (RL), Panammox® effluent (PMX) and photo-Fenton effluent (PF).

Parameter:	**CODs** (mgO_2L^{-1})	**BOD_5/COD_t** -	**NH_4^+** ($mgNL^{-1}$)	**NO_2^-** ($mgNL^{-1}$)	**NO_3^-** ($mgNL^{-1}$)	**TN** ($mgNL^{-1}$)	**Alkalinity** ($mgCaCO_3L^{-1}$)
RL	3720±47	0.09	1963±65	0±0	0±0	2118±151	8633±629
PMX	1775±64	0.03	32.6±15.8	3.6±7.9	125±34.5	290±374	924±246
PF	760	0.14	67.5±2.2	-	71.5±3.3	139±14	942

n.d. not detected

After testing different doses of H_2O_2 and Fe^{2+} for the photo-Fenton treatment, the optimal dosing -which produced the highest values of bCOD- was set at 1000 mg $H_2O_2\ L^{-1}$ and 500 mg $Fe^{2+}\ L^{-1}$. Under these conditions, the evolution of BOD_5, CODs and BOD_5/COD_t ratio during the photo-Fenton treatment was monitored (Figure 1-a). The results show a production and accumulation of readily biodegradable substrate (BOD_5) while COD_s was reduced under the discharge limit (1000 mgCOD L^{-1}). These values, together with BOD_5/COD_t ratio indicate that the quantity of recalcitrant organic matter of the Panammox® effluent was reduced by photo-Fenton treatment, at the same time that the its biodegradability was increased. The increase in the biodegradable organic carbon fraction after the photo-Fenton treatment makes the effluent to be optimal for a subsequent denitrifaction treatment.

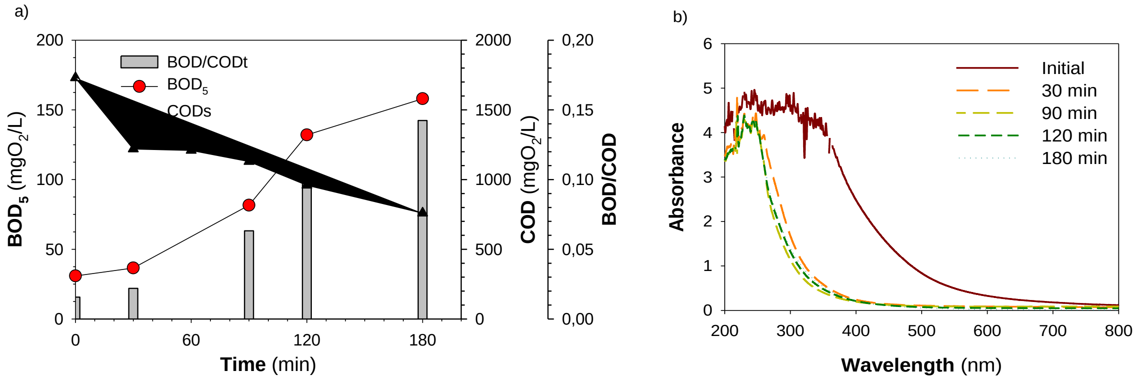

Figure 1. a) CODs, BOD_5 and BOD/COD ratio and b) UV/VIS spectrum evolution during the photo-Fenton treatment of the Panammox® effluent.

In this work, a combined Panammox®/photo-Fenton process was optimized for the treatment of extremely high N-strength wastewater with high refractory COD content. High N and refractory COD removal efficiencies were obtained by minimizing the use of reagents (H_2SO_4 and H_2O_2, Fe^{2+}). The production of bCOD was enhanced to further denitrify the remaining NO_3^- from the anammox process and keep the effluent N and COD concentrations below discharge limits without the need of external C source dosage.

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(P22) Integrated UASB-SBR scheme for the co-treatment of domestic wastewater and organic waste

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Abstract

The combined treatment of domestic wastewater and domestic organic waste (DOW) was investigated in an integrated upflow anaerobic sludge blanket (UASB) coupled to a sequencing batch reactor (SBR). The UASB achieved average COD removal of 82% for domestic wastewater treatment and 84% for the co-treatment of DOW and domestic wastewater, while operating at ambient temperature (22±3°C), with a specific methane yield of 0.22 $m^3CH_4/kgCOD_{removed}$. The subsequent SBR resulted in effective nutrient removal via nitrite with nitritation rate of 5.57±1.45 mgN/gVSS·h, denitritation rate of 6.81±1.99 mgN/gVSS·h, phosphorus uptake rate via nitrite of 6.33±1.92 mgP/gVSS·h and phosphorus release of 5.95±2.21 mgP/gVSS·h. Mass balances for four different scenarios were considered for a hypothetical case study of a treatment facility serving 2000 inhabitants. The treatment technologies included UASB to recover energy from wastewater and from fermented DOW, sequencing batch reactor (SBR) to remove nutrients from UASB effluents, fermentation to produce organic carbon source and membranes coupled to UASB. The option of food waste disposers (FWDs) was also examined. The mass balances showed that the fermented DOW is enough for the denitritation of SBR and to provide carbon source to the UASB increasing the methane production by approximately 10% when source separation of DOW is implemented and up to23% when the FWDs are implemented.

Keywords: Upflow anaerobic sludge blanket; Sequencing batch reactor; nutrient removal via nitrite

INTRODUCTION

Anaerobic treatment of wastewater should be a core technology that can be employed in decentralized sanitation systems for energy recovery. At a household level, black water (faeces and urine), grey water (shower, bath, laundry and kitchen) (Kujawa-Roeleveld and Zeeman, 2006) and domestic organic waste (DOW) are also generated. At decentralized level, the separate collection and anaerobic treatment of the most concentrated black water is an effective way to recover energy from wastewater. The high concentration of black water renders anaerobic treatment with subsequent recovery of nutrients a very attractive treatment option (Latif et al., 2011). In many cases of decentralized sanitation separation of black and grey water is not practiced. Integrating domestic wastewater treatment with DOW treatment increases energy recovery and can be a viable solution. In this work, the application of UASB-SBR was demonstrated for the co-treatment of domestic sewage and DOW at a decentralized community. This work can change perception in favour of local co-treatment of domestic sewage and DOW, thus avoiding the transportation of DOW over long distances.

MATERIALS AND METHODS

The integrated SBR-UASB process was operated to treat (i) domestic wastewater and (ii) combined wastewater and fermented DOW. The UASB inoculum was taken from a full scale UASB treating potato wastewater from Bologna (Italy) and for the SBR inoculum from the municipal plant of Treviso (Italy). The UASB had a working volume of 16 L and the sludge bed was filled up to 35% of its working volume. Internal recirculation of the effluent took place at 10 times the feed flow. The hydraulic retention time (HRT) of the UASB was maintained at 9.5-10 h. The SBR had a working volume of 26 L. It was operated with an SRT of 18 days and a nitrogen loading rate (NLR) of 0.19 kgN/m^3d and a low dissolved oxygen concentration (0.2-0.7 mg/L).The SBR cycle was operated in the following sequence: fill, anaerobic reaction, aerobic reaction, anoxic reaction, sedimentation, decant. Fermentation liquid originating from the organic fraction of municipal solid waste (OFMSW FL) was added during the anoxic and the anaerobic reaction phases. The OFMSW fermentation took place in a batch reactor, at controlled conditions (32-33°C, pH=4.0-4.5). Grinded OFMSW was diluted with secondary effluent up to 6% TS, applied at an organic loading rate (OLR) of 20 kgTVS/(m^3·d) and HRT of 3 d. In situ biomass activity tests were conducted to evaluate the specific ammonium uptake rate (sAUR), the specific nitrite uptake rate (sNUR), the specific phosphorus uptake rate under aerobic and anoxic conditions ($sPUR_{aerobic}$ and $sPUR_{anoxic}$ respecively) and the specific phosphorus release rate (sPRR). Total and volatile suspended solids (TSS, VSS), pH, chemical oxygen demand (COD), ammonium nitrogen (NH_4-N), total Kjeldahl nitrogen (TKN), total phosphorus,phosphate (PO_4-P), nitrite (NO_2-N) and nitrate (NO_3-N) were determined according to standard methods (APHA, AWWA, WEF, 1998) and the anions by ion chromatography (Dionex ICS-900with AS14 as column). Acetic acid, propionic acid and butyric acid were analyzed by gas chromatography (Dionex ICS-1100 with IonPac ICE-AS1 as column).

RESULTS AND DISCUSSION

UASB operation

The UASB was able to effectively remove COD from the domestic wastewater and from the mixture of fermentation liquid and wastewater, while operating at ambient temperature (22±3°C). The average removal of COD was 82% when domestic wastewater was treated and very similar (84%) when fermentation liquid was also introduced.The treated effluent COD concentration wason average 72 mg/L when domestic wastewater was treated and 82 mg/L when fermentation liquid was introduced. The methane yield was 0.22 $m^3CH_4/kgCOD_{removed,}$ avaluewhichlies within the expected range.

Via nitrite nutrient removal

The high vNLR (0.19 kgN/(m^3·d)) in combination with the low DO during the aerobic phase resulted in the complete inhibition of NOB. As a result, the NO_2-N/NO_x-N gradually increased to >97% and was steadily maintained above 99%. As evidenced by Table 1, high nitritation, denitritation and phosphorus removal via nitrite were accomplished. The nitrite concentration in the mixed liquor can potentially inhibit the sPUR. In our case the nitrite levels at the end of the aerobic phase did not exceed 35 mg·L^{-1} and were usually in the range of 10-25 mg·L^{-1}. This seems to affect much more the $sPUR_{aerobic}$ which was much lower than the anoxic phosphorus uptake. Despite the low DO concentration, the sAUR was high, owing to the high vNLR. The average ammonium, nitrogen and phosphorus removal were 84%, 77% and 85% respectively.

Table 1. Nutrient removal rates obtained for the SBR

Kinetic parameter	Units	Average Value ± Standard Deviation
sAUR	mgNH_4-N/(gVSS·h)	5.57 ± 1.45
sNUR	mgNO_2-N/(gVSS·h)	6.81±1.99
$sPUR_{aerobic}$	mgP/(gVSS·h)	2.19 ± 0.82
$sPUR_{anoxic}$	mgP/(gVSS·h)	6.33±1.92
sPRR	mgP/(gVSS·h)	5.95±2.21

Application for a decentralized community?

To demonstrate the feasibility of the UASB-SBR at decentralized level, a fictional case study of a community with 2000 inhabitants was carried out. The main question is whether the quantities of wastewater and food waste are adequately balanced, so that they could be effectively integrated within the UASB-SBR. Four different scenarios were evaluated as alternative ways for the potential co-treatment of DOW and wastewater at decentralized level (Figure 1). Complete mass balances were conducted for a hypothetical community having a population of 2000. The scenarios were:

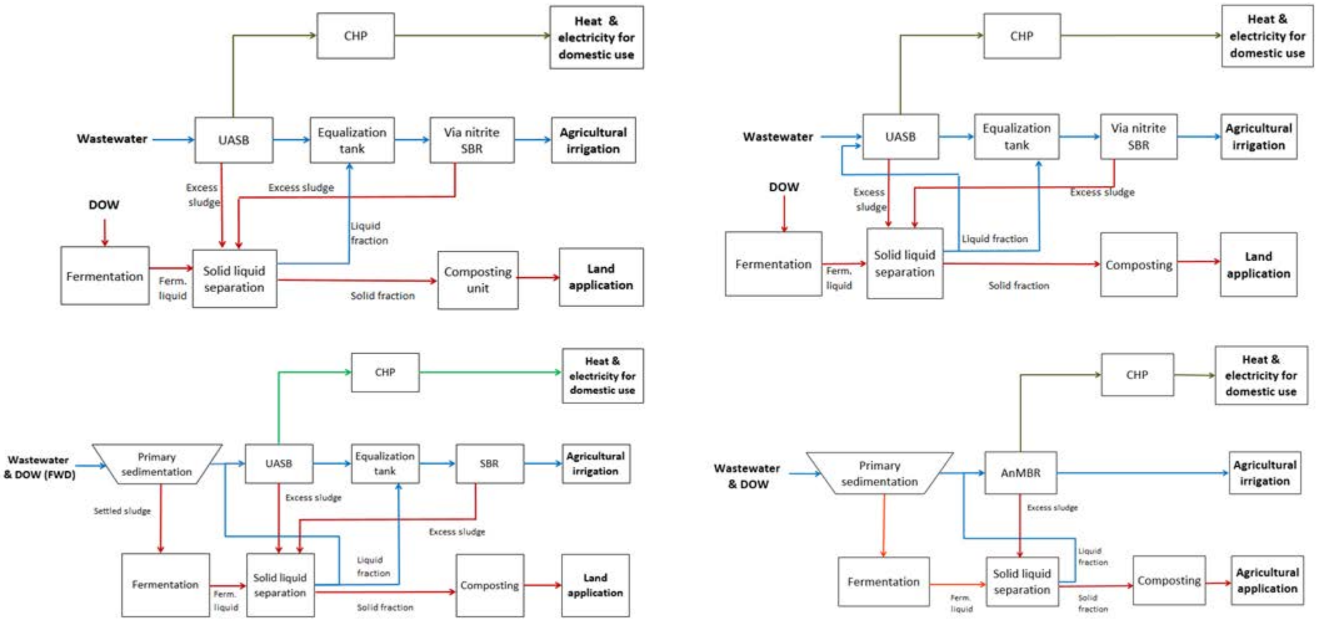

Figure 1: Scenarios A (a), B (b), C (c) and D (d)

- Scenario 1: Integrated UASB-SBR process, where domestic wastewater was treated by UASB to recover energy and then by the SBR to remove nutrients. DOW was fermented and was separated into the liquid and the solid stream. The liquid stream was fed to the SBR. The excess sludge from the SBR and the UASB was also fed to the solid/liquid separation scheme.
- Scenario 2: As scenario 1 with the difference that the fermented liquid was partly fed to the SBR and partly to the UASB. First the needs of denitritation were covered and the surplus of DOW was sent to the UASB to increase biogas production. The excess sludge from the UASB and SBR were fed together with the fermentation liquid to the solid/liquid separation scheme.
- Scenario 3: This case considered the integration of food waste disposers (FWD) within the households so that the raw sewage also contains DOW. Primary settling was carried out to produce primary sludge that was then fed to the fermentation unit.
- Scenario 4:The raw sewage containing DOW was fed to the UASB; then, ultrafiltration membrane was employed as a polishing step. Nutrient removal was not practiced.

The assumptions are based on usual design features for sewage, waste facilities and FWDs. The per capita production of domestic sewage, COD and N load were assumed to be 250 L·(capita·d)$^{-1}$, 120gCOD/(capita·d), 12gN/(capita·d)and 2.4gP/(capita·d). In terms of DOW, the production was assumed to be 0.25 kgDOW/(capita·d), with TS=25% and TVS=90%TS, considering the fact that decentralized communities have lower production of food waste and the source separation system will be about 85%. In the scenarios in which FWDs were implemented, this created an extra load of 60 gTSS/(capita·d), 95 gCOD/(capita·d), 2.1gN/(capita·d)and 0.3gP/(capita·d).Table 2 summarizes the most important parameters for the different scenarios that were considered. When the surplus of the DOW fermentation that is generated is diverted towards the UASB the methane that is produced increases by 10% (Scenario B) compared to the situation where the UASB does not receive any DOW(Scenario A). The integration of FWDs within the sewerage system increases significantly the COD load. Assuming 100% integration of FWDs within a decentralized community and primary sedimentation of effluent, the methane produced increases by 23% compared to scenario A. The primary sedimentation diverts the vast majority of suspended solids (i.e. sewage sludge and FWD solids) towards the fermentation process. In Scenario D, all the fermentation liquid generated by the process is sent to the AnMBR, thus increasing further biogas production. However, this was done at the expense of the treated effluent quality which is characterized by high nutrient levels.

Table 2. Summary of the most important parameters for the 4 examined scenarios

Parameters	Scenario A	Scenario B	Scenario C	Scenario D
Methane produced (m^3/d)	52.9	57.8	64.8	89.1
Electrical energy produced (kWh/d)	196	214	240	330
Thermal energyproduced (kWh/d)	308	336	377	518
Fermented liquid sent to SBR (%)	100	65	40	0
Fermented liquid sent to UASB (%)	0	35	60	100
Energy for fermentation(kWh/d)	29	29	85.9	85.9
Energy requirements for SBR aeration (kWh/d)	86.1	83.4	91.4	-
Energy for composting (kWh/d)	15.9	16.3	21.1	13.7
N treated effluent (mg/L)	9.7	9.7	10.0	67
P treated effluent (mg/L)	2.8	2.8	1.9	9.8
COD treated effluent (mg/L)	51	20	27	83
Moisture of end compost (%)	45	45	40	50
C end compost (% w/w)	38	41	40	31
N end compost (% w/w)	1.9	2.0	1.6	0.8
P end compost (% w/w)	1.0	1.0	0.9	0.2

CONCLUSION

The UASB accomplished 82% removal of COD from domestic wastewater and 84% from combined fermented DOW and domestic wastewater, while operating at ambient temperature 22±3°C. The specific methane yield was 0.22 $m^3CH_4/kgCOD_{removed}$. The SBR effectively removed nutrients via nitrite from the UASB effluent. The average ammonium, nitrogen and phosphorus removal were 84%, 77% and 85% respectively. The mass balances for a hypothetical case study showed that the integration of source separated DOW and domestic wastewater treatment can increase CH_4 production by 10%, while the use of FWDs can increase methane production up to 23%.

ACKOWLEDMENTS

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(S16) Guidelines for the optimal operation of the Hybrid Membrane Aerated Biofilm process for nitrogen removal

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Abstract

Taking into account the upgrading of waste water treatment plans (WWTP) that is required for nutrient removal, the search for more efficient treatment systems has become fundamental for the eco sustainability of WWTPs. In this area, Membrane Aerated Biofilm Reactors (MABRs) research is gaining in importance since they are able to achieve high oxygen transfer and utilization efficiencies. The MABR is a reactor in which the active biofilm is supported on and aerated by a gas permeable membrane. The main limitation of this configuration is the control of the excessive biofilm thickness due to overgrowth of heterotrophs, which limits the diffusion of substrates. The hybrid MABR (HMABR) aims to reduce this problem keeping autotrophic nitrifying biomass on the membranes, and heterotrophic denitrifying biomass within the liquid. In this study, some guidelines for the optimal operation of the HMABR are defined.

Keywords
Gas permeable membranes, hybrid process, nutrient removal, HMABR.

INTRODUCTION

The MABR is a reactor in which the biofilm is supported on and aerated/oxygenated by a gas-permeable membrane (Esteban *et al.,* 2012). The oxygen is able to diffuse straight to the biofilm growing on the other side of the membrane, in contact with the wastewater to be treated. This approach is likely to offer significant advantages over conventional aeration methods. In this configuration, the air does not need to be compressed to overcome the hydrostatic pressure, providing energy savings of up to 70% (Semmens, 2005). The MABR allows for nitrification and denitrification in the same biofilm (Timberlake *et al.* 1988), so it has the potential for the simultaneous removal of biological oxygen demand (BOD) and nitrogen.

The main limitation of this configuration is the control of the excessive biofilm thickness, which has been observed to be thicker than conventional biofilms due to overgrowth of heterotrophs (Casey *et al.*, 2000). Thick biofilms increase the mass transfer limitation and causes heterotrophic competition for oxygen and space in the biofilm resulting in decreased nitrification ability.

The hybrid MABR (HMABR) integrates membrane aerated biofilm process into a completely mixed activated sludge reactor. It has been proposed as an alternative to achieve total nitrogen (TN) removal controlling at the same time biofilm growth (Downing *et al.*, 2007). The critical goal of the HMABR is to maintain nitrifying biomass on the membranes, and achieve denitrification via suspended growth to control the heterotrophic attachment.

In this study, the main objective is to define the criteria for the optimal operation of the HMABR, achieving high nitrification rates that will take place almost exclusively in the biofilm, and an average MLSS concentration typical of a conventional activated sludge process, of about 3000 mg/L so that the heterotrophic denitrification activity occurs mainly in the bulk liquid.

METHODS

Wastewater

The HMABR pilot plant was located at the Environmental Engineering laboratory of CEIT (University of Navarra).The feed water used in this experimental stage, was prepared by mixing different portions of sludge return liquor and primary sludge of an urban raw wastewater which proceeded from municipal WWTP of Apraitz (North of Spain). The feed wastewater showed average values of 35 mg N/L in ammonium nitrogen (NH_4-N), 153 mg/L in soluble COD (sCOD) and 400 mg/L in total suspended solids (TSS). That influent ammonium concentration was fixed in order to operate with non substrate limiting conditions. Prepared wastewater was stored in a 500 L refrigerated tank.

HMABR pilot plant

The HMABR consisted of a 15 L PVC vessel with internal square section of 0.15x0.24 m^2 and height of 0.50 m, in which a single microporous polyethylene chlorinated flat membrane (type 203, size A4, KUBOTA) module was placed. This commercial membrane module is typically used for wastewater microfiltration. According to the instructions given by manufacturers KUBOTA, a hydrophobication treatment was applied before using it. As just one membrane module was used, the total membrane specific surface area was very low, resulting in 7.7 m^2/m^3. A settler of 22 L was located after the HMABR in order to recycle the activated sludge.

Operational conditions and analytical methods

The HMABR was operated for 145 days with an influent flow rate of 24 L/d and a hydraulic retention time of 13.7 h. The target MLSS of around 3000 mg/L (typical of a conventional activated sludge process) was achieved by adjusting sludge wastage. Sludge return ratio was 185%, and average applied loads for nitrogen and organic carbon were 192 gN/m^3d and 289 $gsCOD/m^3d$. Air was supplied to the membrane module at an inlet pressure of 65 mbar.

In this study, because of the low specific membrane surface area, it was necessary to incorporate a NO_3-N dosage to ensure a minimum N-NO_3 concentration in the bulk liquid. Therefore, 1.9 g NO_3-N /d (70 mgNO_3-N /L with respect to the influent flow) was added to the HMABR. In the case of a real plant, there would be enough membrane surface area for nitrification, so that the NO_3-N dosage is not required.

To characterize the behaviour of the HMABR process, samples were taken two times a week from the influent and reactor, and the following parameters were analyzed: total and filtered chemical oxygen demand (tCOD and sCOD), total and volatile suspended solids (TSS and VSS), ammonium (NH_4) and nitrates (NO_3). Daily measurements of pH, temperature and dissolved oxygen in the HMABR were taken.

Ammonium uptake rate (AUR) and nitrate uptake rate (NUR) batch tests were carried out under no substrate and electron acceptor limiting conditions, in order to evaluate the activity of nitrificants and denitrificants separately in both biofilm and activated sludge.

RESULTS AND DISCUSSION

Average results of parameters associated with the behaviour of nitrification and denitrification processes during a stable period, are summarized in Table 1.

Table1. Summary of performance results (average values)

MLSS	Effluent sCOD	Effluent NH_4-N	Effluent NO_3-N	Nitrification rate	Denitrification rate
mg/L	mg/L	mg/L	mg/L	gN/m^2d	gN/m^3d
3253	43	22	14	3	134

For the applied loading conditions and the HRT of 13.7 h used, to achieve the target MLSS concentration typical of a conventional activated sludge process of around 3000 mg/L, the sludge wastage was adjusted obtaining a bSRT of 7.4 days. Due to the nitrate dosage added, almost all influent biodegradable sCOD was removed anoxically in the bulk liquid by denitrificant biomass, limiting the heterotrophic growth and oxygen competition within the biofilm (effluent sCOD was assumed to be inert). In this way, the fact of having no bulk liquid NO_3-N limitations provided an extremely important role in maintaining the desired distribution of biomasses, avoiding that biodegradable sCOD could diffuse further into the biofilm and thus, the attachment and growth of heterotrophic bacteria. An average denitrification rate of 134 gN/m^3d and removal efficiency of 85% was observed. In this case, NUR batch tests resulted in denitrification rates 871% higher in the bulk liquid with respect to the biofilm (90% NUR in the bulk liquid and 10% in the biofilm) so it can be assumed that, as intended, most of the denitrification took place in suspension. High nitrification rates were consistently achieved with an average value of 3 gN/m^2d (maximum of 6 gN/m^2d). This rate is significantly higher than those obtained in previous HMABR studies. An average value of 0.85 gN/m^2d has been reported with a bSRT of 5 days and MLSS of 200 mg/L (Downing *et al.*, 2007), and 1.0 gN/m^2d maintaining bSRT at 2.5 days and MLSS between 50 and 120 mg/L (Downing *et al.*, 2008). Nitrification rates for denitrifying, non hybrid MABRs, were less than 2.6 gN/m^2d (Downing *et al.*, 2008).

Batch tests results showed that AUR were 400% higher in the biofilm than in the MLSS (80% AUR in the biofilm and 20% in MLSS). As AUR tests with MLSS were performed with dissolved oxygen (DO) higher than 6.5 mg/L, while DO in the bulk liquid during experimentation was always less than 0.1 mg/L, it can be considered that nitrificant activity occurred almost exclusively in the biofilm, which was one of the main objectives of the present study.

The high achieved nitrification rates are attributed to 1) operating with non ammonium limiting conditions (NH_4-N concentrations in the bulk liquid were much higher than the half saturation constant, which in addition favoured diffusion into the biofilm by increasing ammonium concentration gradient) and 2) most of the sCOD was removed anoxically in the bulk liquid preventing its diffusion into the biofilm and the inhibition of nitrificant biomass. Further research is needed to evaluate the performance of the HMABR when lower ammonium and nitrate concentrations in the effluent are required.

This relationship between nitrification rates, bulk liquid biodegradable sCOD and NO_3-N concentrations is confirmed when their daily variations (Fig.1) are analyzed. It can be noticed (between day 60 and 120) that high bulk liquid sCOD resulted in lower nitrification rates. Available bulk sCOD is correlated with effluent NO_3-N concentrations. When bulk NO_3-N decreases, influent biodegradable sCOD cannot be removed completely, obtaining higher effluent sCOD concentrations and limiting the nitrification rates.

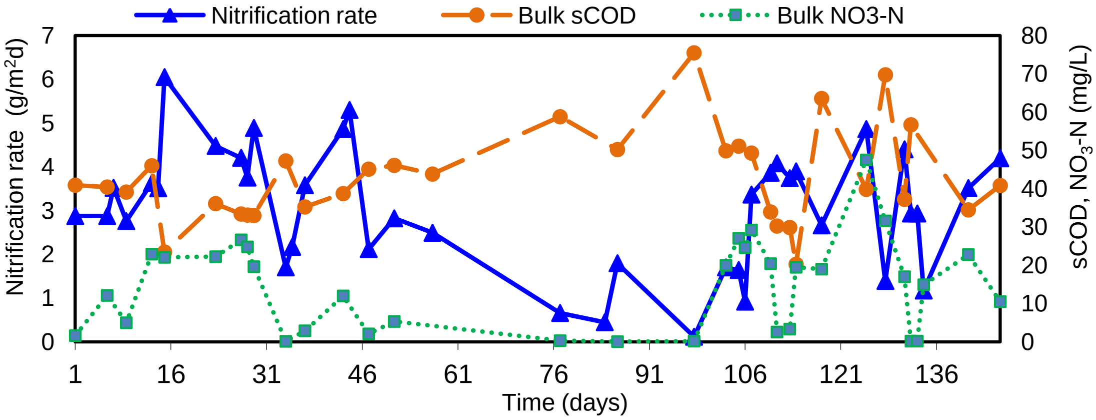

Figure 1. Relationship between bulk liquid sCOD and NO_3-N, and nitrification rates.

CONCLUSIONS

In this experimentation, some criteria for the optimal operation of the HMABR for total nitrogen removal are determined. Effluent NO_3-N concentration has a crucial role to ensure that most of the biodegradable sCOD is removed anoxically in the bulk liquid and thus prevent its diffusion into the biofilm. It is necessary to work with no substrate and electron acceptor limiting conditions, so that an effluent N-NH_4 concentration between 2-4 mg/L and NO_3-N concentration about 1-3 mg/L are required. For this purpose, the MLSS concentration should be adjusted in order to provide the proper denitrification rate.

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(S17) A Robust Biological System for Sewage treatment in Tourist Areas

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Abstract

This study was aimed at evaluating the effectiveness of an innovative compact biological system for treating at pilot scale municipal sewage produced in tourist areas characterised by intense seasonal water demand and wastewater discharge. The results obtained after a long term operation have shown that the proposed system was able to assure average removal efficiencies higher than 90% for COD (chemical oxygen demand), total suspended solids and TKN (total Kjeldahl nitrogen) independently of the influent concentration values and organic loading which ranged from 0.2 to 5.1 kgCOD/m^3·d. Furthermore, the system was characterized by an excess sludge production 80% lower than that of conventional biological systems operating without a primary clarifier; an acceptable level of stabilization of excess sludge was also obtained indicating that a further stabilization process might no longer be required.

Keywords: municipal sewage treatment; organic load variations; sludge production; tourist areas.

INTRODUCTION

Mediterranean tourist areas are characterized by a sharp increase of population during the summer season. This population fluctuation of course affects wastewater quality and quantity. In fact, compared with a common municipal sewage, wastewater coming from tourist areas is usually more concentrated in terms of typical pollutants, more variable in terms of both flow and contaminants concentration, and less disintegrated in terms of particulate matter (Odegaard, 1989). In tourist areas wastewater treatment is usually carried out decentrally by small plants each serving single or group of homes, hotels and other tourist establishments. These systems, mainly based on extended aeration activated sludge processes, suffer from a series of problems, including shock loads, sludge bulking, absence of regular supervision and maintenance, and flow fluctuations, which may lead to poor effluent quality (Christoulas and Andreadakis, 1989). It follows that more reliable and robust wastewater treatment technologies with lower sludge production and better operational flexibility should be provided in tourist areas. Among the new, recently proposed, systems able to comply with this request, one of the most promising is the system developed by the Water Research Institute (IRSA) of the National Research Council of Italy (CNR) whose acronym is SBBGR (Sequencing Batch Biofilter Granular Reactor). The SBBGR system combines the advantages of attached biomass systems (i.e., greater robustness and compactness) with those of periodic systems (i.e., greater flexibility and stability). SBBGR is however a unique system in virtue of the particular type of biomass growing in it (i.e., a mixture of biofilm and granules packed in a filling material) which allows a greater retention of the biomass in the reactor to be obtained (up to one magnitude order higher than that recorded in conventional biological systems). As a result, a notable increase in sludge age is achieved with consequent reduction in sludge production (Di Iaconi et al., 2010) highly desirable in small wastewater treatment plants operating in tourist areas. The overall aim of the present study was the evaluation of the effectiveness of the SBBGR system for treating, at pilot scale, raw municipal sewage coming from a residence located on the Adriatic Sea coast near Bari, a southern Italy town. The effectiveness of this system in coping with the organic load variations typical of tourist areas was also evaluated.

MATERIAL AND METHODS

Figure 1 shows a sketch and photograph of the pilot plant used in the investigation, which consisted of two units: a biofilter and an aerator. The biofilter is the reactive zone of the plant as it contains the biomass; it consists of a cylindrical steel reactor (diameter: 220 mm; height: 3200 mm) filled with wheel shaped plastic elements. The aerator, consisting of a cylindrical steel reactor (diameter: 273 mm; height: 3200 mm), is the zone of the liquid phase (i.e., wastewater); its role is to supply air for the process by means of a blower connected with a diffuser plate located at the bottom of the unit. The biofilter and aerator are hydraulically connected by means of a pump (rec. pump in Figure 1) which continuously recycles the liquid in the aerator through the biomass supporting material of the biofilter. The operation of the system was based on a succession of treatment cycles, each consisting of three consecutive phases: the filling, reaction and drawing phases. During the filling phase, a fixed volume of wastewater to be treated was added to the aerator by means of a filling pump. During reaction phase, the working volume of the aerator was continuously recycled through the biomass supporting material of the biofilter. Finally, the treated wastewater was discharged exploiting the gravity by opening a motorized valve. The plant was then ready to start a new treatment cycle. The operative schedule (filling, recirculation, aeration, drawing) was completely automated, using a programmable logic controller (PLC). A pressure meter, set at the bottom of the biofilter unit, measured on-line head losses due to the biomass growth and captured suspended solids present in the wastewater. When a fixed set value of head loss was reached, a washing step was carried out by compressed air until the headloss was decreased down to a definite value.

Figure 1. Pilot plant sketch (on the left) and photograph (on the right).

Treatment performance was evaluated by measuring several parameters of plant influent and effluent, usually two times per week. The removal efficiencies of all parameters were calculated as a percentage reduction in value between the influent and effluent samples. Chemical oxygen demand (COD), total nitrogen (TN) and total phosphorous (P) were determined using Dr Lange test kits whereas total suspended solids (TSS) and total Kjeldahl nitrogen (TKN) were measured according to standard methods (APHA, 2005).

RESULTS AND DISCUSSION

After biomass generation (start-up phase), the effectiveness of the pilot plant in coping with organic load variations was evaluated. Plant performances (in terms of both average values and value range) recorded during the pilot experimental campaign are summarized in table 1. Looking at this table, it is possible to observe that the COD removal efficiency was always higher than 81% (on average 93%) with residual concentration in the effluent lower than 74 mg/L (on average 41 mg/L) independently of influent COD value, which ranged from 205 up to 2,640 mg/L, and the organic loading rate (OLR) applied to the plant, which was even as high as 5.1 kg COD/m^3·d. This result can be ascribed to the great operation flexibility and stability of the SBBGR system in response to changes in wastewater composition. Regarding total suspended solids, the data reported show that the concentration in the effluent was always lower than 22 mg/L (on average, 9 mg/L) with removal efficiencies higher than 92% (on average 97%), once again independently of the influent TSS value which ranged from 70 up to 1,233 mg/L.

Table 1. Pilot plant performance (in terms of mean±standard deviation and value range)

Parameter		**Mean value (± st. dev.)**	**Value range**
OLR	(kg COD/m^3·d)	1.2 (±1.1)	0.45 – 5.1
COD	influent (mg/L)	708 (±558)	205 – 2640
	effluent (mg/L)	41 (±16)	23 – 74
	removal efficiency (%)	93 (±4)	81 – 97
TSS	influent (mg/L)	395 (±341)	70 – 1233
	effluent (mg/L)	9 (±5)	2 – 22
	removal efficiency (%)	97 (±2)	92 – 99
TKN	influent (mg/L)	67 (±24)	26 – 139
	effluent (mg/L)	5 (±3)	2 – 11
	removal efficiency (%)	91 (±4)	82 – 97
TN	influent (mg/L)	67 (±25)	26 – 139
	effluent (mg/L)	14 (±6)	3 – 25
	removal efficiency (%)	78 (±8)	65 – 92
P_{tot}	influent (mg/L)	5 (±3)	3 – 10
	effluent (mg/L)	3 (±2)	1 – 6
	removal efficiency (%)	28 (±24)	10 – 55

Referring to nitrogen, the results show that the plant was able to remove, on average, 91% of TKN content with residual concentrations in the effluent always lower than 11 mg/L (on average 5 mg/L) independently of the influent value and the organic loading rate applied, thus indicating that a stable nitrification process had been established.

Furthermore, TN removal efficiencies data also highlight the existence of a somewhat extended denitrification process although no planned final anoxic phase was included in the treatment cycle of the plant. In fact, removal efficiencies in the range 65-92% were also achieved thanks to the establishment of a stable simultaneous nitrification-denitrification process favoured by the high biomass concentration and transient conditions (typical of sequential reactors) which generated contiguous anoxic and aerobic biomass layers. It has been reported in previous studies performed using SBBGR technology that the ammonium oxidizers situated in the outer biomass layers carry out the oxidation of ammonium to nitrite/nitrate while denitrifying bacteria located in deeper layers, where oxygen cannot penetrate, reduce these compounds to nitrogen gas by using carbon sources coming from storage or hydrolysis products of influent suspended solids captured during the operation (De Sanctis et al., 2010).

The sludge production was about 0.15 kgTSS/kgCOD$_{\text{removed}}$. This value is much lower (i.e., about 80% lower) than that reported in the literature for extended aeration systems (widely used in tourist areas) operating without a primary clarifier (Schultz et al., 1982). An acceptable level of stabilization of excess sludge was also obtained (a VSS/TSS ratio of about 0.57 was measured) so that a further stabilization process might no longer be required. This is an important result since the sludge produced in these plants is usually transported to a nearby larger treatment plant (which may be located at some considerable distance) where the facilities for sludge treatment are available.

CONCLUSIONS

The results have shown that the proposed system was able to ensure a high degree of operation flexibility and stability in response to the organic load variations typical of tourist areas. In fact, average removal efficiencies higher than 90% (and always higher than 80%) were obtained for COD, total suspended solids and TKN, independently of the influent concentration values and applied organic loading which ranged from 0.2 to 5.1 kgCOD/m^3·d; satisfactory nitrogen removal efficiencies (on average 80%) were also obtained due to simultaneous nitrification-denitrification process. The plant was characterized by an excess sludge production 80% lower than that of the extended aeration systems commonly in use in tourist areas; an acceptable level of stabilization of excess sludge was also obtained indicating that a further stabilization process might no longer be required.

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(S18) Potentialities of Novel PBM membranes in wastewater treatment

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Abstract

The increasing worldwide water demand is pushing more and more the market to find new solutions to be applied for water reuse in several industrial sectors. The development of efficient wastewater treatment technologies can give complete answers, in this direction, to many of the problems related to water purification. In particular, membrane processes devoted to wastewater treatment are gaining more and more attention thanks to their high efficiency, energy saving systems, easy scale-up, and flexibility. In the present work, novel flat membranes produced by polymerisable bicontinuous microemulsion (PBM) technique have been prepared and characterised. PBM membranes were polymerised and also used as coating material for commercial flat polyethersulphone (PES) membranes. PBM membranes, due to their characteristics, are considered ideal candidates for wastewater treatment processes such as Membrane Bioreactor (MBR). PBM membrane modules have been, then, produced to be tested in MBR plant for wastewater removal.

Keywords

Membrane; MBR, Membrane preparation, wastewater treatment

INTRODUCTION

Membranes are traditionally prepared by phase inversion (the most common), melt extrusion, track-etching, sintering etc.. However, in the present work, an alternative approach was proposed for preparing polymeric membranes by polymerisable bicontinuous microemulsion (PBM).

This technique consists on the polymerisation of two immiscible phases (oil and water) stabilised by a surfactant. Among the different types of microemulsion that can be formulated, the bicontinuous range was selected as shown in figure 1. The main advantage is that the structural characteristics of the bicontinuous microemulsion can be conserved and transferred to the polymeric matrix.

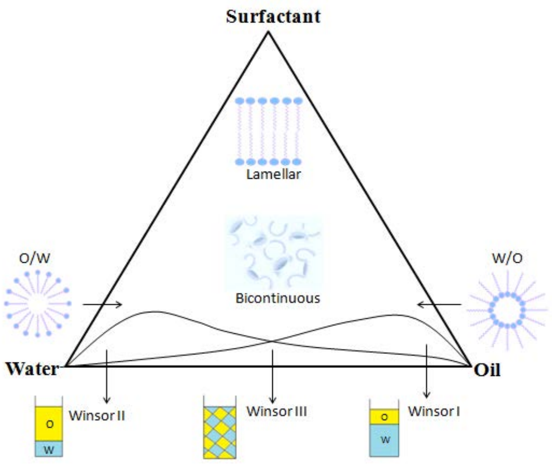


Figure 1. Ternary phase diagram representing some phase equilibria in multicomponent systems.

As shown in figure 1, microemulsions can be in the form of oil-swollen micelles dispersed in a continuous water phase (O/W), or water-swollen droplets dispersed in an oil phase (W/O). In the intermediate region, the structure is not globular anymore but it has a sponge-like structure (bicontinuous microemulsion) where the oil and water domains coexist in interconnected domains.

In bicontinuous microemulsions, the amount of monomer that can be incorporated in the microemulsion can reach 25 wt%, producing stable and clear microlatexes with very small particle size. The organic and aqueous phases coexist in an interconnected network with surfactant molecules localized at the interface of water-oil domains [1].

The PBM has been then employed for coating ultrafiltration PES commercial membranes, for obtaining a highly hydrophilic and antimicrobial membrane, which could be employed in Membrane Bioreactor (MBR) for wastewater treatment. Furthermore, PBM membranes were produced in order to lower fouling and improve rejection of low-molecular micro-pollutants of existing commercial membranes [2]. Optimization of the prepared PBM membranes allowed extending the MBR operation efficiency from high biodegradable organic compounds to wastewaters containing stress-inducing substances.

MATERIALS AND METHODS

The optimal composition of bicontinuous microemulsion was deeply studied based on already existing literature studies as well as the preparation of PBM membranes [3-4]. The critical step was the synthesis of a new cationic AUTEAB surfactant, which was synthesized by following the two-step procedure.

The monomer methyl methacrylate (MMA) was used as oil phase of the system, water was used as aqueous phase and the surfactant AUTEAB was used to disperse the two immiscible phases. The cross-linking agent ethylenglycol dimethacrylate (EGDMA) was also added so to strengthen the final polymer matrix, while the short-chain alcohol 2-hydroxythylmethacrylate (HEMA) was used as co-surfactant in order to facilitate the dispersion of the oil phase and the aqueous phase. Redox-initiators were finally added to the system and the microemulsion was cast, before complete polymerisation, on the surface of a PES ultrafiltration membrane. The PBM coated membranes were then obtained. Sigma Aldrich purchased all chemicals.

RESULTS AND DISCUSSION

The bicontinuous microemulsion as well as the PBM coating membranes were successfully prepared and characterised and the results are reported in the following sections.

Microemulsion characterisation

Conditivity measurements

In order to find the bicontinuous range, microemulsions were investigated in terms of conductivity measurements.

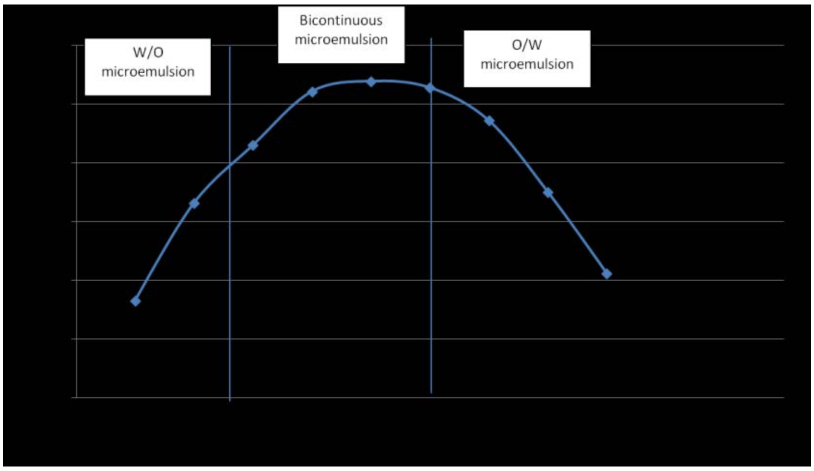


Figure 2. AUTEAB conductivity measurements at different aqueous solutions.

The transition from a w/o to a bicontinuous microemulsion was shown by a sharp increase in the conductivity value [4].

Membrane characterisation

Scanning electron microscopy (SEM) and atomic force microscopy (AFM)

The morphology of the PBM membranes prepared was evaluated by means of SEM and AFM measurements. The existence of a bicontinuous microstructure was revealed and it is clearly visible in the Figure 3a.

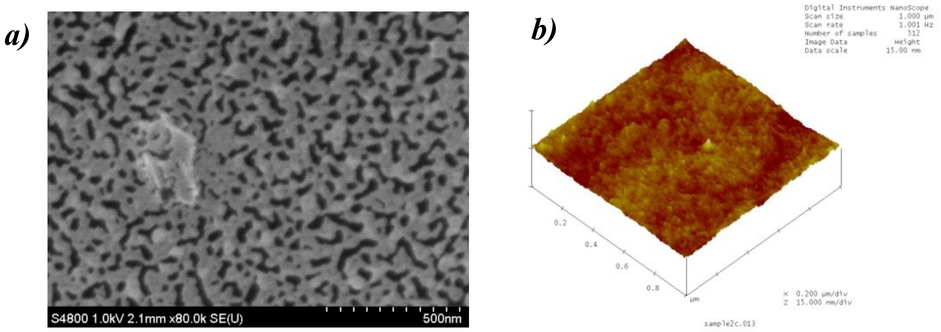


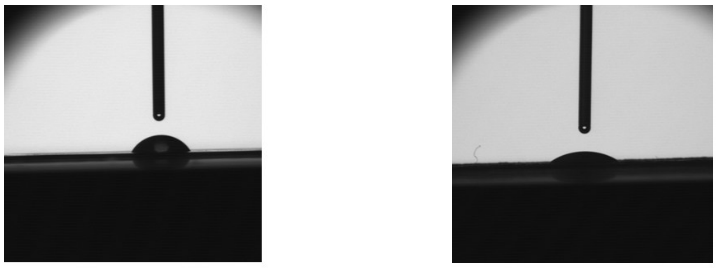
Figure 3. *a)* SEM and *b)* AFM surface of PBM layer coated on PES membrane.

During the polymerisation, the water channels remained unchanged, while the oil channels formed the polymer matrix of the membrane, giving, as final result, an interconnected network of oil (white strips) and water channels (dark strips).

AFM measurements (figure 3b) showed how the overall surface roughness of PBM membranes was much lower in comparison to the one of PES UF commercial membrane. The smoother surface of PBM membranes was at the basis of their tested antifouling properties by limiting the adhesion of organic matter at membrane surface.

Contact angle measurements

The PBM layer causes a decrease in contact angle of about 30% with respect to the pristine UF membrane. The contact angle, in fact, decreases from about 70° (for PES commercial membrane) to 45° (for PBM coated membranes). The higher hydrophilicity of PBM membranes is mainly due to the smoother surface and to the presence of OH groups originating from the HEMA cosurfactant at membrane surface. It is well known that membranes with a higher hydrophilic moiety are less prone to be affected by fouling.



PES commercial membrane

PBM membrane

Figure 5. Water droplet on PES commercial and PBM coated membrane surface.

Water permeability and fouling

The water permeability for PBM coated membrane was about 200 L/m^2 h bar (Figure 6). Permeability was, therefore, about one third lower in comparison to PES commercial membrane (600 L/m^2 h bar). The decrease in permeability was mainly due to the extra PBM layer present on the top of the membrane.

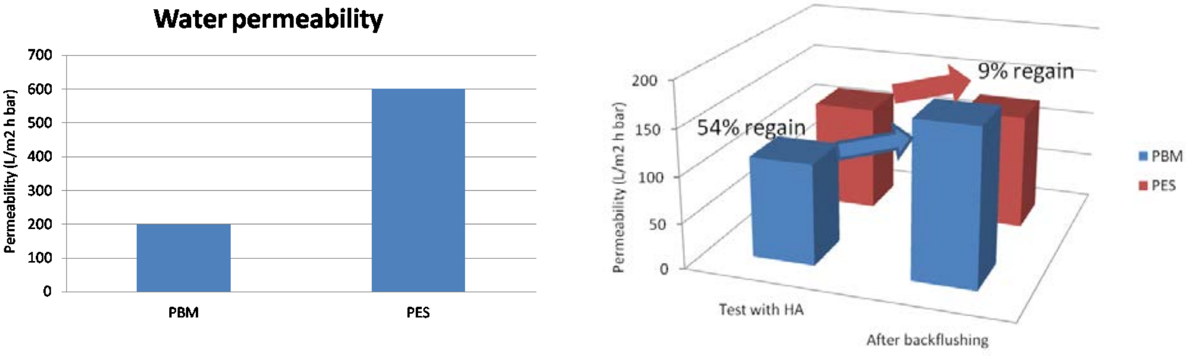


Figure 6. Water permeability and humic acid (HA) foulant tests for PES commercial and PBM coated membrane.

The lower water permeability, was, however, balanced by the good antifouling properties showed by PBM coated membranes. A solution containing the model foulant humic acid (HA) was used in order to measure PBM and PES membranes fouling resistance. After filtration tests it was shown how PBM membranes are more resistant to fouling in comparison to PES membrane due to their smoother surface and higher hydrophilic moiety. Furthermore after back-flushing PBM membranes showed an important regain in permeability (more than 50%) in comparison to PES membrane (9 %) (figure 7).

CONCLUSIONS

AUTEAB polymerisable surfactant was synthesised and successfully used for bicontinuous microemulsion preparation. The microemulsion was, then polymerised, on PES flat UF commercial membranes. It was clearly proved that the bicontinuous structure, under specific conditions of microemulsion composition, was maintained after the polymerisation as demonstrated by SEM analyses. The smoother surface of PBM coated membranes, in comparison to commercial PES membranes, was determined by AFM analyses. Roughness measurements as well as contact angles are considered important aspects contributing to the antifouling property of the novel membrane coating. PBM coated membranes showed better resistance to fouling in comparison to commercial PES membranes when treated with HA. This was mainly due to the very smooth and hydrophilic surface of the PBM coating produced. This resulted in a longer lifetime of PBM membranes in comparison to uncoated commercial membranes and made them ideal candidates in MBR for wastewater treatment.

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(S19) Sustainable Conversion of Fat, Oil and Grease Wastes Produced by Municipal Wastewater Treatment Plant into Biofuels.

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Abstract

Fat, oil and grease produced by oil/water separation at the wastewater treatment plant of Bari West (Southern Italy) were taken, characterized and converted. After chemical activation of this fatty fraction, with the aim of converting the starting calcium soaps into the respective free fatty acids, a direct esterification was carried out under very mild conditions. Working at 345 K under atmospheric pressure, the thermodynamic conversion (more than 90%) of the free fatty acids into the respective methyl esters was obtained in less than 2 h, by using $AlCl_3 \cdot 6H_2O$ as catalyst. Fundamental parameters, such as kinetic and equilibrium constants at different temperatures and activation energy correlated to the use of this catalyst, were also calculated. The biodiesel was purified with a distillation under vacuum, providing a final product conformed to the EN14214 requirements. The convenience of the overall process in terms of costs (0.45 € L^{-1}) and specific thermal energy supply (5.02 MJ Kg_{FAMEs}^{-1}) make such a process a really sustainable and effective example of valorization of a waste.

Keywords
UW-FOG, Biodiesel, bio-wastes valorization, WWTP waste, biorefining, $AlCl_3 \cdot 6H_2O$

INTRODUCTION

Fat, oil and grease in urban wastewater (UW-FOG) often represent a problem not only for deposits' formation that clog the pipelines during sewage transportation to wastewater treatment plants (WWTPs) (Williams et al., 2012), but also for their final management. In fact, once arrived to WWTP, when separated by the influent as an upper emulsion through a flotation step, it becomes a special waste [European Waste Code (EWC) 190809] whose disposal may account for up to 10% of the total sludge disposal costs. Because of this, it is a quite common procedure to treat wastewater by minimizing the preliminary separation of UW-FOG, even though this hampers the successive processes. Such a situation makes it really complex to estimate the real separable amount of UW-FOG from urban wastewater as, in some cases, it is not efficiently collected and in most cases, no units have been installed for the specific removal of this component. Theoretically, considering that the oil concentration in urban wastewater usually ranges from 50 to 150 ppm (Passino, 1980), from a WWTP sized for 100,000 of equivalent inhabitants, about 1600 to 3800 kg of UW-FOG per day might be collected. Such an amount not only cannot be ignored, but it could also be considered as an exploitable resource for biofuel production.

The valorization of UW-FOG has been studied only recently with the aim of producing methane under mesophylic conditions (Martín-González et al., 2011). By contrast, Montefrio et al. (2010) studied the conversion of FOG taken from a grease interceptor (IG-FOG), with a starting FFA content that did not exceed the 15%. Such a grease was efficiently converted into Fatty Acids Methyl Esters (FAMEs), adopting an already known procedure (Canakci et al., 2007) based on a two-step process in which a first acid direct esterification is followed by a basic trans-esterification.

Even though it has been mentioned several times as a possible starting raw material for producing biodiesel, UW-FOG has only scarcely been studied in practice, probably for having a too high FFAs content. In this paper, the conversion process of real waste from WWTPs to FAMEs is presented. The experimental results prove that aluminium chloride hexa-hydrate represents an effective alternative to conventional homogeneous acids, being in the same time equally active and safer than conventional acids, and producing at the end of the process, a potentially (re)usable residual aqueous stream.

MATERIALS AND METHODS

General procedures

All solvents, reagents and standards were RP Aldrich products. A Rotofix 32 Hettige Centrifuge was used for separating out the oily and aqueous phases. GC–MS analyses were carried out by a Clarus 500 gas chromatograph (Perkin Elmer) equipped with a VF-5MS capillary column (20 m; 0.32 mm, 0.25 μm film) interfaced with a Clarus 500 Mass Spectrometer. Quantitative determinations of the reaction solutions were performed using a Varian 3800 GC-FID equipped with a MDN-5S capillary column (15 m; 0.32 mm, 0.25 μm film). Both the GCs were used in on-column mode for determination of heavy compounds. FAMEs characterisation and quantification were carried out according to the EN14103 method (the %RSD calculated on the FAMEs measurements did not exceed the 1.5%). Mono-, di- and triglycerides were determined using the EN14105 method. Waxes were determined using the COI/T.20/ Doc. no.18/ Rev. 2 method, while sterols were analysed using published procedures (Pastore et al., 2013). FFAs were determined through a base titration using a 0.1 N KOH solution, in a diethyl-ether:ethanol 1:1 media, and adopting phenolphtalein as indicator. Soaps were determined through a titration carried out in organic media (diethyl-ether:ethanol 1:1 solution) using a 0.1 N HCl solution and methyl red as indicator.

Preparation of the starting grease

Fresh samples of EWC 190809, taken directly from the Bari West WWTP, were dewatered keeping them for 18 h in a tank from which the excess water was drained off (TS passed from 12.5±0.5% to 22.4±0.5%). The final wet sludge was heated up to 343.15 K and centrifuged at 3000 rpm for five minutes. The upper part (UW-FOG) was put aside and stored for successive operations (12% of the starting material, 53.5% of the starting TS). With cooling down of the temperature, the brown liquid became a semi-solid grey matter that was analysed as a mixture of FFAs (50%), soaps (34%), aliphatic alcohols (0.5%), waxes (0.3%), sterols (0.2%) and traces of glycerides. About 100 g of this semi-solid grey matter were then mixed at room temperature with 5.40 g of HCOOH. The resulting mixture was stirred for 2 h, and 100 mL of hexane were added to separate the oily phase from the obtained calcium salts. The UW-FOG was finally recovered by distilling away the solvent under vacuum. It was never less than 93 g and was mainly made of FFAs (> 82 %).

FFAs conversion into FAMEs under $AlCl_3 \cdot 6H_2O$ catalysis

About 10 g of UW-FOG were directly weighed in a reactor with 9.0 g of methanol. The limpid solution was kept under stirring and heated to the set temperature (nominally 315.15, 330.15 and 345.15 K). After a preliminary control of the starting composition in terms of FFAs ($C_{FFAs,t0}$), 0.8 mL of a methanol solution of $AlCl_3 \cdot 6H_2O$ (prepared dissolving 3.71 g of it in 20 mL of methanol) were directly added into the closed reactor (through the septum using a syringe). In this way, the final ratio of FFAs:MeOH was about 1:10, while the concentration of $AlCl_3 \cdot 6H_2O$ referred to FFAs was 2% molar. The reaction time started at the moment of the addition of the catalyst, and the direct esterification was followed by measuring the concentration of the FFAs ($C_{FFAs,t}$) and of the FAMEs ($C_{FAMEs,t}$) over time.

RESULTS AND DISCUSSION

Direct esterification of FFAs under $AlCl_3 \cdot 6H_2O$ catalysis: the temperature effect

The direct esterification of FFAs with methanol using $AlCl_3 \cdot 6H_2O$ as catalyst (Eq. 1) was investigated at three different temperatures: 315.15, 330.15 and 345.15 K.

$$\mathrm{RCOOH + MeOH \underset{k_{FAMEs}}{\overset{k_{FFAs}}{\rightleftharpoons}} RCOOMe + H_2O} \qquad (1)$$

The profiles of FAMEs and FFAs in the time were determined and reported in Figure 1.

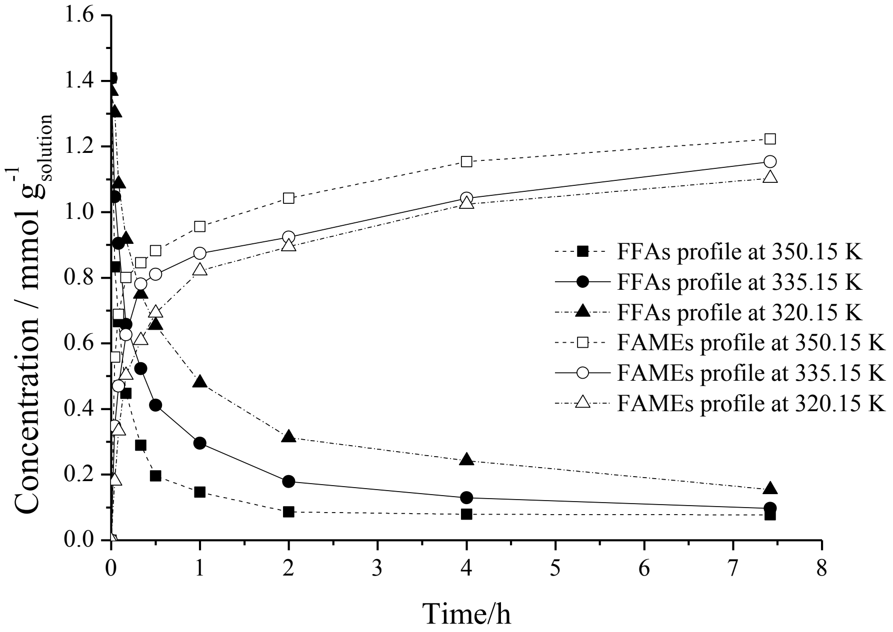

Figure 1. FAMEs and FFAs kinetic profiles determined at 315.15, 330.15 and 345.15 K (MeOH:FFAs:$AlCl_3 \cdot 6H_2O$ 10:1:0.02).

When the temperature was set to 350.15 K, the conversion of FFAs into FAMEs was practically complete (>90%) already after two hours. Having carried out all reactions in batch conditions, the mass balance depended only on the stoichiometry defined in Eq. 1, so that the direct esterification was modelled as a second-order reversible reaction (Berrios et al., 2007). Considering that the velocity could be defined as the disappearing of the reagents or the formation of the products over time, the most accurate acidity decrease was chosen for the modelization. Hence, the rate of the reaction was defined as in Eq. 2:

$$v = -\frac{d\,C_{FFAs}}{dt} = \frac{m_{cat}}{M_{mix}}\left(k_{FFAs}C_{FFAs}C_{MeOH} - k_{FAMEs}C_{FAMEs}C_{H_2O}\right) \qquad (2)$$

where m_{cat} was the amount of the catalyst used in a batch reaction, M_{mix} was the total mass of the solution, k_{FFAs} and k_{FAMEs} were respectively the kinetics constants referred to the esterification and the reversible hydrolysis, while C_{FFAs}, C_{MeOH}, C_{H2O} and C_{FAMEs} were experimentally determined during the reaction.

Under these conditions, Eq. 2 becomes a non-linear differential equation in which the time is the independent variable, while k_{FFAs} and k_{FAMEs} are the variables to be determined. The differential equation was solved through the use of Matlab R2006b and adopting the fourth order Runge-Kutta code. Fixing the k_{FFAs} and k_{FAMEs} values and running the Matlab operator, it was possible to obtain as output the calculated concentration of FFAs at different reaction times. The two correct values of k_{FFAs} and k_{FAMEs} were those that minimized the objective F function defined as follows (Eq. 3):

$$F = \sum_{t=0}^{t_f} \left(1 - \frac{C_{FFAs,calc,t}}{C_{FFAs,exp,t}}\right)^2 \qquad (3)$$

where $C_{FFAs,calc,t}$ was the concentration of FFAs calculated fixing the two constants values and using the mathematical model described, and $C_{FFAs,exp,t}$ was experimentally obtained.

Table 1 reports the values of k_{FFAs} and k_{FAMEs} determined for the three different temperatures.

Table 1. Kinetics and thermodynamics parameters determined for the direct esterification of FFAs using $AlCl_3{\cdot}6H_2O$

T	k_{FFAs}	k_{FAMEs}	Keq
K	$kg^2 kg_{cat}^{-1} mol^{-1} s^{-1}$	$kg^2 kg_{cat}^{-1} mol^{-1} s^{-1}$	
315.15	0.0027±0.0001	0.0040±0.0001	0.675
330.15	0.0056±0.0001	0.0063±0.0001	0.896
345.15	0.0116±0.0001	0.0088±0.0001	1.320

Plotting the $\ln(k_{FFAs})$ and the $\ln(k_{FAMEs})$ vs 1/T, the expected linear trends (with an R^2 even higher than 0.998) was obtained and the activation energies for the production of FAMEs (Ea_{est}) and the back-reaction of hydrolysis (Ea_{hydr}) were calculated, being respectively 43.9 and 24.7 kJ mol^{-1}. These values, in good agreement with the values reported for direct esterification catalysed by sulphuric acid (Berrios et al., 2007), not only shows that $AlCl_3{\cdot}6H_2O$ is as active as the most widely used H_2SO_4, but also suggests that it works as a Brönsted acid.

Scale up of the process

The direct esterification was also carried out starting from a larger amount of UW-FOG (1 Kg) confirming the same results obtained for smaller reactor. At the end, the biodiesel was isolated distilling it under vacuum (424-434 K, 60 mTorr) for a final yield of 72% referred to UW-FOG. The distillate was analysed and found to be conform to EN14214.

CONCLUSIONS

The specific thermal energy of the process, obtained by the ratio between the total thermal energy (502 MJ) and the overall amount of FAMEs finally distilled (about 100 Kg) resulted 5.02 MJ Kg_{FAMEs}^{-1},: really lower than the specific heat of combustion of biodiesel (40 MJ Kg_{FAMEs}^{-1}). An aqueous stream was also coproduced during the process, that contained the aluminium salt used as catalyst and that could have a direct application in WWTP as flocculants, after a proper pH correction to basic values. All these aspects make the proposed valorization of EWC 190809 a really sustainable process, in which a waste is efficiently turned into high-quality biofuels.

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(S20) Bioregeneration of exhaust Granular Activated Carbon from the treatment of Tanker Slops

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Abstract

Petroleum products such as diesel fuels may be released into the marine or coastal environment by discharges of slops, ballast and bilge waters, dry dock activities, and tanker and non-tanker accidents. In addition to containment and recovery of spilled petroleum products, the treatment of seawater in a spilled area may be needed in order to reduce potential damages to aquatic organisms and their habitats. The standard treatment of emulsified oily wastewater is chemical de-emulsification followed by secondary clarifications and granular activated carbon (GAC) filtration. Very little work has been done on the potential bio-regeneration of GAC saturated by salty mixtures of biodegradable and non-biodegradable compounds. This research work investigated the feasibility of a process including physical, chemical and biological process to optimize the treatment while reducing the costs. Specifically this study, as a part of an Italian National Research Project (prot. 2010ARBLT7_007) entitled "*Systems Biology in the Study of Xenobiotic Effects on Marine Organisms for Evaluation of the Environmental Health Status: Biotechnological Applications for Potential Recovery Strategies*", examines the role of specialized microorganisms on the bioregeneration of GAC loaded with the mixture of compounds occurring in slops.

Keywords

bioregeneration; GAC; halophilic microorganisms; hydrocarbonoclastic bacteria;
oily salty wastewater; slops;.

INTRODUCTION

Many industrial sectors are likely to generate highly saline wastewater: these include the agro-food, petroleum and leather industries. Highly saline oily waste(water) are generated by ships mainly in engine-rooms (bilge waters) and by washing oil tanks (slops) in amounts of millions of tons annually. Many of these fluids are very stable emulsion, which make chemical treatment difficult and normal separation processes alone (gravity, flocculation, skimming) rarely effective. The standard method for treatment of emulsified oily wastewater is chemical de-emulsification followed by secondary clarification and granular activated carbon (GAC) filtration. Once a GAC column is exhausted, the GAC must be replaced and disposed of or recycled in some way (i.e., landfilling, incineration, or thermal reactivation). Replacement and disposal of exhausted GAC is quite expensive. A process of biodegradation—where one or more of the SOCs are biodegradable—could lengthen the GAC service life for some SOC mixtures. GAC bioregeneration aims to the recovery of adsorption capacity of activated carbon by the biodegradation of adsorbed organic molecules on the carbon (Rice and Robson, 1982). It has been generally accepted that bioregeneration involves desorption of the adsorbed compounds from activated carbon to bulk solution, followed by biodegradation. This in turn, induces further desorption of the compound into the bulk solution (Hutchinson and Robinson, 1990; Jonge et al., 1996).

Much research has been done on the adsorption of mixtures of SOCs and on the biodegradation and adsorption of mixtures of biodegradable SOCs. Beside very little work has been done on the biodegradation and adsorption of salty mixtures of biodegradable and nonbiodegradable SOCs. Even though biological treatment of carbonaceous, nitrogenous and phosphorous pollution has proved to be feasible at high salt concentrations, the performance obtained depends on a proper adaptation of the biomass or the use of halophilic organisms. In marine oil-polluted sites two predominant halophilic bacteria were identified (Atlas, 1995), by oligonucleotide probes and quantitative fluorescence dot-blot hybridization techniques: the aromatic hydrocarbon decomposer Cycloclasticus pugetii, estimated to make up 23-25% of the total bacteria population in sea water, and the aliphatic hydrocarbon decomposer Alcanivorax borkumensis which formed 4-7% of the bacteria population. In marine water, other investigators (Kargi, 2002; Putz et al.,2005; Yakimov et al., 2007) suggested also further bacteria: Halobacterium (extreme halophile), Marinobacter, Thallassolituus, Oleispira, Pseudomonas sp., Rhodococcus rhodochrous. This study examines the role of a specialized culture of microorganisms on bioregeneration of GAC loaded with a mixture of compounds occurring in slops wastewater.

MATERIALS AND METHODS

Water sampling and Chemical pre-treatment

Grab samples were collected from a floating tank of an oil costal deposit in the Augusta harbour (Sicily). A simple gravity separation was carried in a large (800 l) tank to provide homogenization of the sample for all the following tests and to reduce the effluent concentration of floating oil. A coagulation process was considered as a necessary pre-treatment for the adsorption phase. Best coagulation conditions, as defined through several jar tests, not reported in the paper, occurred utilizing 60 mg/l of Ferric chloride.

GAC saturation

Saturation of GAC was carried out through continuous flow column filtration. The standard experiment utilized a column of 100 cm length filled with 10 g of GAC (about 23 cm) with an empty bed contact time (EBCV) of 18 ml. In each experiment the 1-cm diameter column was packed with Filtrasorb 400 GAC (Calgon Carbon Corporation). The flow rate ranged from 7 to 8 ml/min between the different saturation experiments. Although the difficulties encountered in measuring COD in thevery high salinity waters, this parameter was utilized during the experiments as it is the fundamental parameter to compare with for the respect of the discharge limits.

Bioregeneration experiments

Microorganisms. A strain of Alcanivorax borkumensis strain SK2T (Genebank accession number Y12579; =DSM 11573T) was used in all the experiments. This bacterium grows at 28°C, in aerobic conditions and it is able to grow on many saturated petroleum fraction constituents: straight-chain and branched alkanes, isoprenoids and long side-chain alkyl compounds (e.g. alkylmonocycloalkanes, alkylbenzenes and organic alkyl-sulfuric compounds). Started cultures were prepared by inoculating one loop of microbial cells into 10 ml of ONR7a mineral medium based on the composition of seawater. Nitrogen was provided in the form of NH4Cl, and phosphate was provided in the form of Na2HPO4. After growing in a rotary shaker (New Brunswick C24KC, Edison NJ, USA; 150 rpm) at 25°C for two days, 500 μl of the seed culture broth were transferred into a 250 ml Erlenmeyer flask containing 100 ml of ONR7a medium supplemented with 1% (w/v) sterile tetradecane. The culture was incubated in a rotary shaker (New Brunswick C24KC, Edison NJ, USA; 150 rpm) at 25°C for 5 days.

Bio-regeneration apparatus. Loaded GAC was directly subjected to the recirculation of the mixture pre-emptively filtered on sand. Layout of the experimental setup is shown in Figure 1. The tank containing the bacterial inoculum were maintained, for all experimental period, at the experimental temperature of 25 ± 1°C. Aeration was maintained in continuous using an air pump system (Turbolence 2000 AirPump, Tetra). Bioregeneration was here directly quantified through the comparison of the equilibrium adsorption capacities of fresh and bio-regenerated GAC. In the case of offline systems, where pre-loaded activated carbon is consecutively biologically treated, it could appear easier to determine the extent of bioregeneration. However only very few studies, reporting quantitative measurements of bioregeneration, are described in the literature (Aktas and Cecen, 2007) and no one deals with salty wastewater.

Figure 1. Chemical pre-treatment; Saturation test; Sketch of the bioregeneration apparatus

BIOREGENERATION RESULTS

Results from the bioregeneration tests (a typical trial is reported in Figure 2) showed a good recovery of the adsorptive capacity of the biologically treated GAC. The biodegradation of hydrocarbons involves the oxidation of the substrate by oxygenase enzymes, for which molecular oxygens is required. In this process, alkanes are converted to carboxylic acids that are then biodegraded via β-oxidation, while aromatic hydrocarbon rings are hydroxylated to form diols, the rings are then cleaved with the formation of catechols which are degraded to intermediates of the tricarboxylic acid cycle (Atlas, 1995).

Two mechanisms were here considered involved in the bioregeneration of the granular activated carbon (GAC): a) the concentration gradient mechanism (Aktas and Cecen, 2007) involves organic compounds released from the activated carbon following desorption due to a concentration gradient between bulk liquid and activated carbon surface; organic compound released into the liquid phase are then degraded by microbial activities, causing a lowering of the organic compound concentration in the liquid phase; b) Extracellular enzyme reactions mechanism (Aktas and Cecen, 2007) involves exoenzymes excreted by microorganisms to diffuse into activated carbon pores and react with adsorbed substrates; Then, hydrolytic decay of the substrate may occur or desorption of the resulting enzyme metabolite may take place due to the weaker adsorbability of this metabolite. However, other investigators believe that desorption is a prerequisite for bioregeneration and nondesorbable compounds cannot be bioregenerated (Jonge et al., 1996). According to Xiaojian et al. (1991), the enzyme molecules are larger than the sizes of micropores and thus cannot access to the adsorbed substrate. They estimated that for an enzyme to actively catalyze a reaction inside a pore, the pore diameter must be at least three times greater than the enzyme size. Considering that the average molecular diameter of a monomeric enzyme (molecular weight between 13,000 and 35,000) is above

31–44A°, they concluded that the pore diameter must be larger than 10nm which exclude the micropores (+o2 nm) and some of the mesopores (+¼ 2–50 nm) of activated carbons.

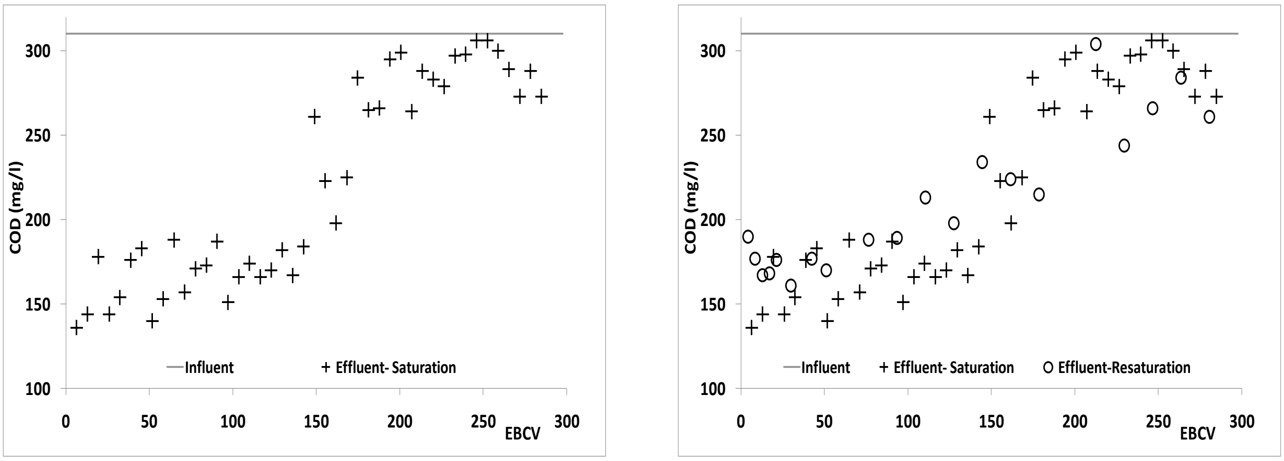

Figure 2. Comparison of the virgin and bio-regenerated GACs adsorption behaviour.

CONCLUSIONS

Tests on bioregeneration of exhaust GAC, carried out in batch units gave encouraging results in terms of COD removal from saturated GAC. Results proved the biological mixture capability of removing efficiently the organic matter adsorbed on the GAC thus increasing the service-life of the GAC without removing GAC from the filter (with consequently reduced management costs). Although biological treatment is usually inhibited by high salt concentrations, results from the present research proved the feasibility of using salt-adapted micro-organisms consortia capable of degrading the main pollutants contained in these oily and salty contaminated waters.

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Efficient Technologies - Non-conventional and emerging contaminants

(Tuesday, 24 June 2014, Aula T3, Polo Zanotto)

(K5) Removal of pollutants from WWTP with plants: options and enzymatic background of phytoremediation of Diclofenac

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Abstract

Pharmaceuticals are a new class of micropollutants posing serious threats to our aquatic environment, and to our water resources. Although modern technologies in waste water treatment (e.g. MBR) have proven elimination of organic pollutants, older WWTPs are still not capable to remove pharmaca completely. Constructed wetlands might represent rather cost and labor saving alternative. In order to test phytoremediation as a tool for the removal of the intensively used NSAID drug Diclofenac which causes massive problems due to its poor elimination in WWTPs, we studied its possible fate in plants. Diclofenac is taken up and undergoes rapid metabolism; already after 3h of exposure the drug and its metabolites could be detected in plant tissues. The drug is activated to a 4'OH-diclofenac and conjugated subsequently in phase II to a glucopyranoside, a typical plant specific metabolite. To our knowledge this is the first time these two painkiller metabolites are shown to occur in plant tissues.

Keywords

Introduction

It has been outlined during recent years that pharmaceuticals and personal care products are constantly accumulating in our environment (Daughton and Ternes 1999, Heberer 2002). A huge number of drugs is used worldwide in human and veterinary medicine and is excreted either unaltered or chemically modified. Pathways for these compounds into the environment are manifold. Manure or sewage sludge contaminated with pharmaceuticals may be introduced into agricultural soils as fertilizers (Boxall et al. 2006), but the biggest sources are effluents of wastewater treatment plants. In many treatment systems, the elimination of a large number of compounds is not sufficient because many pharmaceuticals have very limited sorption properties and tend to pass through wastewater treatment plants which are not optimized for the removal of personal care products, pharmaceutically active compounds and other organic contaminants.

Hence considerable amounts of pharmaceuticals directly enter our surface waters via their effluents. Although concentrations in ground water are still low and a direct toxicological risk for consumers of drinking water has not been identified so far, the contamination of ground and drinking water has to be avoided with view to future generations and their water requirements.

Advanced technologies in waste water treatment like membrane bioreactors (MBR) that integrate biological degradation of organic matter with membrane filtration have proven their more complete elimination of organic pollutants. Pérez and Barceló (2008) could show an elimination of 56 % of the human metabolite 4'OH-Diclofenac in a laboratory scale MBR compared to an elimination of 26% achieved with traditional methods. However compared to biological wastewater treatment facilities e.g. in constructed wetlands MBR represents a rather cost and labor intensive technology.

Diclofenac is one of the most commonly used non-steroidal anti-inflammatory drugs (NSAID) with high economic success in numerous countries of the world. Its removal rate during wastewater treatment processes is low, and it is one of the compounds found most frequently in STP effluents and surface waters with concentrations ranging from ng/l to µg/l.

Only few investigations are available reporting adverse effects of Diclofenac to aquatic organisms. Hong et al. (2007) reported toxic effects on fish (*Oryzias latipes*) under environmentally relevant concentrations of Diclofenac (1 µg/l). Triebskorn et al. (2004) studied the effects of Diclofenac on rainbow trout (*Oncorhynchus mykiss*) on the subcellular level in different trout organs. Based on their results they conclude harmful influence of the drug on renal and gill functionality – even under environmentally relevant exposure situations. The critical impact of Diclofenac on the environment became evident, when the dramatic dieback of the Indian vulture population could be linked to the exposure towards the compound because of visceral gout after consumption of lifestock carcasses.

Data on effects of Diclofenac in plants is even more scarce. Only for few pharmaceuticals uptake and metabolism of the drug into plant cells have been suggested.

After therapeutic use in humans, only 15 % of the Diclofenac is excreted unchanged, but most of the drug undergoes modifications and conjugation reactions. The initial activation reaction in mammals is a hydroxylation at one of the two phenyl rings that is catalysed by P450 monooxygenases. The two most common metabolites are the 3´ and the 4´OH-Diclofenac as well as a double hydroxylated form at 4´and 5´position. Phase two metabolism occurs via glucuronisation at the carboxylic acid group of the molecule. Sulphate and glutathione conjugates occur only in minor quantities. Microbial metabolism on Phase II conjugates within the wastewater treatment process may cause a cleavage of the parent compound and its conjugated biomolecule that could cause a re-release of the biologically active drug.

In plants and animals the metabolism of xenobiotics is similar. Briefly it can be divided into three phases. An initial activation reaction is followed by a conjugation reaction with smaller biomolecules (e.g. glutathione, glucose, amino acids). These hydrophilic and mobile metabolites undergo phase three: storage in the plant vacuole, cleavage or the formation of bound residues.

Aim of the study

The present study aimed at evaluating the uptake of Diclofenac into plants and its metabolism. This was followed using Hordeum *vulgare* (barley), *Brassica juncea* (Indian mustard) and a hairy root cell culture of *Armoracia rusticana* (horseradish) as model species. HPLC-UV/VIS and LC-MS/MS-Analysis was carried out to identify and quantify plant derived metabolites. Specific activities of antioxidative enzymes were determined to evaluate plant stress.

Materials and Methods

A hairy root culture of horseradish (*A. rusticana* L.) transformed by *Agrobacterium rhizogenes* strain A4 was grown in Erlenmeyer flasks in 100 ml full-strength MS medium containing thiamine and inositol for 10 days. Barley and Mustard seeds were surface sterilized with sodium hypochlorite according Götz et al. 2007 before germination on Petri dishes for 3 days. Seedlings were transferred into 2 L plastic containers and grown for 7 days under greenhouse conditions with a light period of 12 hours at 20 °C at daytime and 16 °C during the night. Diclofenac dissolved in methanol was set to a final concentration of 10 µM. After 3 hours root cells were rinsed with deionized and tap water and transferred into drug free growth medium. Samples were taken at 0, 24, 72, and 168 hours after incubation. Plant material was immediately frozen in liquid nitrogen, and stored at −80 °C.

Diclofenac extraction and sample preparation

One half gram of frozen plant material was finely ground under liquid nitrogen and extracted with 1 ml of 0.1 M HCl/Acetonitril (50/50; v/v) and vortexed for 1 minute prior to centrifugation (18,000 x g at 4 °C. 5-(p-Methylphenyl)-5-phenylhydantoin was added to 0.5 ml of the supernatant as internal standard at 10 mg/l in a final sample volume of 200 µl. Phenomonex Strata-X SPE columns (300 mg) were rinsed with methanol and preconditioned with water. 0.5 ml of was loaded to the column. For LC-MS analysis the eluate was dried and dissolved in 200 µl of 0.1 formic acid (v/v).

Analysis

LC–MS analysis was carried out with a HPLC system (Varian ProStar 210) was coupled to an ion trap mass spectrometer (Varian 500MS). HPLC conditions have been described (Huber et al. 2012).

Enzyme preparation and assay conditions

A soluble protein fraction containing glucosyltransferase activity was prepared according to Huber et al. (2012). Proteins were centrifuged after each step and the pellet finally resuspended in 200 mM Tris pH 7.3; 1mM DTE; 2 mM MgCl2. GT-activity for Diclofenac and 4`OH-Diclofenac was assayed in a reaction mixture containing the aglycone (1 mM), 2 mM Uridine diphosphate glucose, 1.25 mM 4-nitrophenyl-β-D-glucopyranoside, 1.25 mM salicin. Reactions were initiated by adding the GT enzyme preparation. Samples were centrifuged for 10 min at 10,000 x g and supernatants were applied to LC-MS analysis.

Cytochrome P450 activity was determined after extraction of microsomes and following the formation of 4´OH-Diclofenac in an in situ assay containing 20 mM sodium phosphate buffer pH 7.4, 20 % glycerol; 0.1 mM NADPH; 3 mM glucose-6-phosphate; 0.4 U glucose-6-phosphate dehydrogenase and 200 µM Diclofenac. Reactions were initiated by adding a microsomal fraction. The formation of hydroxylated Diclofenac was followed as described above.

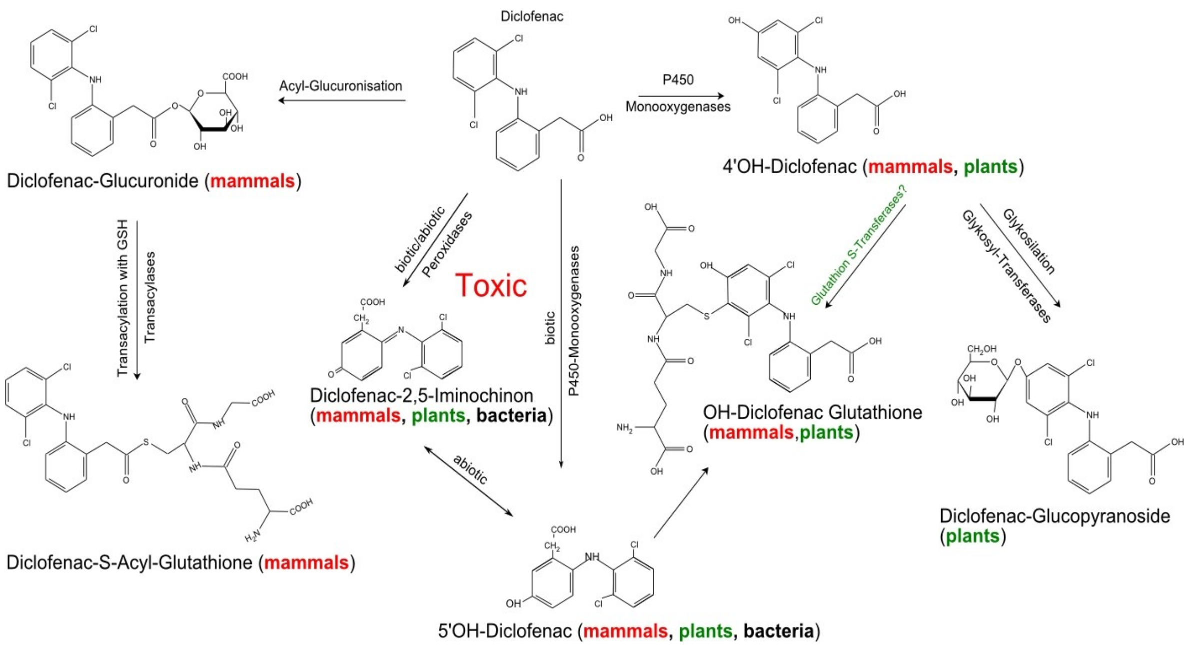
Results and discussion

A first insight in the metabolic pathway of the drug over time was gained when root cells of *A. rusticana* were exposed to 10 µM of Diclofenac for three hours and then transferred into Diclofenac free medium for another seven days. Already after three hours, both, Diclofenac and the hydroxylated metabolite were detectable in the cells at highest levels. Over time both compounds declined within 168 hours (1 week) to less than 20 percent of their initial concentration.

Along the lines for the mammalian system, the formation of the same primary metabolite, hydroxylated at 4´-position could be confirmed in other plant tissues. 4´OH-Diclofenac could be extracted after exposition to Diclofenac at different times. In addition, its formation was recorded in situ by incubating a plant microsomal fraction with Diclofenac in the presence of a NADPH generating system. For Diclofenac and its metabolites, the following mass transitions were detected by MS/MS measurements: 267→196 (5-(p-Methylphenyl)-5-phenylhydantoin, internal standard), 296→250 (Diclofenac), 312→294 (4´OH-Diclofenac), and 474→312 (glucosyl conjugate).

In mammals conjugation with glucuronic acid occurs at the carboxylic group of the Diclofenac resulting in a Diclofenac acyl glucuronide. Glucuronisation does not occur in most plants whereas a glucosidation is described for both – animals and plants. In plants, glucosyltransferases catalyze the conjugation of one molecule glucose with one molecule of hydroxylated Diclofenac. As for the phase I metabolite, this could be confirmed either by extracting the in vivo formed metabolite from different plant tissues or by showing the in situ formation in a glycosyltransferase assay. Indirect proof for the glycosidic nature of the metabolite was delivered in incubation experiments with β-D-Glucosidase. Diclofenac itself was not accepted as a substrate for the conjugation reaction with glucose (data not shown), again in line with the work of Tang and Ma (2005) that showed the same effect in human liver microsomes.

Conjugation with glucose might occur either with the hydroxyl group or the carboxyl groups of the Diclofenac molecule forming an ester or ether bond respectively. Based on the available data and instrumentation, it was not possible to identify the glucosidation site at the Diclofenac molecule. We suggest the formation of an ether glucoside with the glucose bound to the introduced hydroxyl group. The second possible phase II metabolite with the sugar attached via the Diclofenac´s carboxylic group was never observed during our experiments. Fig 1 depicts the metabolism in animals and plants.



In terms of phytoremediation and the treatment of contaminated waste water with plants, the formation of a glucose conjugate might play an interesting role, as glucosides are known to act as precursors to insoluble, bound residues, leaving the xenobiotic compound in a stable and indigestible form bound to the lignin fraction of the cell wall. Further studies are required to investigate inter- and intracellular transport of the conjugates and to elucidate the potential to really incorporate the drug and its sugar conjugates into cell walls. With the present set of data available it is justified to propose the use of plants in wastewater treatment for a more efficient reduction of the effluent load with unwanted pharmaceutical residues to provide a healthier environment.

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(P23) Heterotrophic vs. autotrophic bacteria in the biotransformation and mineralization of pharmaceuticals in activated sludge

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Abstract

The role of nitrifying and heterotrophic bacteria in the biodegradation of pharmaceuticals in activated sludge reactors of wastewater treatment plants (WWTPs) is still unclear. In this work, selective feeding of heterotrophic and nitrifying bacteria, with sodium acetate and ammonium chloride respectively, was performed after spiking 10 pharmaceuticals in 2 types of activated sludge: one with sludge retention times (SRT) of 9 d (mainly heterotrophic) and the other with SRT of 35 d (highly nitrifying). Biodegradation under endogenous respiration was also tested for both types of biomass. The sludge samples were collected from a WWTP with separate oxygen transfer basins for organic matter and nitrogen removal. The heterotrophic sludge biodegraded acetaminophen and caffeine at rates higher than 400 μg/g VSS·d, regardless of whether the heterotrophs and nitrifiers were fed or under endogenous respiration. Results suggest that acetaminophen and caffeine could not only be degraded by cometabolism, but are also used as growth substrate. The nitrifying sludge was not only able to biodegrade these compounds, but also iopromide under any feeding conditions. Sulfamethoxazole was only transformed at a significant rate by active heterotrophs in the nitrifying sludge, probably due to cometabolism of slow growing bacteria that are able to thrive at long SRT. Naproxen showed a similar behaviour with sulfamethoxazole. Ibuprofen was also more rapidly biotransformed in the sludge with the longer SRT. Trimethoprim, erythromycin, diclofenac and carbamazepine were recalcitrant in both activated sludges, regardless of the feeding conditions applied. In the case of iopromide, the parent compound disappeared completely after 24 h in the activated sludge developed at the long SRT and several metabolites were successfully semi-quantified, but biotransformation was only partial with no mineralization, based on experiments using ^{14}C-iopromide. In general, slow-growing heterotrophic bacteria are more effective than nitrifiers for the biotransformation of pharmaceuticals.

Keywords
Activated sludge; biodegradation; micropollutants; mineralization; pharmaceuticals.

INTRODUCTION

Pharmaceuticals are continuously released into the environment through wastewater treatment plants (WWTPs) effluents with hazardous effects such as the spread of antibiotic-resistance bacteria or endocrine disruption of fish in receiving water bodies. Activated sludge reactors have shown to remove many pharmaceuticals, but most of them only partially while others are recalcitrant. Although tertiary treatments like activated carbon filtration or ozonation have proved to be highly effective, improving removal in activated sludge could be a more affordable mean of depleting in wastewater. However, the underlying mechanisms behind the biodegradation of pharmaceuticals in such complex mixed cultures are still unknown. Prediction of the concentrations in effluents from activated sludge has relied on sorption coefficients and biodegradation kinetic constants with only few studies focused on the influence of operational conditions and the type of biomass over these parameters (Kreuzinger et al., 2004; Khunjar et al., 2011). Thus, in order to clarify the influence of the type of bacteria, in this work, selective feeding of heterotrophs and nitrifiers was performed after spiking 10 pharmaceuticals in 2 types of activated sludge: one with sludge retention times (SRT) of 9 d (mainly heterotrophic) and the other with SRT of 35 d (highly nitrifying), collected from a WWTP with separate oxygen transfer stages for organic matter and nitrogen removal.

On top of this, mineralization was also studied for one of the pharmaceuticals by employing ^{14}C-iopromide radiolabelled in the inner iodinated benzene ring. The production of ^{14}C-radioactive carbon dioxide was monitored to test the ability of bacteria in the activated sludge to achieve a complete biotransformation of this recalcitrant X-ray contrast media.

MATERIALS AND METHODS

Experimental setup

The activated sludge for the batch experiments was collected from Amherst WWTP (NY, USA), where organic matter is removed in a 1st stage operating at a SRT of 9 d, thus promoting growth of heterotrophic bacteria, while nitrogen removal takes place in a 2nd stage with a SRT of 35 d, leading to the growth of a highly nitrifying activated sludge.

Several batch experiments were performed with both types of activated sludge, with an initial spike of 1 mg/L of iopromide (IOP), acetaminophen (ACM), caffeine (CAF), trimethoprim (TMP), sulfamethoxazole (SMX), erythromycin (ERY), diclofenac (DCF), naproxen (NPX), ibuprofen (IBP) and carbamazepine (CBZ). Two feeding strategies were followed: heterotrophs were fed with sodium acetate as an organic readily biodegradable substrate while nitrifiers were fed with ammonium chloride and sodium bicarbonate. Endogenous respiration was also tested.

Besides, mineralization of IOP was assessed. After spiking 1 mg/L of radioactive ^{14}C-IOP (with a total radioactivity of 3 μCi) in a 100 mL of activated sludge, two alkaline traps with 1 M sodium hydroxide connected in series were used to collect the carbon dioxide from the off-gas and the radioactivity was measured by liquid scintillation counting (LSC) both in the mixed liquor and the alkaline traps after 7 d.

Analytical techniques

Samples were collected and filtered through 0.45 μm polypropylene filters. The concentrations of the 10 selected pharmaceuticals were determined using isotope dilution mass spectrometry. An Agilent 1100 liquid chromatography (LC) system coupled to an Agilent 6410 Triple Quad mass spectrometer (MS) with electrospray ionization (ESI) source, was used in all analysis. Detection was performed under positive mode multiple reaction monitoring (MRM) to ensure high ionization efficiency and low background. Metabolites were also determined considering bibliographic parent and daughter ion transitions for the selected pharmaceuticals.

Conventional parameters of wastewater treatment were also determined: pH, dissolved oxygen (DO), ammonia nitrogen, nitrite, nitrate, total organic carbon (TOC), volatile and total suspended solids (VSS and TSS). Heterotrophic and nitrifying activities were determined by following the decrease rate of DO concentration after spiking the activated sludge with 200 mg COD/L equivalent of sodium acetate and 20 mg $N\text{-}NH_4^+$/L of ammonium chloride, respectively.

RESULTS AND DISCUSSION

The heterotrophic sludge showed an average activity of 0.73 g COD/g VSS·d while nitrifying activity was despicable at 0.01 g N/g VSS·d. High biotransformation rates of ACM and CAF (>400 μg/g VSS·d) were obtained, while lower rates were observed for IBP, NPX and IOP (30-120 μg/g VSS·d). No biotransformation was observed for the other pharmaceuticals: CBZ, DCF, ERY, SMX and TMP. Also, very little effect of the different feeding conditions applied was observed (Table 1).

Table 1. Biodegradation rates of the 10 selected pharmaceuticals under the different feeding conditions tested (no feeding for endogenous respiration, acetate for heterotrophs and ammonium/bicarbonate for nitrifiers) for the 2 types of activated sludge from Amherst WWTP: 1st stage heterotrophic (SRT of 9 d) and 2nd stage nitrifying (SRT of 35 d).

		Biodegradation rate (ug/g VSS·d)									
	Feeding	IOP	ACM	CAF	TMP	SMX	ERY	DCF	NPX	IBP	CBZ
1st stage	-	79	5,035	761	0	12	0	0	63	114	0
	Acetate	59	4,098	429	0	31	0	0	37	93	0
	Ammonium/ Bicarbonate	57	4,806	736	0	31	0	0	57	112	0
2nd stage	-	3,378	893	868	0	0	65	0	143	374	0
	Acetate	3,136	2,850	1,122	0	1,348	38	0	526	3,718	0
	Ammonium/ Bicarbonate	1,958	2,127	612	0	0	33	0	716	2,992	0

The activated sludge from the 2nd stage, operated at a longer SRT of 35 d, showed a nitrifying activity of 0.12 g N/g VSS·d, while the heterotrophic activity was considerably lower (0.15 g COD/ g VSS·d) than in the 1st stage. ACM, CAF, IBP, NPX and specially SMX were biodegraded at the fastest rate when heterotrophs were fed with acetate, suggesting that slow-growing heterotrophs are responsible for their cometabolic biotransformation. Nitrifiers, when fed with ammonium and bicarbonate, were also able to cometabolize IBP, NPX and ACM. The significant high removal rates observed under endogenous respiration for IOP, ACM and CAF suggest that these compounds might be used as growth substrate by some type of bacteria developed in the activated sludge. In the case of CAF, paraxanthine and theobromine were determined as the main metabolites, which were subsequently biotransformed as well. Complete mineralization of some of these compounds might be possible as bacterial strains capable of growing exclusively on ACM and CAF have already been isolated (Summers et al., 2012; Zhang et al., 2013).

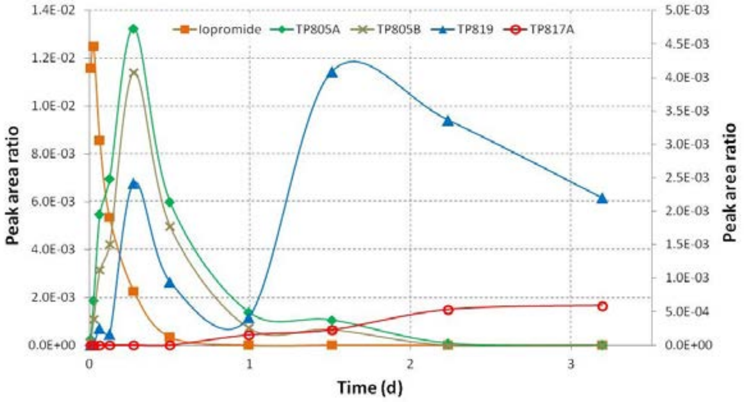

Figure 1. Relative areas of IOP (left axis) and their metabolites M805A, M805B, M819 and M817A (right axis) to the internal standard (d^{10}-CBZ) in the activated sludge from the 2nd stage.

Concerning IOP, no mineralization was observed as the radioactivity measured in the alkaline traps, where the carbon dioxide was collected from the off-gas of the bioreactor, was at background levels. The radioactivity remained in the liquid phase of the activated sludge. The ^{14}C-IOP was only radiolabelled in the inner iodinated benzene ring, proving that biotransformation occurred only in the side chains. Several metabolites were found: oxidation of the primary alcohols led to the formation of carboxylic acid groups in the phase I metabolites M805A, M805B and M819 (Perez et al., 2006). Further oxidation of M819 in the tertiary amine chain formed the phase II metabolite M817A (Kormos et al., 2011), which started to build up in the mixed liquor once M819 peaked (Fig. 1). Batt et al. (2006) remarked the influence of nitrifiers in the high removal efficiency of 97% obtained in a batch experiment with the same nitrifying activated sludge from the 2nd stage of the same WWTP. However, the lower biodegradation rates obtained when the nitrifiers were activated by feeding ammonium suggest that slow-growing heterotrophic bacteria, also favoured under long SRT, might be the key players in the biotransformation of IOP.

CONCLUSIONS

Slow-growing heterotrophic bacteria developed at long SRT seem to play a major role in the biotransformation of IOP, ACM, SMX, NPX and IBP. Biodegradation rates under endogenous respiration, in the absence of primary substrates for bacterial growth, are very high for IOP, ACM and CAF, suggesting that some type of bacteria might be able to use them as growth substrate. Cometabolism by heterotrophs is the most likely biodegradation mechanism for NPX, IBP and especially SMX, as their removal rates highly increased when acetate was fed as easily biodegradable growth substrate for heterotrophs. Nitrifiers seem only capable of cometabolizing ACM, IBP and NPX. In the case of IOP, while its biotransformation is fast, no mineralization was observed, based in the experiment with radiolabelled ^{14}C-IOP.

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(P24) Removal of micropollutants in a nitritation/anammox process

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Abstract

Pharmaceutical and personal care products (PPCPs) are extensively used and are thus, present in the aquatic environment, including surface, ground water, municipal and industrial effluents. Significant research work is available on the removal of PPCPs in conventional wastewater treatment plants and on some advanced biological processes, such as membrane bioreactors, but there are limited applications of the anammox process for their removal. In the present study, the occurrence and fate of 19 selected PPCPs was determined in an ELAN®reactor, in which ammonia oxidation and anammox processes were simultaneously carried out in a single-stage under limiting oxygen conditions. The removal mechanisms and the influence of the anammox activity on PPCPs removal was evaluated. The ELAN® process achieved high removal (>80%) for the studied estrogens, naproxen, ibuprofen, bisphenol A and celestolide, while it was not effective for the removal of carbamazepine (<7%), diazepam (<7%) and fluoxetine (< 30%). Biodegradation was the dominant removal mechanism, while sorption contributed to some extents to the removal of musk fragrances, fluoxetine and triclosan. The sorption was strongly dependent on the particle size, with the smaller floc size facilitating the actual sorption of the target compounds. The operation time enhanced the intramolecular diffusion of the PPCPs in the sludge granules, resulting in the increase of their concentration in the solid phase. The removal of ERY was strongly correlated to the anammox activity.

Keywords

PPCPs; biodegradation; sorption; nitritation/anammox; particle size; biomass activity

INTRODUCTION

The detection of pharmaceutical and personal care products (PPCPs) in the aquatic environment (surface water and groundwater) and in wastewater effluents is an emerging issue due to the lack of information on the potential impacts associated with their occurrence, fate and ecotoxicological effects (Ellis et al, 2006; Loos et al., 2010). Their removal in wastewater treatment plants (WWTPs) depends on the biological treatment process that is applied (Carballa et al., 2004). Several research works compare the efficiencies of biological processes for the elimination of selected pharmaceuticals, often focusing on the conventional activated sludge process (CAS) or on membrane bioreactors (MBRs) (Reif et al, 2011). However, there is no literature available on the fate and the removal of PPCPs in the autotrophic nitrogen removal over nitrite process. Several parameters can affect PPCPs removal (transport and transformation) in activated sludge processes, such as the hydraulic retention time (HRT), the solids retention time (SRT), pH, redox conditions and temperature (Banzhaf et al., 2012; Fernandez-Fontaina et al., 2012), which could explain the disparity of PPCPs removal efficiencies that are reported in literature even for similar technologies. The ELAN® ("ELiminación Autótrofa de Nitrógeno", in Spanish: autotrophic nitrogen removal) process, developed by Aqualia with the know-how of the University of Santiago de Compostela, where nitritation/anammox are carried out in a single reactor, was studied for the removal of 19 PPCPs. ELAN® is suitable process to treat wastewater characterized by a low COD/N ratio, having less oxygen requirements than the conventional process and without any external carbon source requirements.

The objective of this work was to assess the effect of important parameters, such as HRT, sludge particle size and nitrifying activity on the removal mechanisms of 19 selected PPCPs in an ELAN$^{®}$ process treating the anaerobic supernatant from digested sewage sludge. The combined effect of degradation, sorption and volatilization in the removal of the PPCPs was evaluated.

MATERIALS AND METHODS

The removal of 19 PPCPs was studied in an ELAN$^{®}$ (Vazquez-Padin, et al, 2013) pilot plant (200 L) treating the supernatant of the anaerobic sludge digester of the Lagares WWTP in Vigo (NW of Spain). The sequencing batch reactor (SBR) was operated in cycles of 3 hours with a volumetric exchange of 25%. The reactor was operated at 29 ºC and volatile suspended solids (VSS) concentration of 7-9 g_{VSS}/L. The oxygen concentration was maintained above 0.6-1.2 mg/L, in order to have a microaeration in the surface of the granule and anoxic conditions inside the granule. The influent ammonium concentration varied from 700-1000 mgN/Ld. Nine sampling campaigns were carried out in six months to determine the dissolved and sorbed PPCPs concentrations by GC/MS and LC/MS/MS. The selected compounds were 3 musk fragrances (galaxolide HHCB, tonalide AHTN and celestolide ADBI), 4 antibiotics (sulfamethoxazol SMX, trimethropim TMP, erythromycin ERY and roxithromycin ROX), 4 hormones (estradiol E2, estrone E1 and ethynilestradiol EE2), 4 antiphlogistics (ibuprofen IBP, naproxen NPX, diclofenac DCF), 2 antidepressant (fluoxetine FLX, citalopram CTL), an antiepileptic (carbamazepine CBZ), a tranquilizer (diazepam DZP), an antibacterial and antifungal agent (triclosan TCS) and a synthetic compound to produce plastics and epoxy resins (bisphenol A BSF). PPCPs were spiked in concentrations between 0.1 and 20 μg/L.

RESULTS AND DISCUSSION

Occurrence, fate and removal of PPCPs in ELAN$^{®}$ process

PPCPs were readily removed in the ELAN$^{®}$ process, except FLX, DCF, CBZ and DZP, which displayed a recalcitrant behaviour (Table 1) and are characterized by low solid-liquid coefficient (K_d) and biodegradation constant (k_{biol}), that explains their low removal by this process (Table 2). In the case of IBP, estrogens and BSF, the removal efficiency was higher than 90%. In agreement with these results, the anammox process was found to be beneficial for the removal of IBP from black water in an upflow anaerobic sludge blanket (UASB) – partial nitritation (PN) – anammox system, contributing by 77% in the substance removal (Graaff et al., 2011). In the present study, the main removal mechanism was biodegradation. Sorption onto the sludge was negligible, except in the case of musk fragrances and TCS, as these substances have a lipophilic character (Table 1 and 2). The biodegradation was similar to pure nitrifying reactors (Suarez et al, 2010; Fernandez-Fontaina et al, 2012). In the case of SMX, a higher removal was obtained in the ELAN$^{®}$ compared to the nitrifying reactors. SMX is strongly dependent on the reduction potential (Banzhaf et al, 2012) and its removal is higher under anoxic conditions than under aerobic conditions (Hai et al., 2011). The examined process exhibited moderate performance for the removal of most of the examined antibiotics (ERY, ROX, TMP). Volatilization was negligible for the vast majority of the target pharmaceuticals, except ADBI.

Table 1. PPCPs removal efficiencies in ELAN$^{®}$ process (Anammox activity: 700-1000 mg N/d)

	ADBI	HHCB	AHTN	CBZ	DZP	IBP	NPX	DCF	FLX
Influent (μg/L)	15.1	7.9	19.2	17.3	19.0	18.9	8.8	16.8	3.1
Effluent (μg/L)	2.25	1.7	4.2	16.3	18.3	0.4	1.5	10.3	2.2
Sorption (%)	5	9	15	1	0	0	0	0	4
Volatilization (%)	13	0	0	0	0	0	0	0	0
Biodegradation (%)	65	67	55	6	6	98	80	36	26
Total removal (%)	82±2	76±5	70±11	7±1	6±1	98±1	80±1	36±1	29±1

	ROX	SMX	TMP	E2	E1	EE2	BSF	TCS	CTL	ERY
Influent (μg/L)	6.1	0.3	7.1	0.5	1	0.8	14.6	7.1	0.1	3.3
Effluent (μg/L)	3.0	0.2	4.1	0.0	0.0	0.1	0.7	2.0	0.0	0.8
Sorption (%)	1	0	0	0	0	0	0	13	0	1
Volatilization (%)	0	0	0	0	0	0	0	0	0	0
Biodegradation (%)	50	57	44	98	100	87	96	62	67	74
Total removal (%)	50±1	57±2	45±1	98±1	100±1	87±1	96±1	75±13	67±1	75±1

E2 and DCF concentrations in the treated effluent (Table 1) are lower that the surface water limits specified within the Decision 2455/2001/EC. In the case of EE2 the concentrations are higher than the specified surface water limits. In the case of inland surface water the treated effluent concentration is only 2.9 times higher than the limit and with the dilution factor could reach lower than the limit with the surface waters. However, in the case of other surface waters, the treated effluent concentration is 14.3 times higher than the limit and could be a problem. To conclude, advanced physical and chemical post-treatment must be coupled with the ELAN® process in order to further eliminate persistent PPCPs, which are not susceptible to biodegradation.

Table 2. PPCPs biological constants (k_{biol}, L/g_{VSS}d) and sorption coefficients (Kd, L/kg_{TSS})

	ROX	ADBI	HHCB	AHTN	IBP	NPX	DCF	FLX	SMX
k_{biol}	0.3	1.3	0.8	0.5	38	0.9	16.8	0.1	0.3
Kd	130	4020	6070	9500	ND	ND	ND	870	60

	TMP	E2	E1	EE2	BSF	TCS
k_{biol}	0.2	27.0	53.5	2.0	33.0	0.7
Kd	70	ND	ND	310	620	10090

Biotransformation

During the process, a high variability in the PPCP removal was observed, as well as in the nitrogen removal. IBP, BSF and TCS were strongly dependent on the nitrification activity (Figure 1).Higher nitritation activities due to the enhanced production of ammonium monooxygenase enzyme are mainly responsible for the cometabolic degradation of several PPCPs, such as HHCB, IBP, AHTN, NPX, ERY, TMP, ROX and FLX (Fernandez-Fontaina et al., 2012). A correlation between the nitrifying biomass activity and PPCPs biodegradation was found for these compounds (Figure 2b) and agrees with previous findings of Fernandez-Fontaina et al. (2012) for IBP. In the case of IBP, the high removal efficiency can be related with the anammox activity (Graaff et al., 2011). In a previous work performed in an upflow anaerobic sludge blanket (UASB) – partial nitritation (PN) – anammox system, the two last autotrophic stages contributed by 93% in the substance removal, while the anaerobic step adversely affected the removal (de Graaff et al., 2011).

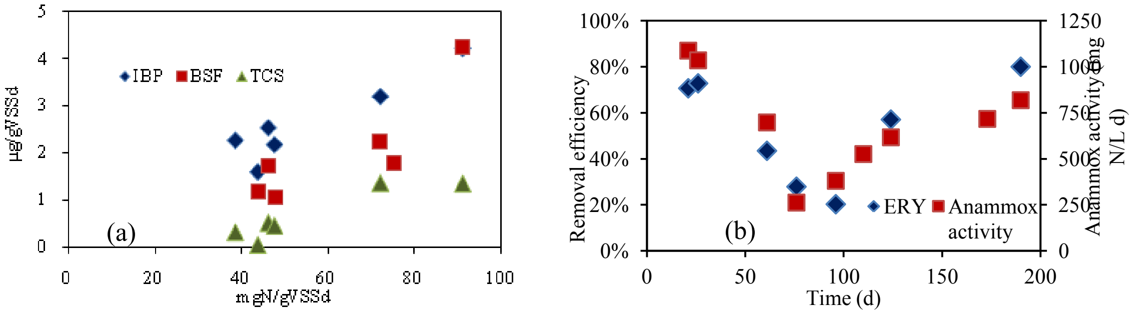

Figure 1. a) Influence of the nitrification activity on IBP, BSF and TCS removal efficiencies, b) Influence of the anammox activity in ERY removal efficiency

Sorption

Musk fragrances and triclosan are lipophilic compounds, and are thus characterized by high sorption coefficients. In fact, the contribution of sorption to their removal ranged 5-15% (Table 1). The concentration of musk fragrances in the solid phase was influenced by the contact time and the size of the granules. The sorption coefficient was continuously increasing with time (Figure 2). PPCPs need to penetrate the granule to be sorbed inside; thus a fast sorption onto the surface was followed by an intramolecular diffusion (Shi et al., 2011). After two months of operation, an increase of the particle size (from 2.9 mm to 4.5 mm) was observed, as well as a decrease in the musk fragrances concentration in the sludge (Figure 2) due to the decrease in the specific surface of the granule,. After four months, the opposite effect was observed and the concentration in the solid phase increased, since the particle size was reduced from 4.5 to 2.3 mm. The effect of the particle size was previously reported by Reif et al. (2011) who found higher AHTN concentration on the sludge in the MBR than in CAS process due to the lower sludge particle size in the MBR.

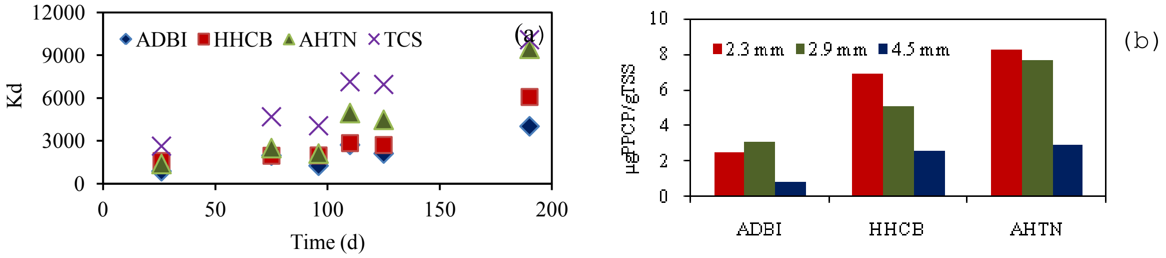

Figure 2. (a) Kd values during ELAN® operation, (b) Influence of particle size in the concentration in the solid phase

CONCLUSIONS

The ELAN® process was found to remove estrogens, NPX, IBP, BSF and ADBI by more than 80%. On the contrary, the process was not effective for the removal of CBZ (<7%), DZP (<7%) and FLX (< 30%). Biodegradation was by far the most important removal (i.e. transformation) mechanism. Sorption contributed at some extent to the removal of ADBI, HHCB, AHTN, FLX and TCS and volatilization only to the removal of ADBI. Sorption efficiency of lipophilic compounds was dependent on the biomass particle size and the solid-liquid contact time. IBP, estrogens and BSF were highly biodegradable by the ELAN® biomass. The values were similar to an activated sludge process with nitrifying biomass. The increase of nitritation capacity favoured the removal of IBP, BSF and TCS. The removal of ERY correlated well with the anammox activity.

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(P25) Removal of micropollutants from secondary effluents through biological filtration/adsorption systems

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Abstract

In this work, the removal mechanisms of 18 pharmaceuticals and personal care products (PPCPs), including endocrine disrupting compounds (EDCs), during post-treatment of secondary effluents in biological filtration/adsorption systems was assessed. The influence of empty bed contact time (EBCT), ranging from 0.2 to 3.2 d, and type of secondary effluent (anaerobic and aerobic) was evaluated. Two filters (one packed with sand and the other with granular activated carbon (AC) as filtering media) and two biofilters (with the same packing materials and inoculated with activated sludge) were tested. According to the results obtained, micropollutants were classified in three different categories depending on the behaviour experimented: I) biodegradation and high adsorption onto AC and sand, II) biodegradation, high adsorption onto AC but low or null adsorption onto sand, and, III) only adsorption onto AC. EBCT did not affect the removal efficiencies in the range tested. Most of the organic micropollutants studied (around 65%) presented null adsorption onto sand whereas all compounds showed adsorption onto AC. Therefore, biodegradation is crucial for the elimination of biodegradable compounds in the sand biofilters, obtaining similar removal efficiencies as in the AC reactors.

Keywords
Biofiltration; EBCT; granular activated carbon; organic micropollutants; sand filtration

INTRODUCTION

Organic micropollutants are synthetic or natural trace contaminants present in wastewaters at low ($\mu g\ L^{-1}$) to very low concentrations ($ng\ L^{-1}$). Within this large group of substances, pharmaceutical and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) have seen increased scientific interest in recent years. Since they have not been considered during the design of wastewater treatment plants (WWTPs), removal of organic micropollutants during the conventional wastewater treatment is only partial, thus being discharged into receiving water bodies (Joss et al., 2008). Although conclusive information does not exist about the toxicology impact of these pollutants in nature, different works have demonstrated the effects of PPCPs on the environment (Roig, 2010). As a consequence, in July 2013, the European Commission approved the monitoring of three pharmaceutical compounds (17α-ethinylestradiol, 17β-estradiol and diclofenac) in surface waters before taking a final decision on their inclusion in the list of priority substances. In order to improve the quality of the effluents discharged and to reduce their potential environmental impact, post-treatment systems are recommended. Most studies are focused on advanced oxidation process and only recently, some authors have evaluated the efficiency of sand filters and biological activated carbon filters to remove PPCPs from treated wastewater (Hernández-Leal et al., 2011; Reungoat et al., 2011). However, no much attention has been paid to the removal mechanisms responsible for PPCPs elimination in such systems. Hence, the main aim of this work was to evaluate the removal of selected PPCPs during the post-treatment of secondary effluents by means of biological filtration/adsorption systems. Moreover, the main mechanisms responsible for their elimination and the influence of the type of secondary effluent and empty bed contact time (EBCT) were investigated.

MATERIALS AND METHODS

Organic micropollutants

Three antiphlogistics (ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF)), four antibiotics (erythromycin (ERY), roxithromycin (ROX), sulfamethoxazole (SMX) and trimethoprim (TMP)), an antidepressant (fluoxetine (FLX)), an antiepileptic (carbamazepine (CBZ)), a tranquillizer (diazepam (DZP)), three musk fragrances (galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI)) and five EDCs (estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), bisphenol A (BPA) and triclosan (TCS)), were selected in this work. These substances were spiked into the reactor feedings at concentrations ranging between 1 and 40 µg L^{-1}.

Secondary effluent characteristics

Two types of secondary effluent were tested: effluent from anaerobic treatment of sewage (experiment 1) and effluent from conventional activated sludge treatment (experiment 2). The characteristics of the two synthetic feedings are shown in Table 1.

Table 1. Average characteristics of the secondary effluents used in the experiments.

	Anaerobic effluent (experiment 1)	Aerobic effluent (experiment 2)
pH	7.0 - 7.5	7.3 - 7.8
COD (mg/L)	450 - 600	40 - 130
N-NH_4^+ (mg/L)	8.5 - 11.5	0.6 - 1.4
N-NO_3^- (mg/L)	0.3 - 2.2	3 - 10
P-PO_4^{-3} (mg/L)	10 - 11	0.5 - 1.5
Alkalinity (mg/L)	450 - 550	6.5 - 8.5

Experimental set-up

Four column reactors (two filters and two biofilters) of 4.6 L of total volume were used (3 L of filtering bed). Granular activated carbon (AC) and sand (S) were used as filtering media (Table 2) in the filters (ACF and SF) and biofilters (ACB and SB), respectively. The influent was introduced into the bottom of the reactors using peristaltic pumps and the effluent was obtained from the top by liquid displacement.

Table 2. Characteristics of the filtering bed.

	Sand	Granular activated carbon
Particle size (mm)	1 - 2	1.0 - 2.3
Bulk density (kg/m^3)	1,416	480
Bed porosity	0.43	0.44

Before the start-up, the biofilters were inoculated with activated sludge from the nitrification/denitrification tanks of a WWTP operated under the Biodenipho process for nutrient removal. The biomass concentration in the biofilters was around 5 g VSS L^{-1} (referred to the bed volume) and aeration was supplied through an air diffuser placed at the bottom of the columns. Instead, no biomass or aeration was placed into the filters and inhibitors of biological activity such as sodium azide (NaN_3) and allylthiourea (ATU) were continuously spiked into the feeding from day 21 of operation on to avoid growth of biomass, thus limiting the removal mechanism to adsorption. The reactors were operated under different values of EBCT: 3.2, 1.6 and 0.8 d in experiment 1 (anaerobic effluent) and, 0.8 and 0.2 d in experiment 2 (aerobic effluent). Temperature was kept constant at 25ºC during the two experiments.

Analytical techniques

Influent and effluent samples were taken twice a week for ammonium, COD, nitrate, nitrite and solids determinations according to Standard Methods (APHA, 1999). Conductivity, dissolved oxygen and pH were measured using selective electrodes. Two sampling campaigns were conducted at each EBCT to determine PPCPs concentrations in the influent and effluent of the reactors. Samples were filtered through 0.45 µm glass fiber filters, employing solid phase extraction as preconcentration technique prior to quantification using LC/MS/MS and GC/MS/MS as described by Serrano et al. (2011).

RESULTS

According to the results obtained, the micropollutants studied could be classified in three categories based on their behavior (Figure 1):

I) Compounds that showed biodegradation and high adsorption onto AC and sand (Figure 1a): ADBI, AHTN, HHCB and TCS. Lowering EBCT led to a decrease in the removal efficiency of all compounds of this category in the sand filter.

II) Compounds that experimented biodegradation, high adsorption onto AC but low (Figure 1b) or null adsorption onto sand (Figure 1c): SMX, E2, IBP, NPX, FLX, ERY, ROX, BPA, TMP, E1 and EE2. The modification of EBCT did not affect the removal efficiencies in any of the treatment systems evaluated.

III) Compounds that showed only adsorption on AC (Figure 1d): CBZ, DZP and DCF. No effect of EBCT was observed in the range tested.

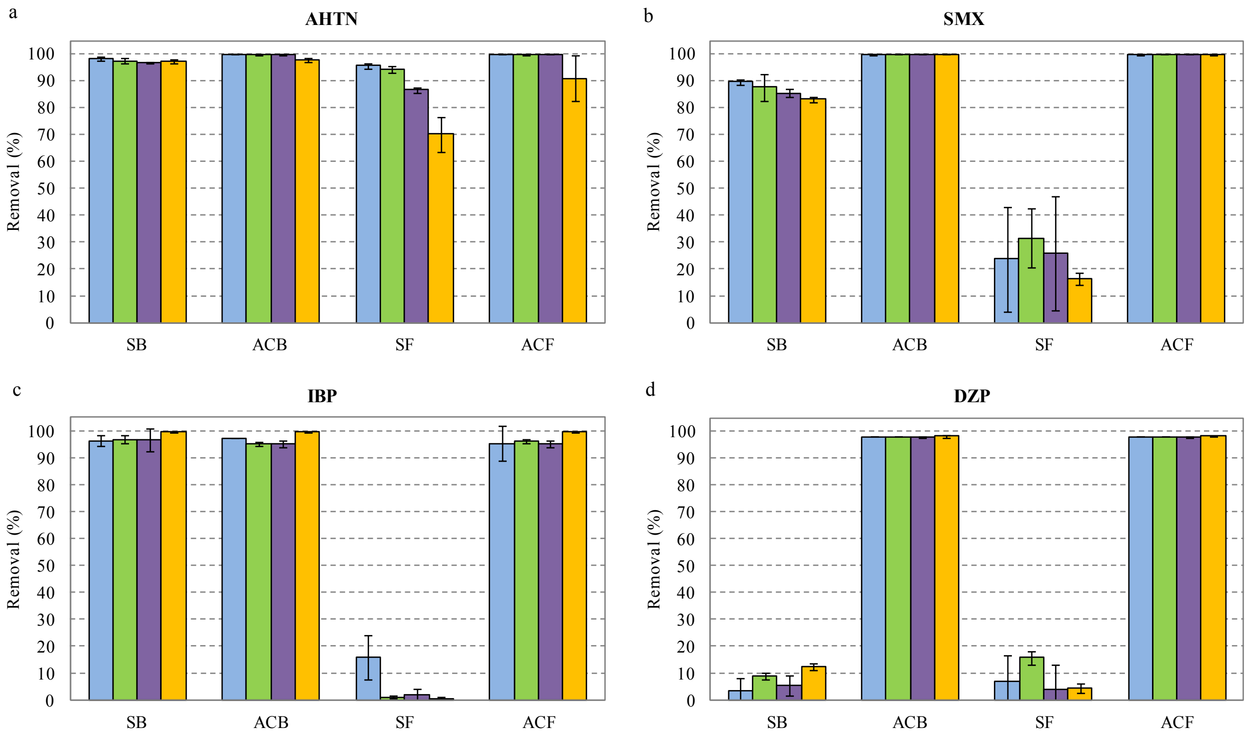

Figure 1. Removal efficiencies of PPCPs at different EBCT during experiment 1 with anaerobic

secondary effluent. 🟦 EBCT: 3.2 d (without ATU or NaN_3 in SF and ACF); 🟩 EBCT: 3.2 d; 🟪 EBCT: 1.6 d; 🟨 EBCT: 0.8 d. SB: sand biofilter, ACB: activated carbon biofilter, SF: sand filter, ACF: activated carbon filter.

The growth of biomass on the filters during the first fifteen days of operation increased the removal efficiencies of some easily biodegradable compounds, such as IBP and FLX. Overall, the PPCPs removal efficiencies achieved in this work were similar to the values obtained by other authors (Hernández-Leal et al., 2011; Reungoat et al., 2011) who studied the removal of PPCPs in effluents from conventional activated sludge treatment through biological filtration and adsorption systems. So far, no references have been found about the use of these systems to treat effluents from anaerobic treatment of sewage.

The second experiment is ongoing. Four sampling campaigns have been already conducted. The results of the first two campaigns are being analysed and the samples of the last two campaigns are being processed. The results of this experiment will enable the comparison between the two types of secondary effluent as well as to determine the critical EBCT value.

CONCLUSIONS

Most of the tested micropollutants are biodegradable and with a great potential to adsorb onto activated carbon. Moreover, EBCT did not affect the removal efficiency of most micropollutants in the range studied.

Only 35% of the selected PPCPs presented adsorption on sand. Therefore, biodegradation is crucial to improve the removal of the biodegradable and easily biodegradable compounds (E2, IBP, NPX, FLX, ERY, BPA, ROX, E1, EE2) in sand biofilters, obtaining similar efficiencies to those achieved in the AC reactors. In conclusion, the biodegradation potential developed in the biofilters is crucial for the economic sustainability of this tertiary treatment as a barrier for the entrance of PPCPs in the environment, extending the lifespan of the adsorption media, and activated carbon might only be required for the removal of the most recalcitrant compounds (CBZ, DCF and DCF).

ACKNOWLEDGEMENTS

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(P26) Occurrence and removal of pharmaceuticals in pressure sewers

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Abstract

The occurrence of 43 pharmaceuticals and 2 metabolites of ibuprofen was evaluated at the inlet and the outlet of a pressure sewer main in order to asses if complex in-sewer processes affect the pharmaceuticals concentrations during their pass though the main. The target compounds were detected at concentrations ranging from low ng/L to a few µg/L, which is in the range commonly found in wastewater influents of the studied area. For most compounds, the changes in concentrations between two sampling points were negligible (i.e. from -10 to 10 %). A higher decrease in concentrations during the pass through the main, i.e. 25-60 %, was observed for diltiazem, citalopram, clarithromycin, bezafibrate and amlodipine. Negative removal was calculated for sulfamethoxazole (-66 %) and irbesartan (-58 %) that may be due to conversion of conjugates back to their parent compounds in the sewer. From these results, it is evident that microbial transformation of pharmaceuticals begins in sewer.

Keywords

Pharmaceuticals, wastewater, pressure sewer main

BACKGROUND

Pharmaceutical compounds have received much attention in last two decades due to their documented presence in the environment and concern about their potential adverse effects to humans and wildlife. This was largely owing to the development of advanced analytical instruments and sample preparation techniques, which enabled the trace-level detection of these compounds in different environmental compartments including wastewater, surface and groundwater, sediment and soil (Kümmerer, 2009). Numerous studies have shown the presence of pharmaceuticals in raw wastewater and wastewater treatment plant (WWTP) effluents, and these have been considered a primary source of pharmaceuticals to the environment. Therefore, the efficiency of commonly applied wastewater treatments regarding the elimination of pharmaceuticals has become an actual topic focus of scientific research. The occurrence and removal of pharmaceuticals has mostly been studied in WWTPs, from influent to effluent, and in different stages of wastewater and sludge treatment. However potential transformation of pharmaceuticals in sewer system, before they enter WWTPs, has received no attention although recent studies have confirmed the importance of complex microbial, chemical and physicochemical in-sewer processes (Hvitved-Jacobsen et al. 2013). Therefore, the aim of the study was to evaluate the occurrence and removal of forty-five pharmaceuticals, belonging to different therapeutic groups (e.g. nonsteroidal anti-inflammatory agents and analgesics, lipid modifying agents, psycholeptic and antiepileptic drugs etc.) during their pass through a pressure sewer main.

MATERIALS AND METHODS

Description of the sewer system. The studied sewer main is situated at the end of a small catchment area in the coastal region of Catalonia (Spain) prior the l'Escala WWTP. The catchment serves around 3,000 inhabitants during winter, and up to around 35,000 during summer months. The sewer system served approx 10,000 population equivalents during the sampling period (wastewater flow: 1505±26 m^3/day). Table 1 shows main characteristics of the monitored sewer main, with one wastewater pump station and no lateral inputs or withdrawals along the sewer line until the WWTP. Infiltration and inflows in the sewer system can be considered negligible as the studied pipe was commissioned only two years ago.

Table 1. Main characteristics of the pressure sewer main

Length (m)	7620
Inner diameter (mm)	500
Flow rate (m^3/h)	62.7
Hydraulic retention time (h)	21±2

Sampling. Wastewater samples were collected daily as twenty-four hour composite samples, at a pumping station (inlet) and at the influent of WWTP L'Escala (Catalonia, Spain) (outlet). The sampling was carried out over five consecutive days in July 2013. The weather was dry and stable. The temperature of wastewater was 22.3 (±0.5) °C at both sampling points. Time proportional samples (4 inlet and 4 outlet samples) were collected employing portable automatic samplers programmed to collect a 50 mL of wastewater each 10 min. The outlet sampling (i.e. WWTP influent) was adjusted for the 21-hour Hydraulic Retention Time (HRT). The collected portion of samples was maintained at 4°C. The samples were extracted and processed immediately upon arrival to laboratory and latter analyzed during the following week.

Analysis of pharmaceuticals. Collected wastewater samples were analyzed using a Waters Acquity Ultra-Performance^{TM} liquid chromatography system (Waters, Milford, MA, USA) coupled to a 5500 QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) with a turbo Ion Spray source, according to an analytical method for the detection of pharmaceuticals in wastewaters (Gros et al. 2012). Quantitative analysis was performed by internal standard approach. Instrumental intraday precision of the applied method was < 8 % (n=6, 68% CI). Method quantification limits ranged from 4-37 ng/L. Relative recoveries of the analyzed compounds during the method ranged from 40-122 % (n=6).

Uncertainty estimation. The uncertainty of chemical analysis was calculated from the relative recoveries, triplicate analysis of wastewater samples and intra-day instrumental precision. The chemical standards mixture was prepared just before the analysis, so the error associated with the stability of the solution was considered negligible. The uncertainty due to sampling was estimated by considering the population served by the sewer and their pharmaceutical consumption pattern, and the applied sampling procedure as proposed by Ort et al (2010).

RESULTS AND DISCUSSION

Occurrence. Concentrations of the target pharmaceuticals, i.e. 43 pharmaceuticals and 2 metabolites of ibuprofen, in analyzed wastewater samples ranged from low ng/L (e.g. 6-7 ng/L of glibenclamide) to a few µg/L (e.g. 4-6 µg/L of ibuprofen). In general, the detected concentrations are in the range of those previously reported for WWTP influents of the studied area (Gros et al. 2012). Figure 1 summarizes the concentrations of the compounds at the inlet and the outlet of the pressure main during the sampling period. Uncertainty was not included in the graphs, but the compounds with larger sampling uncertainty than 20 % are underlined. Day-to-day variations in the measured concentrations were between 3 and 16 % for 80% of the analyzed compounds. Higher day-to-day variations in concentrations (20-60%) were observed only for erythromycin, sulfamethoxazole, trimethoprim, bezafibrate, cimetidin, and thiabendazole. This may be associated with the consumption of these pharmaceuticals in the studied area, which is connected with the results in a way that lower consumption introduces higher sampling uncertainty (Ort et al. 2010a).

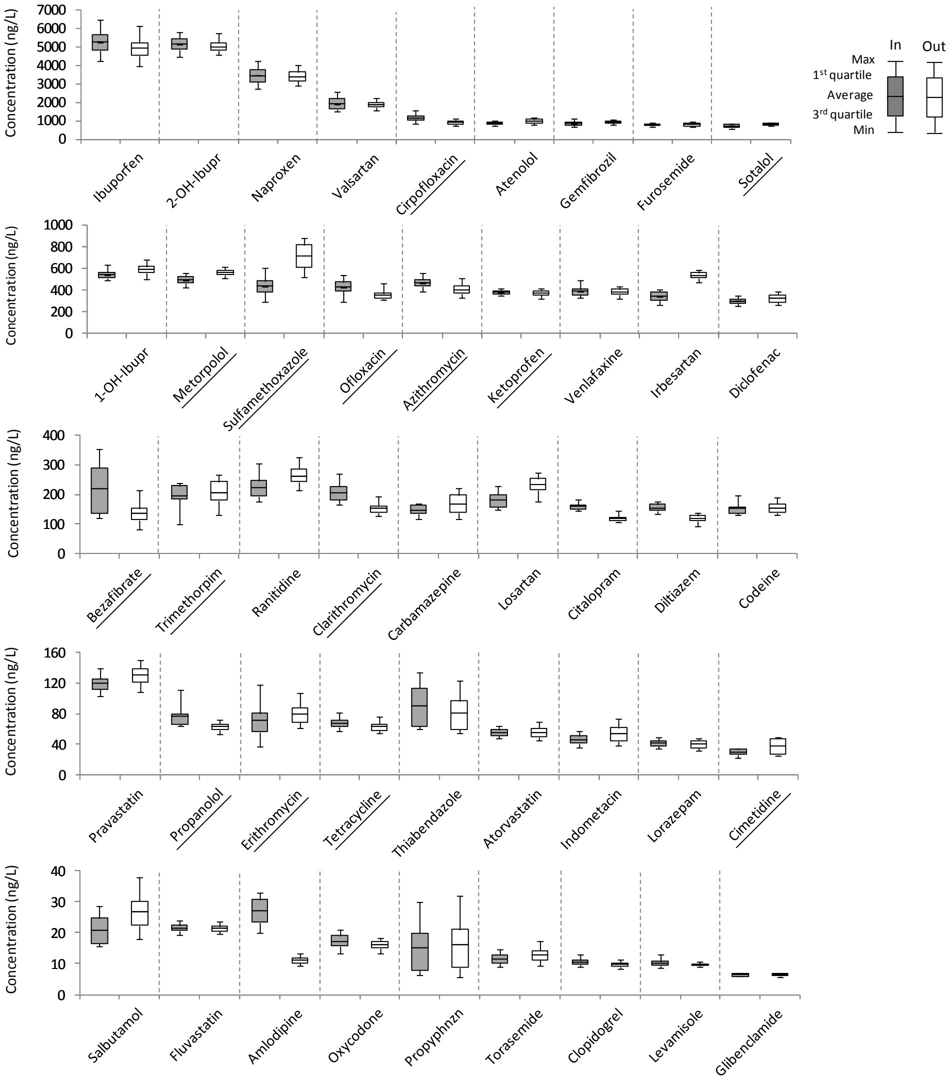

Figure 1. Concentrations of pharmaceuticals detected in wastewater collected at the inlet and the outlet of the studied sewer main. The concentrations are given as minimum, 1st quartile, average, 3rd quartile and maximum data calculated from four concentration values for each sampling site.

Removal. Here, the term "removal" refers to the reduction of pharmaceuticals from the inlet to the outlet of the sewer main, due to a combination of different processes: chemical and physical transformation, biodegradation and sorption to solid matter. The removal was calculated pair-wise for each sampling day, and then averaged. It is based on the analysis of the aqueous fraction of wastewater samples because considerable sorption could be expected only for the antibiotics azithromycin, ciprofloxacin and tetracycline, according to their literature values of sorption coefficients for primary/secondary sludge. Figure 2 depicts the calculated removal (%). For most compounds, the average removal ranged from -10 to 10%, which could be considered negligible when compared with the overall uncertainty associated with the concentration values. Slightly higher removal was observed for diltiazem (23%; 12-31% (mean; min-max)), citalopram (25 %; 11-36 %), clarithromycin (26%; 22-31%) and ciprofloxacin (21%; 2-31%), bezafibrate (32%; 12-62%), and amlodipine (59%; 54-67%). However, because of relatively high sampling uncertainty and day-to-day variation in removal efficiencies of the compounds, these percentages should be taken as rough estimates of removal. The observed removal could be attributed mainly to biochemical processes, except for ciprofloxacin, for which sorption to organic particulate matter cannot be neglected.

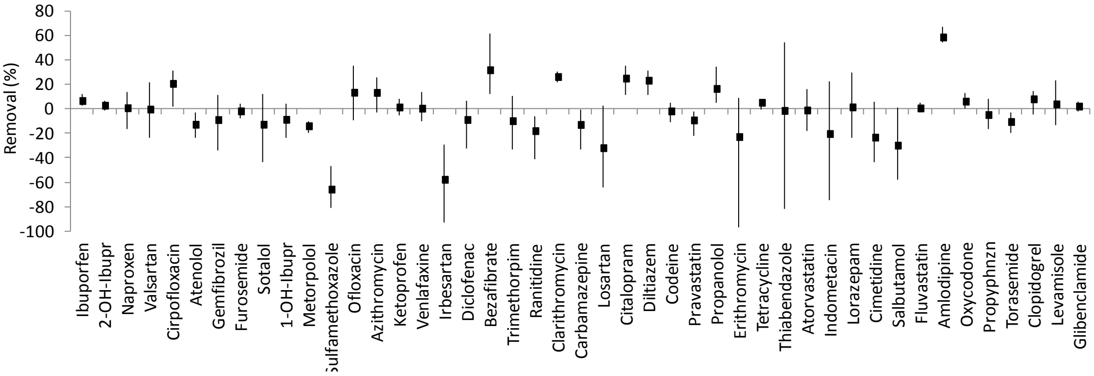

Figure 2. Removal of pharmaceuticals during the pass through the pressure sewer main (■: average value; bars: minimum and maximum removal efficiencies for the sampling days)

A significant increase in the concentrations ("negative removal") of sulfamethoxazole (-66±15 %) and irbesartan (-58±25 %) were observed during the pass through the sewer main. The known metabolism pathways of sulfamethoxazole and irbesartan involve glucuronidation (van der Ven et al. 1995), and thus we could assume that the "negative" removal was due to the cleavage of the conjugates by microbial community present in sewer wastewater. Nevertheless, the conjugates were not analyzed and further research is therefore required.

In the literature, the removal of pharmaceuticals has been principally reported for aerobic conditions. Considering that the nature and the process rates for the transformation of wastewater organic matter under anaerobic conditions are quite different compared with aerobic transformation rates, and that the configuration and the SRT (SRT=HRT=21h) in the force main differ much from commonly studied wastewater treatments. The transformation of pharmaceuticals in pressure sewers has not been reported before, and this information is crucial to improve effectiveness of sewage-epidemiology approach for monitoring patterns of pharmaceuticals use.

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(P27) Metoprolol and its metabolites: biological transformation in activated sludge experiments and detection in full scale WWTPs.

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Abstract

Metoprolol (MTP) is a compound of concern due to its high consumption, pseudopersistence and potential ecotoxicity. Activated sludge batch experiments were performed to investigate MTP biological transformation and the formation of its known transformation products (TPs) under different treatment conditions. Additionally, two previously unknown TPs were identified and their plausible structures were proposed based on the tentative identification. MTPA had the major ratio formation for the TPs identified along the experiments (up to 40% of initial MTP concentration after 96 hours treatment) and its persistence through biological treatment was proved. Ecotoxicity studies, using *Vibrio fischeri* bioluminescent bacteria in an acute toxicity test, showed that these compounds are not toxic with the exception of o-DMTP. Finally, MTP and MTP TPs were measured in a full scale membrane bioreactor and in a full scale conventional urban waste water treatment plant and the results were compared with batch experiments.

Keywords

Emerging contaminants; pharmaceuticals; wastewater; biological treatment; transformation products; ecotoxicity.

INTRODUCTION

β-blockers are a highly consumed group of pharmaceuticals, broadly detected in influent wastewater treatment plants (WWTPs) and with incomplete removal (Verlicchi et al., 2012). Among β-blockers, metoprolol (MTP) is of particular concern due to its high consumption, high persistence in WWTPs and for its potential ecotoxicity at μg/l level. Low elimination rates are usually described for MTP in conventional WWTPs (between 0-31%; Lacey et al., 2012). MTP predicted non effect concentration is 0.1 μg/l (rainbow trout liver structure alteration) while lower toxicity (mg/l order) was proved for algae test or Daphnia magna (Orias and Perrodin, 2013). Very few data are present on MTP metabolites toxicity with any kind of test. MTP is metabolized in mammals into three main metabolites named metoprolol acid (MTPA), α-hydroxymetoprolol (α-HMTP) and O-desmethylmetoprolol (O-DMTP). Human MTP metabolites can also be originated by microbial biodegradation (Barclay et al., 2012). MTPA is also generated as biodegradation product from atenolol (Radienovic et al., 2008). Very few studies have focused on MTP metabolites presence in activated sludge systems and WWTPs (Kern et al., 2012).

The study presented in this work is the first thorough study about the occurrence and generation of MTP, its known metabolites (O-DMTP, MTPA and α-HMTP) and new TPs, at laboratory scale and at full scale WWTPs. MTP biodegradability was evaluated under different treatment conditions in activated sludge batch experiments. The presence of MTP and its TPs were monitored by liquid chromatography coupled to both, tandem mass spectrometry (LC-MS/MS) and to high resolution mass spectrometry (LC-HRMS). Additionally, the presence of MTP and known and previously unknown TPs was monitored in two full scale WWTPs. Finally, the evaluation of the ecotoxicity of MTP and its three known metabolites was also performed along the batch studies.

MATERIAL AND METHODS

Batch experiments with activated sludge. Batch experiments were performed in activated sludge samples from the WWTP of Celrà (Spain, 20,000 I.E., 2,100 m^3/d, 48h HRT, 20-22d SRT). 1 ml of MTP, MTPA or atenolol stock solutions was spiked to obtain the desired concentration. The bottles were at controlled temperature (20°C) and under dark conditions. A control experiment without target compound (blank) was carried out. The samples were taken at different times (up to 96h) by means of glass syringes, filtered (nylon membrane filter, 0.45 µm) and stored at -20°C.

MTP biodegradation experiments, at 1 mg/l of MTP and 1 g TSS/l, were performed at aerobic, anaerobic and anoxic conditions. Different initial concentrations of MTP (10 mg/l, 1 mg/l and 10 µg/l) were also investigated in aerobic conditions at 1 gTSS/l. Higher TSS concentration (3 gTSS/l) was tested in aerobic conditions, at 1 mg/l of MTP, in order to elucidate the biomass impact. Finally, biodegradation assays for MTPA and atenolol (1 mg/l) were performed under aerobic conditions at 3 gTSS/l. All the experiments above described were performed in triplicate.

Monitoring of MTP and its TPs in urban WWTPs. Two different WWTPs were monitored: Campdorà (Spain, 40,000 m^3/d, 24h HRT, 25 d SRT) with conventional treatment and Terrassa (Spain, 7,500 m^3/d, 17 h HRT, 32 days SRT) with MBR technology. Influent and effluent samples from both WWTPs were collected during 3 consecutive days, taking into account the corresponding shift times between influent and effluent wastewaters. All samples were pre-filtered through 1 µm, filtered (0.45 µm) and stored at -20°C before solid phase extraction (SPE).

Analytical methodology. Samples collected from batch experiments were diluted to obtain a final metoprolol concentration equal to (or less than) 100 µg/l. WWTPs samples were pre-concentrated by SPE using an extraction method adapted from Gros et al., 2012. Pharmaceuticals analyses were done by means of UPLC instrument coupled to 5500 QqLit, triple quadrupole–linear ion trap mass spectrometer (5500 QTRAP, Applied Biosystems) with Turbo V ion spray source. Unknown transformation products generated during degradation experiments were investigated with an on-line turbulent flow chromatograph coupled to a hybrid linear ion trap high resolution Orbitrap mass spectrometer (TFC-LTQ Orbitrap Velos, ThermoFisher Scientific Company).

Toxicological analyses through *Vibrio fischeri* bioluminescence inhibition test. A bacterial bioluminescence test was applied for ecotoxicological purposes (ISO11348-3, 1998). First MTP and its metabolites were tested; then, mixture of MTP and its metabolites in Milli-Q water were tested in order to mimic the concentrations detected at each sampling time of the batch experiment (1 mg/l and 3 gTSS/L) but discarding the effect of the wastewater matrix. The concentration of toxicants in the test which caused a 50% of the reduction in light (Inhibition = 50%) after exposure for 15 min was designed as the EC50 value. Tests were performed at 15°C.

RESULTS AND DISCUSSION

Monitoring of MTP in batch experiments

MTP degradation under anoxic and anaerobic conditions was minimal (lower than 2% in 24h). Major removal was obtained under aerobic conditions with higher elimination at higher biomass concentration (Figure 1). Further experiments were performed, also under aerobic conditions, with 1 gTSS/l but at different initial concentrations of MTP: 10 mg/l, 1mg/l and 10 µg/l, the latest one chosen in an effort to mimic the usual levels of MTP in wastewaters. At 10 µg/l total removal of MTP was achieved before 96h while lower removals were observed at higher MTP concentration. This result, in contrast with usual poor removal in WWTP (Lacey et al., 2012) is probably due to usual low HRTs for typical modern WWTPs compared to the reaction time here applied (96h).

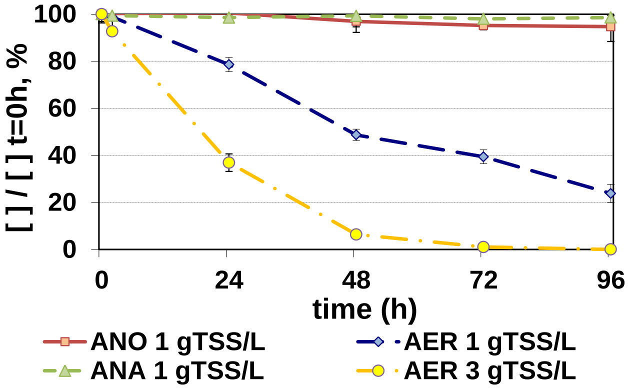

Figure 1. 1 mg/l initial MTP concentration (normalised to the initial time spiked concentration) at aerobic (AER), anoxic (ANO) and anaerobic (ANA) conditions.

Identification and monitoring of MTP TPs formed during batch experiments

O-DMTP, MTPA and α-HMTP presence was confirmed (batch experiment at 1 mg/l MTP and 3 gTSS/l). In addition, 2 unknown TPs were tentatively identified and their chemical structures proposed. MTPA was the TP generated at the highest extend, up to 40% of MTP initial concentration, after 48h treatment and with no alteration till the end of the experiment (96h). An additional batch (at 1 mg/l MTPA and 3 gTSS/l, aerobic conditions) confirmed MTPA persistence. α-HMTP and O-DMTP were formed at lower than 5% of MTP initial concentration and tend to be eliminated over time after achieving a maximum level after 24h. TP1 and TP2 were generated later during the experiment timeframe.

Toxicity test with *Vibrio fischeri*

The toxicity units (TU, expressed as the percentage of 1/EC50) of MTP, α-HMTP and MTPA were below 3%. The only compound showing slightly higher toxicity was O-DMTP (5.57%). The TUs of the samples mimicking the batch experiments (1 mg/l MTP and 3 g TSS/l) did not show any significant differences, being all of them below 3%, and without any apparent synergic effect.

Monitoring of MTP and its metabolites in a WWTPs

MTP, O-DMTP, MTPA and α-HMTP as well as 5 commonly used β-blockers were quantified in wastewater influent (WWI) and wastewater effluent (WWE) of Girona and Terrassa WWTPs. MTP was not eliminated in Girona WWTP (conventional treatment, table 1) whereas MBR technology (WWTP Terrassa) was more efficient (around 54% MTP removal). O-DMTP was not detected in WWI neither in WWE. α-HMTP was found at 36 ng/l or below in WWI, but not in WWE. This is the first study reporting the presence of α-HMTP in full scale WWTPs. MTPA was detected up to 298 ng/l in WWI with an MTP/MTPA ratio matching with the excretion ratios. Atenolol was the β-blockers compound found at the highest concentration.

Table 1. Target compound concentrations in Girona WWTP (ng/l (± RSD); nd: not detected).

Compound	1st DAY		2nd DAY		3rd DAY	
	WWI	WWE	WWI	WWE	WWI	WWE
Atenolol	1295±10	920±47	4067±103	717±20	3327±173	358±4
MTP	31±3	33.8±	35±3	35±4	24±3	27±2

		0.6				
MTPA	206±27	2506±91	282±32	2280±44	298±20	1561±95
α-HMTP	<LOQ	nd	32±2	nd	36.1±0.7	nd
O-DMTP	nd	nd	nd	nd	nd	nd

MTPA concentration greatly increased during WWTP. MTPA persistence cannot explain itself this result that may be attributed to its generation from other β-blockers. Atenolol, in particular, has been described to be transformed into MTPA (Kern et al., 2012, Radjenovic et al., 2008). A batch experiment (1 $mg_{ATENOLOL}$/l; 3 gTSS/l) confirmed the rapid transformation of atenolol into MTPA.

CONCLUSIONS

MTP total removal was obtained after 96 h in aerobic condition at environmental relevant MTP concentration (10 µg/l) and 1 gTSS/l. Higher removals were observed at higher TSS. Biodegradation of MTP resulted in the formation of 3 known TPs identified as the metabolites O-DMTP, MTPA and α-HMTP as well as 2 newly identified TPs. MTPA was the major transformation product (up to 40% of initial MTP concentration after 96 hours treatment) demonstrating its high persistence through the treatment. The rest of TPs were detected at less than 5% of initial metoprolol concentration. O-DMTP exhibited more acute ecotoxicity for *V.fischeri* than MTP and the other MTP metabolites tested. MTPA, was detected in effluent and influent water of full scale urban WWTPs at much higher levels than MTP itself; α-HMTP was found at low concentrations in both WWTPs, while O-DMTP was not detected.

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(S21) Removal of emerging pollutants through UV irradiation: the role of wastewater characteristics

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Abstract

Non-steroidal anti-inflammatory drugs (NSAIDs) and endocrine disrupting chemicals (EDCs) are compounds which present significant scientific interest due to their toxicological and chemical characteristics and their persistent detection in the aquatic environment. Pharmaceuticals and personal care products are used in large quantities around the world and wastewater treatment plants are a well known source and one of the most significant pathways for their transfer to the aquatic environment. The objective of this study was to evaluate the role of wastewater characteristics on the degradation of NSAIDS and EDCs through UV irradiation. Bench scale batch experiments were conducted using secondary treated wastewater samples being irradiated by a low pressure UV system in order to achieve a UV dose of 150 mJ/cm^2 and to assess the effect of pH, humic acids and total suspended solids (TSS) content on processes performance. According to the results, UV disinfection at a dose of 150 mJ/cm^2 can effectively remove Ketoprofen and Diclofenac. The effect of wastewater pH on disinfection is rather minimal for pH values between 6-10. Regarding the effect of TSS concentration on the degradation of EDCs and NSAIDs, it seems that the removal of the target compounds which are distributed mostly in the particulate phase decreases with increasing TSS concentration. Furthermore, it can be stated that humic acids concentration in wastewater is not a crucial parameter affecting process efficiency. Finally, Diclofenac's UV-degradation by-products were identified for three UV doses. Based on the results eight UV-degradation by-products of Diclofenac were identified with their concentrations being increased as UV irradiation contact time increases.

Keywords
Diclofenac by-products; endocrine disruptors; pharmaceuticals; UV; wastewater treatment

INTRODUCTION

Emerging contaminants are compounds which present significant scientific interest due to their toxicological and chemical characteristics. Several studies report the frequent detection of these compounds into the aquatic environment in wastewaters, surface waters, ground waters and in some cases in the drinking water (Jonkers et al., 2012; Martínez Bueno et al. 2012). Wastewater treatment plants (WWTPs) are a well known source and one of the most significant pathways for their transfer to the environment (Samaras et al., 2009). Endocrine disrupting chemicals (EDCs) and non-steroidal anti-inflammatory drugs (NSAIDs) are two important groups of emerging pollutants due to persistent detection in the aquatic environment. It is well evidenced that most of these chemicals are only partially removed through biological treatment and therefore being detected in secondary effluents (Verlicchi et al., 2012). Recently Noutsopoulos et al., (2013) evaluate the effectiveness of alternative wastewater disinfection methods to degrade both EDCs and NSAIDs. In the context of this study the authors examine the effect of UV dose on process performance. According to their results the authors report that UV irradiation at doses usually adopted for wastewater disinfection purposes is effective for the degradation for some of these compounds.

In view of the above the objective of this study was to assess the role of wastewater characteristics such as pH, humic acids (HA) and total suspended solids (TSS) concentration on the degradation of EDCs and NSAIDs through UV irradiation and to study the UV by-products of Diclofenac. The target compounds of this study, their main physicochemical properties along with their abbreviations are listed in Table 1.

MATERIALS AND METHODS

Materials

Methanol (MeOH) and ethyl acetate were of high performance liquid chromatography (HPLC) grade (Merck, Darmstadt, Germany) and were used as received. BPA (>97%) was purchased from Fluka (Buchs, Switzerland), whereas TCS (>97%) and deuterated BPA (BPA-16) were purchased from Fluka (Heidelberg, Germany). Analytical standards of NP, NP1EO, IBF, NPX, KFN, DFC, and meclofenamic acid (MFC) were supplied by Dr Ehrenstorfer (Germany). All compounds were used without further purification (minimum purity >99%). Stock solutions of individual compounds were prepared in methanol at 1 g/L and kept at −18°C.

UV Batch Experiments

Several UV batch experiments were performed in triplicates in 3 L reactors. All batch experiments were performed in secondary treated wastewater samples spiked with the target compounds (NP, NP1EO, NP2EO, TCS, BPA, DCF, NPX, KFN, IBF) at a concentration of 1 μg/L. A collimated UV source consisting of one low pressure lamp, was employed to assess dose response curves for each sample tested. The intensity of UV radiation was measured using an IL 1700 radiometer with an SED 240 detector. Average UV intensity was calculated using Beer's Law taking into account the reduction of UV light through the depth of the sample. UV dose (Ct) was calculated as the product of the intensity and the contact time. pH adjustment was done with phosphate buffer solution.

Analytical Methods

For the determination of the EDCs and NSAIDs, wastewater samples before and after UV disinfection were analyzed using a chromatographic method developed by Samaras et al., (2011). For the qualitative and quantitative analyses, an Agilent Gas Chromatograph 7890A connected to an Agilent 5975C Mass Selective Detector (MSD) was used. For the identification of DCF UV-degradation by-products, a Thermo Liquid Chromatography - High Resolution (HR) - Mass Spectrometry (LC-HRMS) instrument was used. The LC system consisted of an Ultra-High Performance LC pump (Accela, Thermo) incorporating a column thermostat and an autosampler, interfaced to a Linear Ion Trap - Orbitrap (LTQ-Orbitrap) hybrid Fourier Transform Mass Spectrometer (FTMS) (San Jose, CA, USA).

Table 1. Target compounds and their main physicochemical properties

Compound	Short	Molecular type	MW	pKa	logKow
Naproxen	NPX	$C_{14}H_{14}O_3$	230.27	4.15	3.22
Ibuprofen	IBU	$C_{13}H_{18}O_2$	206.29	4.59	3.72
Ketoprofen	KFN	$C_{16}H_{14}O_3$	254.3	4.45	3.12
Diclofenac	DCF	$C_{14}H_{10}C_{l2}NO_2 \cdot Na$	318.14	4.14	4.5
Triclosan	TCS	$C_{12}H_7C_{13}O_2$	289.54	7.9	5.4
Bisphenol-A	BPA	$C_{15}H_{16}O_2$	228.29	10.2	3.4

Nonylphenol	NP	$C_{15}H_{24}O$	220.35	10.28	4.48

RESULTS AND DISCUSSION

Effect of pH. In order to assess the effect of pH on process performance, experiments were performed at three pH values (6, 7.5 and 10) at three different doses 70 - 150 – 1000 mJ/cm^2. According to the results, it was observed for all target compounds that their removal rate was practically independent to pH (for the pH range examined). Only TCS exhibits higher degradation rate when pH value increases and especially when pH value is higher than compound’s pKa (7.9). This result is in agreement with the results by other research teams (Sanchez-Prado et al., 2006).

Effect of humic acids. In order to evaluate the effect of humic acids presence in wastewater on the removal of target compounds through UV-irradiation, UV experiments were performed with secondary treated wastewater samples with a humic aid content of 20 mg/L at a UV-dose of 150 mJ/cm^2. Based on the results it can be stated that the removal of the selected compounds seems not to be significantly affected by the presence of humic acids in the wastewater samples.

Effect of TSS. The effect of TSS content in wastewater on the degradation of target compounds through U-irradiation was examined for three alternative TSS concentrations (0 mg/L, 10 mg/L and 70 mg/L) at a standard dose of 150 mJ/cm^2. Based on the experimental results it can be stated that the effect of TSS on the removal of the target compounds through UV-irradiation depends on compound’s affinity to the aqueous or the solid phase (expressed by logKow). Compounds which are distributed mostly in aqueous phase (e.g. BPA) shown no significant variation on their removal during UV disinfection in the presence of different TSS concentrations. In contrast, compounds where a significant portion of them is presented in the particulate phase (TCS and NP) exhibit a significant decrease on their removal as TSS concentration increases.

Identification of UV-degradation by-products of DCF. The detection and identification of DCF’s UV-degradation by-products were performed for three UV doses (70- 150 – 1000 mJ/cm^2). The results are presented in Figure 1. Based on the results, eight by-products were identified for the three alternative doses (C-2 (8-chloro-9H-carbazole-1-acetic aldehyde), 8-chlorocarbazole-1-acetic acid, carbazole-1-acetic acid, 8-hydroxy-carbazole-1-acetic acid, E-2-[3-2(2,6-dichloro-2-hydroxyphenylimino)-6-oxocyclohexa-1,4, dienyl] acetic acid, 2-(8-hydroxy-3-oxo-3H-carbazol-1-yl) acetic acid, hydroxydiclofenac and 9-H-carbazole-1-carbaldeyde). As shown in Figure 1, C-2 was found to be the major UV-degradation product while more by-products are produced as UV dose increases. The increase of the degradation by-products is related to the increased degradation of DCF with the increase of UV-dose.

CONCLUSIONS

Batch experiments were performed in order to assess the effect of pH, humic acids and total suspended solids (TSS) content on UV disinfection of selected compounds from wastewater samples. Regarding the effect of pH on EDCs and Phs, it seems that removal rate for most of the target compounds is insignificantly affected during UV-radiation. Only TCS was found to be more unstable when pH value increases from 6 to 10 which probably connected with the pKa value of the compound. The effect of humic acids concentration on the fate of the substances through UV disinfection is minimal. Removal of the target compounds, due to UV radiation, which are distributed mostly in particulate phase decreases with increasing TSS concentration, while UV efficiency is not affected by TSS concentration for the polar target compounds. Finally, a detection and identification of 8 by-products of Diclofenac has been done for that three doses of UV radiation and C-2 (8-chloro-9H-carbazole-1-acetic aldehyde) found to be the major for UV dose of 70 mJ/cm^2.

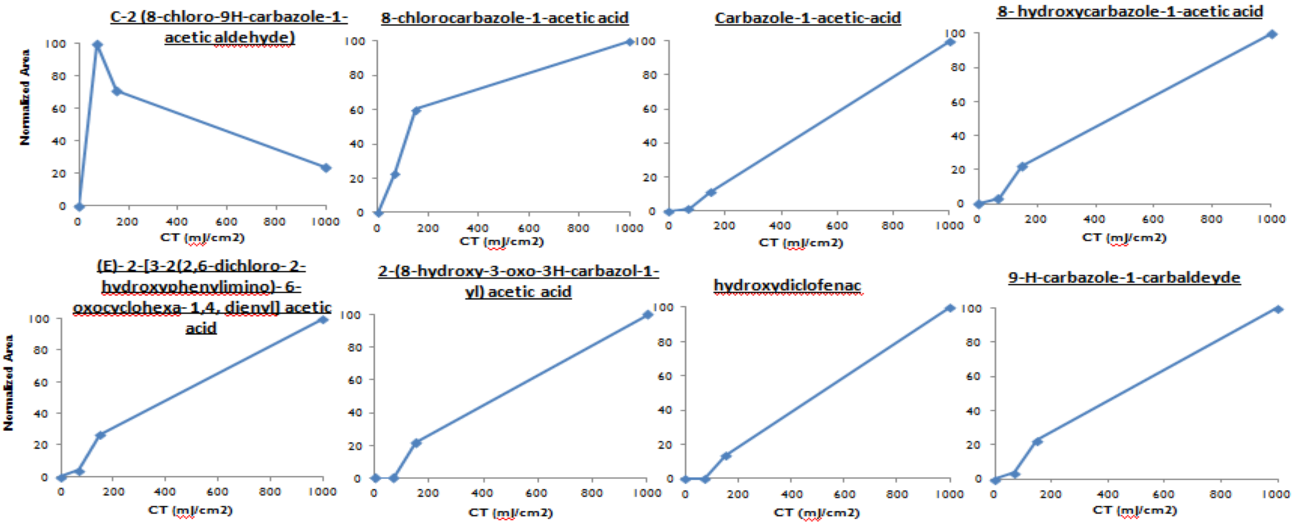

Figure 1. UV-radiation by-products of DCF

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(S22) Optimization of Homogenous and Thin-Film Photocatalytic Degradation of Ampicillin (AMP) by means of Nom Effect and Toxicity Evalution

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Abstract

Following the biometabilization and excretion from body(around %10) mechanisms of human and animals that are given medication via antibiotics and other pharmacauticals, surface and urban wastewater streams become a target posing substantial impacts on the environment and human health.

Since most of antibiotics have been demostrated to be low degradable in biological treatment systems advanced oxidation processes (AOPs) have gained an essential attraction to oxidize them. Among AOPs photo-catalytic (PC) oxidation drew a particular attention in academic studies with the advantage of being green technology regarding of solar energy use. Known with their varying types of mechanisms effective for preventing microbial acitivity, NP use multiple mechanisms simultaneously thus make development of bacterial resistance unlikely.

Thus this study aimed to investigate the effect of natural organic matter (NOM) on photocatalytic degradation of ampicillin under UV-A irradiation of 125 W (UV-A Power Supply 482) within a range of 315-400 nm wavelength both in heterogenous and homogenous thin-film studies. Effects of TiO2 dose, pH, NOM origin and concentration, concentration of ampicillin on the reaction rate were investigated. Degradation efficiency was assessed by means of variations in UV absorbance besides mineralization was assessed by organic carbon removal via TOC and COD analyses. Ammonia, nitrate formation during photocatalytic degradation were monitored as a function of irradiation time. Analyses of oxidation by-products at the end of each experiment is achieved by LC-MS/MS. Daphnia magn and Ceriodaphnia dubia acute toxicity was performed according to ISO 6341 method using 24 h new born daphnids for 24 and 48 h exposure time. In this context it was able to be estimate how consistent the chemical assays with the results of potential detoxification of ampicillin and it's oxidation by-products.

Keywords

Ampicillin; degradation; demineralization; detoxification; ecotoxicity homogenous photocatalysis; oxidation by-products; thin film, TiO2

INTRODUCTION

Due to adequate removal rates of pharmaceuticals obtained by conventional biological processes, urban waste water treatment plants (UWWTP) become the main source of surface water contamination [7]. Arised from varying sources like antibiotic industry, hospital effluents and excretion from human and livestock, antibiotics with their high consumption rates can reach and pose severe hazards and risk to the aquatic environment [2]. Continous release of almost low concentrations of pharmaceuticals in aquatic environemtens leads to increases of synergistic effects with other pharmaceuticals&chemicals or spesifically development of antibiotic resistant bacterias in the case of antibiotic release [3]. Adoption of advanced oxidation processes (AOPs)in the tertiary treatment of UWWTPs can significantly contribute to enhanced pharmaceutical removals [5].

AOPs can be generally defined as aqueous phase oxidation methods destructing the target pollutants through mechanisms based on the intermediacy of highly reactive species such as hydroxyl radicals [4] Based on ROS and radical formation mechanisms, photocatalysis is less guided compared to biochemical reactions in terms of reaction pathways, leading to nonspecific reactions and myriads of reaction products. Arising from biopersistence of its many organic contents, pharmaceuticals can be induced to form only a limited degree of transformation [4]. Besides mineralization is a slow process with producing more stable by-products than the pharmaceuticals to total oxidation, nonetheless posing risks by being more readily biodegredable [5]. UV Irradiated TiO2 shows cell membrane damaging properties via ROS generating mechanism while non-irradiated TiO2 also have bactericidal effects. Incorporating different types of metals into the same thin film (TF) [**Error! Reference source not found.**,7].

The disapperance of the drug itself may be misleading by means of treatment efficiency hence subsequent conventional parameters including TOC (total organic carbon), COD (chemical oxygen demand) need to be measured. That will secure to come to a solid conclusion on the overall efficiency and the safe use or reuse potential of the treated sample [4].

Ampicillin (AMP) is used in human and veterinary medication applications known to get its structural antimicrobial properties from beta-lactam ring. The aqueous solutions of AMP are known to be degraded through photo-fenton and TiO2 based homogenous photocatalysis processes [2].

This subject became our subject of investigation within the context of comparing TF and homogenous PC removal efficiencies of TiO2 based reactor in the presence of different origin and concentrations of NOM, as well transformation products are measured to compare the quality of treated samples which may result in toxic.

MATERIALS AND METHODS

Reagents

TiO_2 based TFs were deposited by means of sol-gel technique. Ethanol (Merck), Glacial Acetic Acid (Merck), Nitric Acid (Merck) and Titanium (IV) n-butoxide (Fluka) were of analytical grade and used as received. KSV Nima Medium Dip Coater Unit was used for thin film fabrication. The films were grown by single stage dip-coating on quartz glass substrates. As-prepared wet films were first annealed at 300 °C for and finally, the films were calcinated at 500 °C for 3 h [8]. AMP was purchased from Sigma Aldrich at standart quality. Chemical structure of AMP is given in Figure 1.

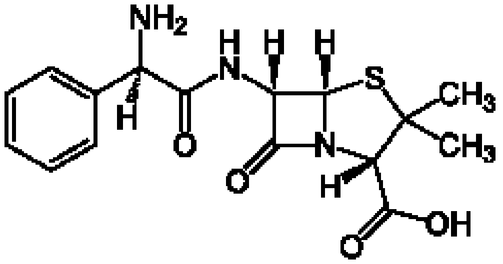

Fig. 1 Structure of ampicillin (CAS 56-75-3).

Experimental set-up

Photocatalytic experiments were carried out at room temperature in a 200 mL stirred cylindrical Pyrex dish filled with varying volumes of aqueous solution at different 2 min pre-sonicated TiO2 (0.25, 0.5, 1, 2 g/L) and AMP concentrations (5, 10, 20 mg/L). While quartz substrates, placed on the surface level of the petri dish, the way that the thin-film coated side in contact with the solution. Exposure to UV irradiation maintained by a UV-A irradiation of 125 W lamp (UV-A Power Supply 482) within a range of 315-400 wavelength.

Analytical Methods

Optimum concentrations for AMP and doses for TiO_2 were determined as an output of chemical and toxicity analysis. Optimum values for NP doses are used as an instructive information for the thin-film fabrication.

The evolution of UV absorbance under dark conditions was monitored in order to observe adsorption of organic matter and AMP on catalyst/thin film surfaces using Shimadzu Lamda 1800 instrument. Samples were filtered through 0.45 µm Millipore Millex-HA cellulose based membrane filters to remove catalysers before spectrophotometric analysis. TOC was measured using a Shimadzu TOC analyzer (6KVA model) at Central Laboratory of Namık Kemal University (NABILTEM). COD experiments were performed according to Standard Methods [1]. Transformation products of AMP degradation were monitored via LC-MS/MS analysis at NABILTEM. Ammonia and nitrate analyses carried out in order to monitor their formation during photocatalytic degradation as an indivative of on-going mineralization reactions.

Ecotoxicity tests

Acute toxicity of AMP and it's aqueous treated samples were assessed on two freshwater crustaceans *Daphnia magna* and *Ceriodaphnia dubia* which are two primary consumers in the aquatic chain.

Daphnia magna immobilization:*D. magna* were inoculated in a temperature constant vivarium at Environmental Engineering Department's Laboratory according to ISO method 6341 [9]. The pH of the medium was 8.0 and the total hardness was 250 mg/L (as $CaCO_3$). Tests were performed in the dark at 20 ^{0}C. For aqueous solution, 5 concentrations in a geometric series were tested in the concentration range first established in a preliminary test. New born daphnids (<24 h) were exposed to four detergents. Experiments were performed as four replicate and 5 daphnids were tested in each replicate. Acute toxicity was assessed for 24 and 48 h of exposure time by means of immobilization percentage determined by dividing total immobilized organisms to total number of test organisms.

Ceriodaphnia dubia immobilization: *C. dubia* kits were kindly provided from another laboratory and incubated for having nauplii in 48 h in standard solutions, than they were inoculated in the constant temperature kept vivarium to perform acute toxicity tests run with the same conditions with *D. magna* [9].

RESULTS AND DISCUSSION

Degradation and demineralization

Photolysis did not exhibit any significant removal while dark experiments showed that there was around 35-40% of AMP removal. Adding catalyst to the reactor under illumination by UV-A shifted the removal efficiency to over 85-90% for 20 mg/L AMP using 2 g/L TiO2 during around 2 h illumination period. Increasing catalysts dose resulted in highering removal efficiency of AMP in heterogenous reactor in accordance with the previous studies [3,4,7].

The oxidation time took longer for lower doses of TiO2 based sol-gel TF applications while time could decrease when TiO2 dose was optimized as expected [8]. Removal capacity of TF was affected by by-products formation too.

Detoxification

Both mobility of *D. magna* and *C.dubia* was affected by exposure of untreated and treated AMP aqueous solutions. The concentration of AMP influenced toxicity much since the formation of oxidation by products was higher at higher initial AMP concetrations [7]. The variety of by products dependent on the treatment scheme and TF system was found to be very effective to combat with the formation of by products as confirmed by LC-MS/MS analysis.

Chemical analyses

Formation of ammonia and nitrate concentrations increased in parallel to the oxidation time in both processes. However, ammonia was not suspected to cause the toxicity at oxidation pH and occurred concentration [7]. LC-MS/MS spectra indicated that AMP was removed effectively by both processes while oxidation products formation was lesser in the TF treated samples at lower AMP initial concentrations. However at higher catalysts doses and AMP concetrations by products increased and reaction time took longer to stabilize their occurrence. The presence of NOM promoted the formation of by products and descreased system performance [4,7].

CONCLUSION

It has become an obvious need to integrate biological systems with a tertiary AOPs process to degradate emerging pollutants which are not removed efficiently in the conventional systems. Ampicicllin, as a beta lactam group of antibiotic, is one of those mostly consumed pharmaceuticals in Turkey too.

Photocatalysis as known green and sustainable technology, is attempted in this study to remove AMP from syntheitic aqueous solutions considering also the effect of NOM. Heterogeneous and homogenous TF systems were applied successively to obtain safe effluent provided by *Daphnia magna* and *Ceriodaphnia dubia* ecotoxicity tests as well as chromatographic measurements.

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(S23) Removal of non-steroidal anti-inflammatory drugs from water through photodegradation

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Abstract

Non-steroidal anti-inflammatory drugs are compounds which present significant scientific interest due to their toxicological and chemical characteristics and their persistent detection in the aquatic environment. Bench scale batch experiments were conducted to evaluate the effect of hydrolysis and photodegradation on the fate of selected non-steroidal anti-inflammatory drugs in the aquatic environment and to assess the effect of pH, humic acids and nitrates content on processes performance. Solar irradiations were carried out at the National Technical University of Athens, Greece (latitude 37°58' N, altitude 160 m above sea level) during May 2013. For the determination of the target compounds, water samples before and after being irradiated for several time intervals were analyzed. Exposure to sunlight was continuous and similar experiments were carried out in the dark to account for hydrolysis. According to the results, photodegradation is the major mechanism for the removal of Diclofenac, Ketoprofen and Naproxen which shown half-lives lower than 6 h. On the other hand, the photodegradability of Ibuprofen was minimal. The effect of water pH on photodegradation kinetics is rather minimal for pH values between 6-8. Among all parameters examined, photodegradation of the target compounds is mostly adversely affected by high humic acids content in water. The effect of both nitrates and humic acids on the fate of the target compounds in the aquatic environment seems to be an amphoteric phenomenon which is in reference with the absorption spectrum of each substance and the produced photosensitizers.

Keywords

endocrine disruptors; humic acids; non-steroidal anti-inflammatory drugs; photodegradation; water

INTRODUCTION

Emerging contaminants (ECs) is a rather diverse and heterogeneous group of chemicals consisting of pharmaceuticals and personal care products, steroids and hormones, drugs, fragrances, surfactants, flame retardants, perfluorinated compounds, complexing agents, etc. Several studies reported the frequent detection of these compounds into the aquatic environment in wastewaters, surface waters, ground waters and in some cases in the drinking water (Jonkers et al., 2012; MartínezBueno et al., 2012). In the environment, ECs are substances released from domestic, industrial, and agricultural sources (Yan et al., 2010). Wastewater treatment plants (WWTPs) are a well known source and one of the most significant pathways for their transfer to the aquatic environment (Samaras et al., 2009). It is well evidenced that these chemicals are only partially removed through biologically treatment of wastewater and therefore being disposed in the aquatic environment. Besides the fact that these compounds are detected in low concentrations (to the order of ng/l) (Ratola et al., 2012), some of them, such us anti-inflammatory drugs (NSAIDs) present significant scientific interest due to their toxicological and chemical characteristics. A literature review has shown that so far there are limited data regarding the fate of these compounds during their disposal to the aquatic environment. More specifically few studies report on the photodegradability of these compounds (Andreozzi et al., 2003; Pal et al., 2010).

In view of the above the objective of this study was to investigate the effect of hydrolysis and photodegradation on the fate of selected NSAIDs in the aquatic environment and to assess the role of some parameters such as water pH, humic acids (HA) and NO_3-N concentration on processes performance. The target compounds of this study, chosen as representatives of NSAIDs, their main physicochemical properties along with their abbreviations are listed in Table 1.

MATERIALS AND METHODS

Materials

Methanol (MeOH) and ethyl acetate, of HPLC grade (Merck, Germany), were used as received. BSTFA+1% TMCS solution (Supelco, USA) and pyridine (Carlo Erba-SDS, France) were used for silylation. Analytical standards of the target compounds NPX, DCF, IBU and KFN were supplied by Dr Ehrenstorfer (Germany). All compounds were used without further purification (minimum purity >99%). Stock solutions of individual compounds were prepared in methanol at 1 g/L and kept at -18^{o}C. HPLC grade water was prepared in the laboratory using a Milli-Q/Milli-RO Millipore system (USA).

Photodegradation Batch Experiments

Solar experiments. Solar irradiations were carried out at NTUA, Greece (latitude 37°58' N, altitude 160 m above sea level) during May 2013. Photodegradation batch experiments were performed in triplicates in 2 l reactors. Reactors were 2 mm thick Pyrex cylinders of 16 cm high and 14 cm in diameter, whose outer side was covered with two layers of silver foil sheet. All batch experiments were performed in buffered pure water spiked with the target compounds (presented in Table 1) at a concentration of 2 μg/l. pH adjustment was done with phosphate buffer solution in order to achieve the desirable pH value. The measured pH never varied by more than 0.2 units during the course of the experiments. Exposure to sunlight was continuous and samples were taken at t=0 and in regular intervals, solutions were homogenized with a glass rod and samples collected for GC-MS analysis. To investigate hydrolysis, similar experiments were carried out in the dark. The incident solar light intensity was measured with a pyranometer (Kipp and Zonen CM11pyranometer) at spectral range 305–2800 nm continually over the irradiation period.

Analytical Methods

For the determination of the target compounds water samples before and after solar exposure were analyzed using a chromatographic method developed by Samaras et al. (2011). Samples were acidified to pH 2.5, and extracted using C18 SPE cartridges. The eluates of the extraction were evaporated to dryness, and the dried residues were subjected to derivatization reaction using BSTFA (1% TMCS) and pyridine. For the qualitative and quantitative analyses, an Agilent Gas Chromatograph 7890A connected to an Agilent 5975C Mass Selective Detector (MSD) was used.

RESULTS AND DISCUSSION

The effect of photodegradation and hydrolysis on the removal of target compounds in aqueous solutions has been examined. Removal of the compounds was treated as first-order kinetics (until 90% degradation been achieved). The rate constant from the dark tests subtracted from the overall rate constant determined from the irradiated solutions to give the direct photolysis rate constant. Experimental half-lives ($T_{1/2}$) were determined independently of the k pseudo-constants (Table 1). Regarding photodegradation, estimation of direct photolysis rate constants and half-lives was impossible for IBU, DFC and KFN. Results for each target group are presented in Figure 1. Based on the results, KFN presents the lowest half-life (<0,25hr) and photodegradates in a very short time which makes it not possible to calculate the rate of photolysis. Also, DCF presents a rapid decline (over 60%) in the first hour of irradiation time. Similar effect of sunlight irradiation on KFN and DCF have also been reported by Matamoros et al. (2009) and Tixier et al. (2002). On the other hand, in the case of IBU, the determination of the kinetic equations, photolysis rate and half-life were not estimated because the substance did not exceed 50% of removal either under sunlight or in the dark. The rate constant from dark experiments, which is identical to the hydrolysis, was equal to rate constant from irradiated experiments and that indicated that the major mechanism of IBU was hydrolysis.

Table 1. Kinetic constants (k) and experimental half-lives ($T_{1/2}$) for photodegradation of the target compounds.

Compound	Short form	Molecular type	MW	pKa	k (h^{-1})	$T_{1/2}$ (h)
Naproxen	NPX	$C_{14}H_{14}O_3$	230.27	4.15	-	<1
Ibuprofen	IBU	$C_{13}H_{18}O_2$	206.29	4.59	-	-
Ketoprofen	KFN	$C_{16}H_{14}O_3$	254.3	4.45	0.115	6.0
Diclofenac	DCF	$C_{14}H_{10}C_{l2}NO_2\cdot Na$	318.14	4.14	-	<0.25

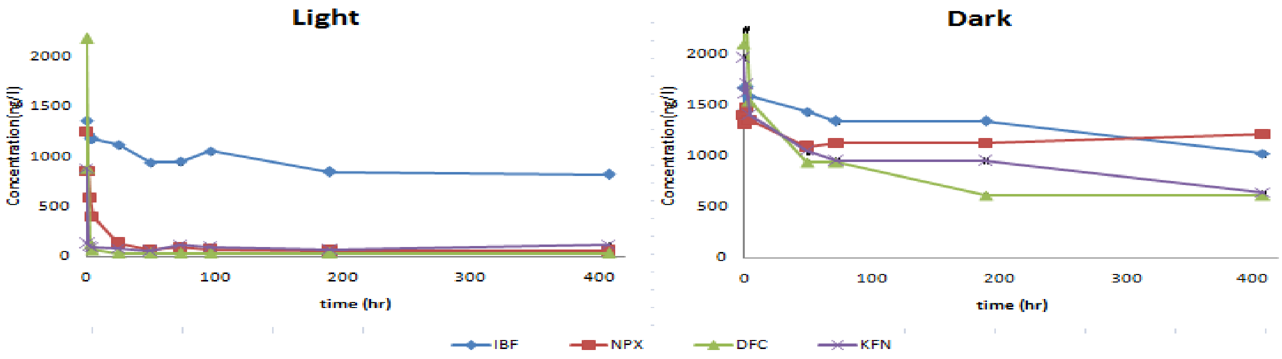

Figure 1. Photodegradation of the target compounds under light conditions and dark conditions

Effect of pH. In order to assess the effect of pH on process performance experiments were performed at three pH values (6, 7 and 8). According to the results, it was observed for all target compounds that their photodegradation rate was practically independent to pH (for the pH range that was studied).

Effect of humic acids. In order to evaluate the effect of the presence of humic acids on the removal of target compounds through photodegradation similar experiments were performed in water samples with a humic aid content of 20 mg/L. Based on the results it can be stated that the presence of humic acids in water inhibits most target compounds' photodegradation rate and this is because chromophoric moieties of HA compete with the compounds for irradiation absorption due to their spectra overlap, thereby inhibiting the direct photolysis. However this is not true for IBU which photodegradation rate seems not to be affected by the presence of humic acids in the water samples.

Effect of nitrates. The assessment of the effect of nitrates on photodegradation rate of the target compounds was examined for three alternative nitrates concentrations (0 mg/L, 1 mg/L and 10 mg/L). Based on the results, it can be stated that the effect on the removal of most of the target compounds is minimal and their degradation rates were similar in all tested nitrate concentrations. This is not valid for NPX which exhibit higher degradation rate with the increase of nitrate concentration. This is possibly based on the reaction of these compounds with the photochemically produced hydroxyl radicals (•OH).

CONCLUSIONS

Batch experiments were performed in order to assess the effectiveness of sunlight to remove selected anti-inflammatory drugs from water samples. According to photodegradation and hydrolysis experiments at neutral pH, DFC and KFN were found to be very unstable, with half-lives value lower than one hour. This indicates that photodegradation is the major mechanism for the removal of these compounds in the environment. On the other hand, IBU presents very low photodegradability. Among various parameters, the presence of humic acids seem to affect photodegradation rate, whereas the effect of pH and nitrates is rather minimal for most of the target compounds. The effect of nitrates and humic acids on the photodegradation rate of the substances is in accordance to the absorption spectrum of each substance and the produced photosensitizers.

ACKNOWLEDGMENTS

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(S24) TiO_2-assisted photocatalysis for selected Endocrine Disrupting Compounds removal from treated municipal wastewater

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Abstract

This work studied the degradation of selected endocrine disrupting compounds by means of photocatalysis. Lab-scale experiments with TiO_2 as photocatalyst took place, while filtered secondary effluent was the aquatic medium. For most of the EDCs the removal rate was higher than 90% for both concentrations of photocatalyst used except for clofibrate (50%) and norethindrone (70% and 30% for 0.5g/L and 0.1g/L TiO_2 respectively). For most of the compounds, the kinetics of oxidation followed a second order model.

Keywords

Photocatalysis; advanced oxidation processes; endocrine disrupting compounds

INTRODUCTION

Endocrine disrupting compounds (EDCs) are chemicals, natural or synthetic, which can affect the endocrine system of human, wildlife and aquatic organisms (Jiang et al., 2013). Pharmaceuticals, personal care products and plastics are the main sources of EDCs in the environment. Due to their continuous entry in the environment, the toxicity and the unknown side effects, EDCs are classified in the group of emerging micro-pollutants. The most frequently detected EDCs are estrogens (estrone, 17β-estradiol, ethinylestradiol, norethindrone), androgens (androsterone, stanolone), plasticizers (Bisphenol A, 2,4-Di-tert-butylphenol), carbamazepine, iminostilbene, triclosan, the group of fibrates (clofibrate, clofibrate methyl, clofibric acid) and chlorophenols (2,4-Dichlorophenol, 2,3,4-Trichlorophenol, 4-Chlorophenol). EDCs enter the municipal wastewater treatment plant (WWTP) mostly from human use. Elimination of the majority of the endocrine disrupting compounds during wastewater is often insufficient resulting in contamination of natural water bodies. EDCs have been detected in drinking water (carbamazepine 30 ng/L (Ternes, 2001)), in surface water (carbamazepine 6,3 μg/L (Ternes, 1998), triclosan <1-100 ng/L (Xie et al., 2008), clofibric acid 0.55-103 ng/L (Nunes et al., 2008)) and in the influents and effluents of WWTPs (clofibrate 0.8 μg/L, clofibric acid 1.6 μg/L, norethindrone 0.28-1.01 μg/L, ehtinylestradiol 42ng/L, Bisphenol A) (Nunes et al., 2008; Ternes, 1998; Tabak et al., 1981).

Several promising options for the EDCs removal from treated municipal wastewater are now available including Advanced Oxidation Processes (AOPs). AOPs are more sufficient than conventional treatment processes. Photocatalysis is one type of AOPs in which an electron of a semiconductor is promoted by UV light from the valence band to the conduction band. This results in the formation of hydroxyl radicals. The most commonly used photocatalyst is TiO_2 because of its stability and low cost. The objectives of this work were to study the degradation of selected endocrine disrupting compounds by means of photocatalysis. Lab-scale experiments with TiO_2 as photocatalyst took place, while filtered secondary effluent was the aquatic medium.

MATERIALS AND METHODS

Materials

Degussa P25, consisting of 80% anatase and 20% rutile TiO_2, was used. The surface area of Degussa

P25 is $50 m^2/g$.

The following EDCs were studied: 4-Chlorophenol, Iminostilbene, 19-Norethindrone, 2,3,4,-Trichlorophenol, 2,4-Dichlorophenol, Estrone, Carbmazepine, Clofibrate, Triclosan, Clofibric acid, Bisphenol A, 17-beta-Estradiol and 17-beta-Estradiol.

Secondary effluent samples were collected from the Chania Municipal Wastewater Treatment Plant (Chania, Crete, Greece). The samples were filtered through GF/C 47mm Whatman filters. The characteristics of the sample are given in Table 1.

Table 1. Characteristics of the secondary effluents samples

TSS	BOD	COD	TOC	pH	Conductivity
4 mg/L	4 mg/L	25 mg/L	3.2 mg/L	6.58	1.82 mS/cm

Photocatalysis experiments

For the photocatalytic experiments the secondary effluent samples were spiked with the selected EDCs, which were previously dissolved in ultrapure water without the use of organic solvents. The experiments were conducted in a lab-scale photocatalytic reactor. The photoreactor system was a quartz cylinder with an annular cross-sectional area. This annular space surrounded a 9W UV lamp. Cooling of the photoreactor took place by circulating water. Two different concentrations of TiO_2 (0.5 and 0.1g/L) were studied.

Analytical methods

Analysis of EDCs was performed by Solid Phase Micro-Extraction (SPME) coupled with Gas Chromatography (Shimadzu 17 A Model GC)-Mass Spectroscopy (Shimazdu QP5050A model MS detector) (Antoniou et al., 2009). 10 mL of water sample was placed in a vial (15 mL, Supelco). 2.3g sodium chloride were added and the pH was adjusted to 3 with the addition of H_2SO_4 0.1N. The sample vials were sealed with screw cap and PTFE-silicon septa and placed in a water bath, in order to maintain a constant temperature. The needle of the SPME device pierced the septum of the vial and the fiber was exposed for 60 min to the sample at 50^oC, while the sample was stirred with a PTFE-coated magnetic bar. The fiber was then withdrawn into the needle and immediately transferred into the GC injector. The analytical column was Sigma-Aldrich Supelco SLB^{TM} 5 MS fused silica capillary column (30m×0.25mm×0.25μm of film thickness). Injections were performed in the splitless mode and the carrier gas (helium) flow was 1.0 mL/min. The method had very good repeatability, since the RSD% ranged from 2.03-18.03%. The detection limits of the compounds ranged from 0.0055-1.44μg/L and the relative recoveries in the secondary effluents samples were high (76-134%). Dissolved Organic Carbon (DOC) was monitored with a Shimadzu 5000A TOC analyzer.

RESULTS

Figure 1 presents the removal rates of the specific EDCs by means of photocatalysis for two photocatalyst levels: 0.1 and 0.5 mg/L. For most of the EDCs the removal rate was higher than 90% for both concentrations of photocatalyst except for clofibrate (50%) and norethindrone (70% and 30% for 0.5g/L and 0.1g/L TiO_2 respectively). Estone, 17β-estradiol, Bisphenol A and clofibric acid showed very high removal rates for 0.5g/L TiO_2 in less than 30min. Despite the high removal rates for the selected EDCs only 26.8% and 2.9% (0.5g/L and 0.1g/L TiO_2 respectively) of the initial DOC was removed by photocatalysis after 6h. This indicates that the DOC did not compete with the EDCs. Among the two different concentration of photocatalyst, 0.5g/L of TiO_2 is more effective than 0.1g/L since degradation required less reaction time.

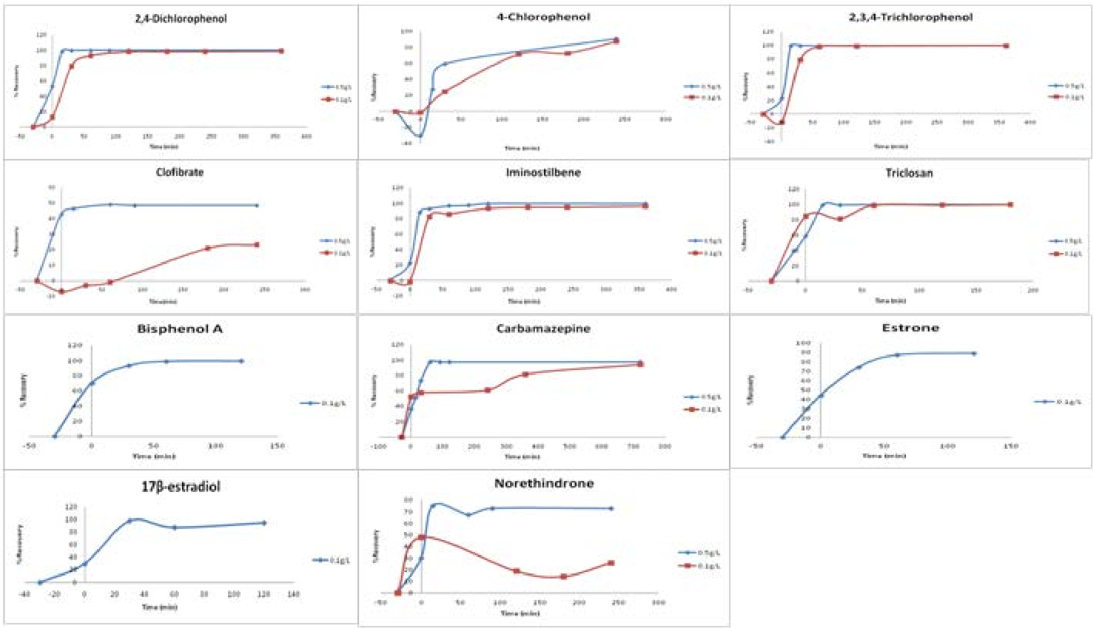

Figure 1. Removal of selected EDCs by photocatalysis. Photocatalyst concentration: 0.5g/L (blue line) and 0.1g/L TiO_2 (red line)

In general, the removal of ECDs by photocatalysis could be affected by various parameters, such as the type of EDC, type of photocatalytic reactor, initial concentration of EDCs, type of photocatalyst, radiation intensity, etc. Hyun-Seok et al. (2009), have shown that triclosan has been effectively (80%) removed in 60min with 0.1g/L TiO_2. Czech et al. (2013) have shown approximately 80% photoremoval for estrone after 4h of photocatalysis by using a different kind of TiO_2 (TiO_2-S21).

The removal of 2.4-Dichlorophenol, 4-Chlorophenol, 2,3,4-Trichlorophenol, clofibrate, iminostilbene, triclosan, Bisphenol A and estrone followed a second order kinetic model, while first order kinetics were more suitable for carbamazepine. For some EDCs it was not possible to find a suitable kinetic model due to their low levels.

CONCLUSIONS

Photocatalysis proved to be an efficient method for EDC removal from secondary effluent. The high dose of the photocatalyst (0.5 g/L TiO_2) was more effective than the lower dose (0.1g/L). For most of the EDCs the removal rate was higher than 90% for both concentrations of photocatalyst except for clofibrate (50%) and norethindrone (70% and 30% for 0.5g/L and 0.1g/L TiO_2 respectively). For most of the compounds, the kinetics of oxidation followed a second order model.

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(S25) Removal of heavy metal ions from wastewater using industrial waste sludge

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Abstract

In former Sisak Steelworks steel pipes were galvanized by hot-dip galvanizing procedure through immersing in molten zinc. Until year 2000, 900.000 tonnes of galvanized pipes were produced. In one phase of the process, preparation of pipes by chemical treatment, around 70.000 m^3 of neutralization sludge were generated and disposed of in the landfill site.

The physical-chemical properties of sludge were determined using X-ray diffraction technique (XRD), scanning electron microscopy (SEM) equipped with the EDS detector and Brunauer-Emmett-Teller method. Preliminary results indicate that the investigated industrial waste sludge is a non-hazardous with relatively high surface area and can be used for removal of heavy metal ions (Cr_{TOT}, Ni^{2+}, Cu^{2+} and Zn^{2+}) from wastewater.

Keywords

Neutralization sludge; removal; heavy metals; wastewater

INTRODUCTION

On the territory of Croatia industrial landfills are numerous and certain danger to the environment pose the metallurgical and metal processing industries whose waste such as slag, dust, sludge and similar could be dangerous sources of pollution. In former Steelworks in town Sisak galvanization of steel pipes were conducted by process of hot-dip galvanization by immersing in molten zinc. The procedure of pickling with sulphuric acid in the phase of the pipes preparation for galvanization caused emergence of neutralization sludge. In this phase of chemical preparation of pipes 70.000 m^3 of sludge were created from year 1970 to 2000. Through the years it were disposed in the landfill site what today constitute one of the “industrial lagoons” overgrown by vegetations.

In this paper, characterization of waste sludge was performed by means of XRD, SEM-EDS analysis and Brunauer-Emmett-Teller (BET) method. Also, investigation of possible application of waste sludge, as low cost sorbent, for heavy metal removal was performed.

Experimental

The sample of neutralization sludge was taken on middle part of lagoon on depth of 10 to 100 cm. After removing organically parts sludge was dried, homogenized and reduced by method of quartering. The morphology and chemical compositions of the waste sludge were determined by means of the scanning electron microscopy (Tescan Vega) equipped with the EDS detector. The mineral composition of waste sludge was analysed by X-ray diffraction, using a Shimadzu diffractometer XRD 6000 with CuKα radiation (40 kV, 30 mA, 0.02° steps from 5° to 65°). Specific surface area of powders was determined by a Brunauer–Emmet–Teller (BET) N_2 gas adsorption-desorption isotherm obtained at 77 K on a Micromeritics ASAP 2000 equipment (previously degassed at 50 °C under a dynamic vacuum). Removal of heavy metal ions (Cr_{TOT}, Ni^{2+}, Cu^{2+} and Zn^{2+}) from wastewater was monitored by flame atomic absorption spectrometer (AAS), AA-6800, Shimadzu.

RESULTS, DISCUSSION AND CONCLUSION

According to results of XRD and SEM-EDS analysis (Figure 1) neutralization sludge is consist of $CaSO_4$ x 2 H_2O – gypsum, $CaSO_4$ x 0.5 H_2O – calcium sulfate hydrate, Fe_2O_3 – hematite and FeO(OH) – goethite. Results of surface area properties obtained by BET method are shown in Table 1.

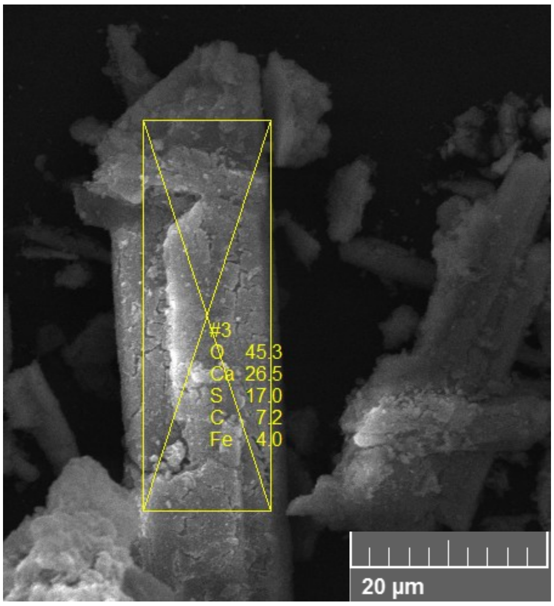

Figure 1. SEM-EDS image of neutralization sludge with corresponding EDS analysis of O, Ca, S, C and Fe.

Table 1. Results of surface area properties.

Surface area, m^2 g^{-1}	S_{BET}	39,8
Pore volumes, cm^3 g^{-1}	V_p	0,0923
Micropore volumes, cm^3 g^{-1}	V_{mp}	0,0009
Average pore diametar, nm	d_p	8,5

Table 2. Amount of removal of heavy metal ions (Cr_{TOT}, Ni^{2+}, Cu^{2+} and Zn^{2+}) by industrial waste sludge as function of contact time.

t / h	µg M^{n+} /g sludge			
	Cr_{TOT}	Ni^{2+}	Cu^{2+}	Zn^{2+}
0.5	0.95	7.1	104	97
1	0.95	8.3	106	99
5	0.95	8.85	112	104

The heavy metal removal efficiency depends on the chemical composition and surface properties of sludge (Lopez et al., 1998 and Rađenović et al., 2013). Results of surface analysis and mineral composition indicates the possibility of using neutralization sludge in removal of heavy metal ions from wastewater of galvanization process what was also confirmed by AAS analysis. Initial concentration of Cr_{TOT}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions in wastewater of galvanization process was 0.019 mg dm^{-3}, 0.191 mg dm^{-3}, 2.86 mg dm^{-3} and 2.189 mg dm^{-3}, respectively. Removing of metal ions from the wastewater was performed by mixing of the sludge with the wastewater (ratio Solidus/Liquidus = 1 g/50 cm^3) at different contact times (0.5, 1 and 5 h). Obtained results are presented in Table 2. Equilibrium contact time was found to be 30 min.

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(K6) Removal of Micropollutants from Secondary Effluents and Sludge by Various Processes in Rural and Peri-urban Areas

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Abstract

The present work details the results of a comprehensive study dealing with the fate of several families of micropollutants (with various physicochemical properties) through tertiary treatment processes of water and through sludge treatments. Powerful and sensitive analytical techniques were used: 16 metals and 39 organics (pharmaceuticals, polycyclic aromatic hydrocarbons, alkylphenols, pesticides) were analysed in wastewaters; 14 metals and 62 organic hydrophobic micropollutants were measured in sludge (estrogenic hormones, polychlorinated byphenyl, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, alkylphenols and other organics).

We studied treatment processes adapted for rural areas involving low energy-consumption: trench system, polishing pond, horizontal subsurface flow constructed wetlands with various adsorbing materials (i.e. expanded clay, zeolite, activated carbon, apatite, gravels) running at tertiary stage of water treatment; and sludge drying reed-bed operated at two different resting periods.

Our results show that the trench system was not efficient for additional removal of refractory micropollutants. The polishing pond had higher removal efficiencies (between 30 and 70%) for some pharmaceuticals due to indirect photodegradation. The horizontal subsurface flow constructed wetland (HSSF-CW) built with activated carbon showed almost full-removal during more than 330 days for pharmaceuticals, pesticides, several metals and nonylphenoxyacetic acid. For the HSSF-CWs built with expanded clay or zeolite, we obtained removal efficiencies of 70% for half of studied pharmaceuticals and alkylphenols mono- and di-ethoxylates. The removal efficiencies of other substances were much lower than the ones measured with activated carbon, but they were still higher than the ones measured with gravel (filter designed for denitrification) or apatite (designed for phosphorus removal). Due to better oxygen conditions, the sludge drying reed-bed with low frequency of sludge input resulted in better removal for organic micropollutants than the sludge drying reed-bed with high frequency of sludge input.

Keywords
Emerging and priority micropollutants, energy-free process, rural areas.

INTRODUCTION

Reducing the inputs of micropollutants to the environment by wastewater treatment facilities is expected to protect the quality of aquatic systems and drinking water resources. Conventional treatments plants usually remove several micropollutants by biodegradation and/or by adsorption onto sludge (Miège *et al.*, 2009; Martin Ruel *et al.*, 2010; Choubert *et al.*, 2012). But several refractory micropollutants are always measured in treated effluents discharged to the environment (e.g., several pharmaceuticals, pesticides and nonylphenoxyacetic acid). Energy-consuming processes involving oxidation or adsorption on activated carbon are widely studied (Lester *et al.*, 2011) and proposed to stakeholders as a solution to face micropollutants problem in urban areas. Alternatively, in the context of rural and peri-urban areas, energy-free tertiary treatment processes like ponds or constructed wetlands were shown to remove pharmaceuticals in planted or unplanted systems (Matamaros *et al.*, 2008; Tchobanoglous and Leverenz, 2011; Li *et al.*, 2014) or adsorbent materials (Dordio *et al.*, 2010; Tahar *et al.*, 2013). Nevertheless, the fate of other families of micropollutants in these processes is still poorly documented. Also, sludges from secondary wastewater treatment are often treated by drying reed-beds in small treatment plants, before being applied on land for crop growth. The possible reduction of hydrophobic micropollutants like hormones, polycyclic aromatic hydrocarbons (PAH), alkylphenol (AKP), polychlorinated byphenyl (PCB) and polybrominated diphenyl ethers (PBDE) in such process is of particular concern.

The present work determines the removal efficiencies of various priority and emerging substances by a wide range of energy-free processes devoted to the context of rural areas (involving passive aeration supply) for tertiary water treatment and for sludge treatment. Special care was taken to ensure the reliability of sampling, analysis and calculation of removal efficiencies.

MATERIAL AND METHOD

Studied processes

Seven tertiary treatment processes were evaluated:

- 1 trench system of 80 meters-long, built on not-permeable soil (450 P.E.), hydraulic retention time (HRT) of 10 minutes;
- 1 polishing pond of 2,570 m^2 (1000 P.E.), HRT of 15 days;
- 3 unplanted⍰ horizontal subsurface flow constructed wetlands (HSSF-CW) at pilot-plant scale, one was filled with activated carbon (HRT = 1.5 h), one with expanded clay and one with zeolite (HRT = 24 h);
- 2 unplanted HSSF-CW of 60 m^2 each (50 P.E), one filled with gravel designed for denitrification, and one filled with apatite designed for phosphates precipitation (HRT = 24h).

Two sludge drying reed-beds were evaluated: one operated with a high frequency of sludge input (with 2 days feeding period and 14 days resting period), and the other one with a low frequency of sludge input (with 2 weeks feeding period and 14 weeks resting period).

Sampling

Influent and effluent water samples were taken in the inlet and outlet of each studied treatment stage. Automatic refrigerated samplers equipped with Teflon tubings and glass containers were used to set-up flow-proportional composite samples during dry weather conditions for each treatment plant. Sludge samples were collected at 2 depths (middle and bottom of a sludge blanket of 70 cm), twice for each site at 2-year interval.

Chemical analysis

Reliable analytical methods with low limits of quantification (LQ) were applied for the analysis of 55 micropollutants in the dissolved phase of wastewater: 16 metals, 19 PAH, 5 AKP, 4 pesticides and 11 pharmaceuticals (2 antibiotics, 4 betablockers, 5 analgesics/antidepressors), and among them 17 are priority substances of the water framework directive (WFD). Also, 76 micropollutants were analysed in the particulate phase of sludge, including 14 metals, 19 PAH, 4 AKP, 5 estrogenic hormones, 7 PCB, 18 PDBE and 9 other organics including di-2-ethylhexyl phthalate (DEHP), di-butylphtalate, triclosan, galaxolide, tonalide and bisphenol A.

RESULTS AND CONCLUSIONS

Concentrations of micropollutants in tertiary influents and sludge

In the 14 samples of tertiary influents (=secondary effluents) of rural areas, we quantified 14 metals and 31 organic micropollutants. Moreover, 10 organic micropollutants were always quantified at concentrations above 0.1 µg/L, including 8 pharmaceuticals (metoprolol, propranolol, sotalol, sulfamethoxazole, carbamazepine, ibuprofene, paracetamol, diclofenac), one AKP (nonylphenoxyacetic acid (NP1EC)) and the aminomethylphosphonic acid (AMPA). Other measured micropollutants were never quantified (e.g. 6 PAH and 12 antibiotics). Two metals (tin, uranium) and 2 pesticides (isoproturon, glyphosate) were measured in 50% of influent samples.

In the 6 samples of sludge from drying reed-beds, we quantified all metals and 48 organic micropollutants. We only quantified one hormone (estrone) and the 4 other studied were never quantified (17β-estradiol, 17α-ethinylestradiol, estriol and 17α-estradiol) for which the limit of quantification (LQ) was below 5 ng/g of dry matter (DM). PCB and most PBDE were always quantified at very low concentrations, respectively below 20 ng/g DM and 50 ng/g DM (except BDE209 between 800 and 6000 ng/g DM). Benzothiazole, tertbutylphenol and pentachlorophenol were never quantified (LQ of 200 ng/g); whereas galaxolide, tonalide and triclosan were always quantified, with a maximum concentration of 350, 16 and 12 ng/g DM, respectively. Di-butylphtalate, DEHP and bisphenol A were quantified in 50% of sludge samples.

Removal efficiencies of micropollutants by tertiary treatment processes

For the overall tertiary treatment processes, removal efficiencies (Rw) could be determined for up to 15 metals and up to 18 organic micropollutants. The numbers of Rw in each range (<30%; 30-70%; 70-90%; >90%) are shown Figure 2 for each studied tertiary treatment.

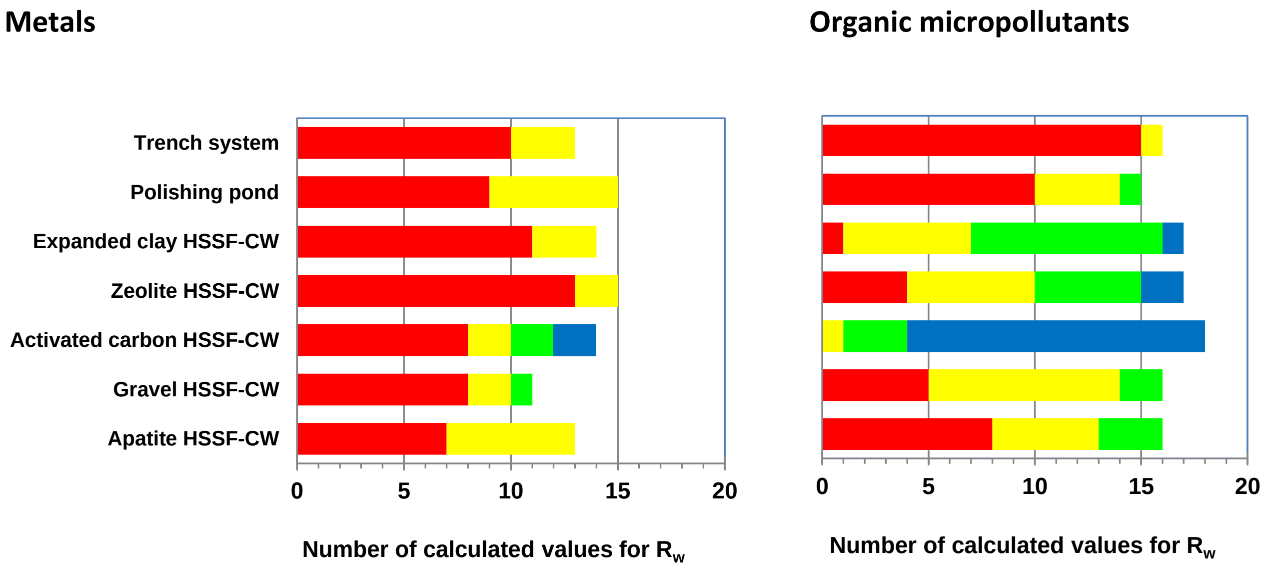

Figure 2. Classification of removal efficiencies (Rw) for various tertiary water treatments
<30% (■); 30-70% (■); 70-90% (■); >90% (■)

The trench system showed low removal efficiencies (Rw<30%) for a majority of refractory micropollutants. Only some Rw were between 30 and 70% due to adsorption on clay (cobalt, zinc, cadmium) or photodegradation (ibuprofen, paracetamol). The polishing pond showed higher Rw values (between 30 and 70%) for 5 pharmaceuticals (diclofenac, sotalol, propranolol, atenolol, roxythromycin) due to indirect photodegradation (half-life time around 4 to 20 h) during the HRT of 15 days. Other micropollutants had their concentrations unchanged in the process and stil above 0.5 µg/L (e.g. carbamazepine, AMPA and NP1EC).

For activated carbon horizontal subsurface constructed wetlands (HSSF-CW), removal efficiencies of organic micropollutants around 100% during more than 330 days for 3 metals (chrome, cobalt, cuivre), all studied pharmaceuticals, pesticides and NP1EC (by-product of alkylphenol polyethoxylates). Only nonylphenol and other metals obtained lower removal efficiencies. For expanded clay HSSF-CW or zeolite HSSF-CW, removal efficiencies of micropollutants were > 70% for half of the studied pharmaceuticals (propranolol, sotalol, sulfamethoxazole, diazepam, ibuprofen, carbamazepine (except zeolite)) and 2 alkylphenols (octyl- and nonylphenol). The removal of other substances were much lower than the ones measured with activated carbon; nonetheless, Rw were much higher for expanded clay HSSF-CW than for gravel HSSF-CW designed for denitrification, or apatite HSSF-CW designed for phosphorus removal.

Removal efficiencies of micropollutants by sludge drying reed-beds

For the sludge treatment, removal efficiencies (Rs) could be determined for up to 15 metals and up to 34 organic micropollutants. The numbers of Rs in each range (<-30%;-30 to +30%; >30%) are shown on Figure 3 for each sludge treatment.

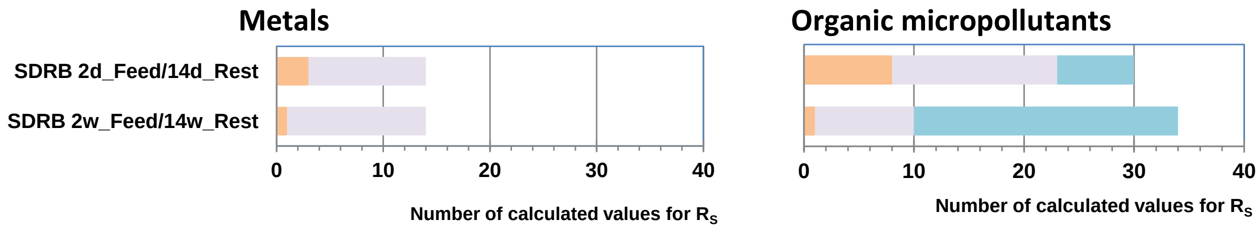

Figure 3. Classification of removal rates (RS) for the 2 sludge drying reed-beds <-30% (■);-30 to +30% (■); >30% (■)

Due to good oxygen conditions in the SDRB with low frequency of sludge input (2w_Feed/14w_Rest), this process had a majority of Rs > 30% due to biotransformation in aerobic conditions (i.e., for estrone, nonylphenol, 7 PAH, 7 PCB, 5 PBDE and 3 other organics (galaxolide, tonalide, triclosan)). Nevertheless, the Rs values only reached a maximum of 50% for some of the substances concerned (e.g. PAH, nonylphenol, estrone, galaxolide, triclosan, DEHP). The SDRB with high frequency of sludge input (2d_Feed/14d_Rest) had a majority of Rs values between -30% and +30% (as oxygen was lacking, micropollutants could not be biotransformed and concentration were unchanged,). Similar Rs values were measured whatever the studied SDRB: >30% for nonyphenol mono- and diethoxylates, DEHP; between -30% and +30% for metals.

Future research

In addition to source-reduction policy, we demonstrated the efficiency of some low-cost treatment processes for removal of refractory micropollutants before release of effluents in the environment. Future research will focus on the economic and environmental benefits of low-cost adsorbents in horizontal subsurface flow constructed wetlands. Also, other tertiary treatments are under study for refractory micropollutants, like successive low depth natural basins or trench with soil infiltration.

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(P28) Micropollutants Removal in MBR Reactors: A comperative study

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Abstract

Over 1 billion people is estimated short of potable water. Membrane Bioreactors (MBR) can facilitate reuse of wastewaters and create additional resource provided they produce safe water. Removals of selected endocrine disrupter compounds (EDCs), namely, diltiazem, progesterone, estrone and carbamazepine, as model micropollutants, were comparatively investigated in two full scale and one pilot scale MBR plants. The natural EDCs, estrone and progesterone, could be effectively treated in these plants. Flux rates had marginal effects on the removals. Carbamezapine was not removed in any of the MBR plants; whereas ditltiazem could be removed in one of the three plants studied, possibly by adsorption onto the membranes. The painkiller Acetamiophen was removed by biodegradation in all three plants. Studies on activated sludge plants, CAS and BNRs, revealed a totally different picture where all five EDCs were almost entirely removed by both biodegradation and adsorption onto sludge.

Keywords

EDCs, Endocrine Disruptors removal, MBR, Pharmaceuticals

INTRODUCTION

Currently over 1 billion people is estimated short of adequate potable water and this is expected to increase to 2.5 billion in the year 2025. Membrane Bioreactors (MBR) are now accepted as important tools to extend availability of water by facilitating reuse of wastewaters. Apart from the membrane materials, Sludge Retention Time (SRT) and liquid flux rate are the two important parameters for controlling the MBR process. In this study, removal of selected endocrine disrupter compounds (EDCs), namely, diltiazem (Dtz), progesterone, estrone and carbamazepine (Cbz), as model micropollutants, were comparatively investigated at differing flux rates in two full scale and one pilot scale MBR plants. Summary of the performance characteristics of the studied plants are given in Table 1.

ANALYTICAL METHODS

All the tested plants were effectively operating and producing effluents acceptable for unrestricted re-use. Composite samples were drawn from influents, effluents and grab samples were collected from sludge wastage line. Additional liquid samples were drawn from the MBR aeration tanks in the case of METU plants. Aeration tank samples were decanted for 30 mins. and supernatants were analyzed for the micropollutants to differentiate between biodegradation and membrane effects. Liquid samples were analyzed after concentrating and cleansing by SPE technology and using LC/MS/MS according to a published method by the authors. Dried sludge samples were initially extracted by sonication and then followed the same route as with the liquid samples.

Table 1. Characteristics of the studied MBR plants.

	ClearBox (Pilot)	**VRM Plant**	**Konacik**
Storage tank volume (m^3)	0.35	10	115
Aeration Tank Volume (m^3)	0,75	85	Anox: 180 Aerobic: 600
MBR tank volume (m^3)	0,75	23	64 x 2
Membrane Type	plate and frame	plate and frame	Plate and frame
Total Membrane Area	3(m^2)	540(m^2)	2560(m^2)
Membrane Material	polyethersulfones	PES	PES
Nominal Pore Size (µm)	0.038	0.038	0.04
Sludge Retention Time	10(days)	10(days)	25(days)
Flux (L/h-m^2)	13.3-26	13.3-30	18
SRT (d)	10	10	25
HRT (h)	18	18	16
Type	Flat sheet/ vacuum/ Static /	Flat sheet/ vacuum/ rotating	Flat sheet/positive pressure / Static
MLVSS	4-8 gL^{-1}	4-8 gL^{-1}	4 gL^{-1}
Flow	1 m^3 d^{-1}	200 m^3 d^{-1}	1100 m^3 d^{-1}
N-Removal	NO	NO	YES
Feed	domestic ww	domestic ww	domestic ww

RESULTS AND DISCUSSION

Konacik Plant

As can be seen in fig. 2 diltiazem and carbamezapine, the two most commonly prescribed pharmaceuticals as blood thinners and antiepileptics, respectively, are not at all treated in this plant. Whereas the pain killer acetaminophen is completely removed. The anaylsis of sludge samples did not reveal any significant accumulation of acetaminophen in sludge indicating that it was more or less completely biodegraded

METU VRM Plant

The diltiazem behaved rather odd in the VRM plant as it was present in the supernatants but totally absent in the final effluents. It is evident that diltiazem was not removed biologically in the aeration tank as the concentration in the influents and *supernatants* were more or less identical in most of the samples. However diltiazem was totally absent in the filtered effluent meaning that it was totally removed in this system either biologically under low D.O. conditions prevailing in the VRM chamber or by adsorption onto the membranes. Yet Konacik plant or the pilot plant at METU, which shares the same influent and seed sludge as with the VRM, did not show this behavior. This remains to be explored. Removals of other selected EDCs, in the METU VRM plant are depicted in fig. 4. As can be seen from this figure the natural hormones, estrone and progesterone, and the pain killer acidaminophen were completely removed in this plant. Sludge analysis revealed no residuals of these suggesting complete biodegradation. Whereas, carbamezapine was not removed at all.

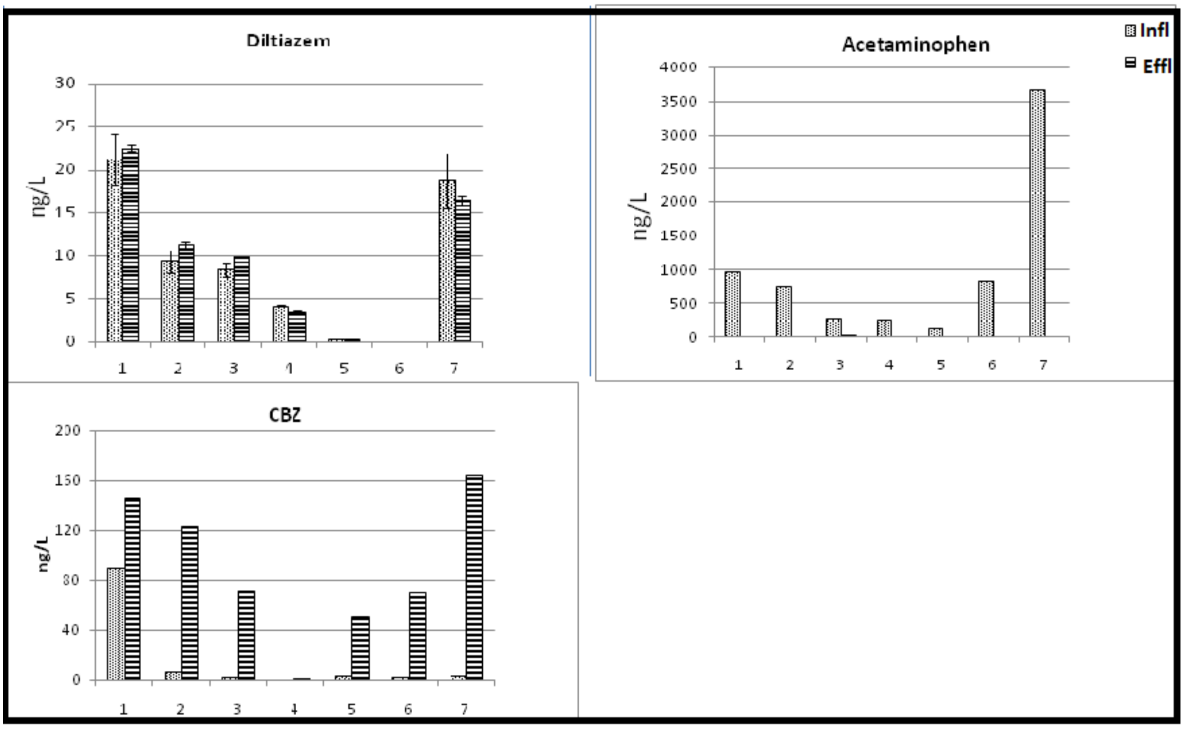

Figure 2. Removals of selected micropollutants in Konacik MBR plant.

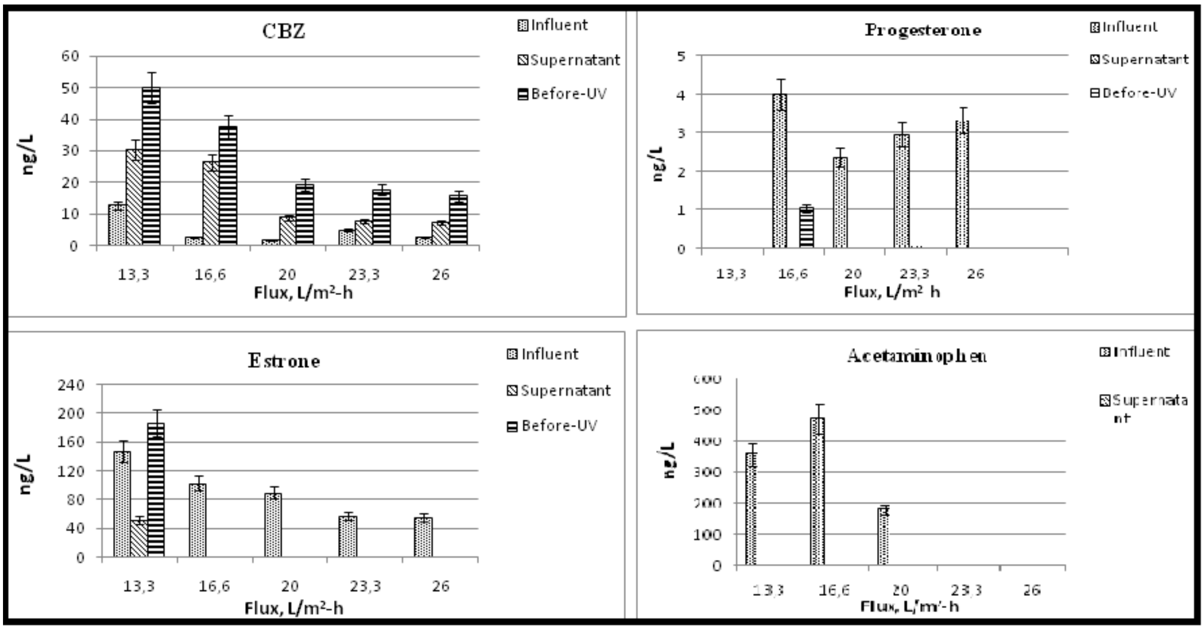

Figure 4. Removals of selected micropollutants in METU-VRM MBR plant.

METU (ClearBox) Pilot MBR Plant

Removals of selected EDCs in the pilot MBR are depicted in fig. 5. It is readily seen from this figure that the natural hormones, estrone and progesterone, and the painkiller acetaminophen were completely eliminated from effluents by way of biodegradation since both supernatants and permeates did not contain any of these. Whereas carbamezapine was not removed at all in this plant, which is consistent with the other MBR plants. Diltiazem was also not removed in this plant as influent, supernatant and effluent concentrations were identical.

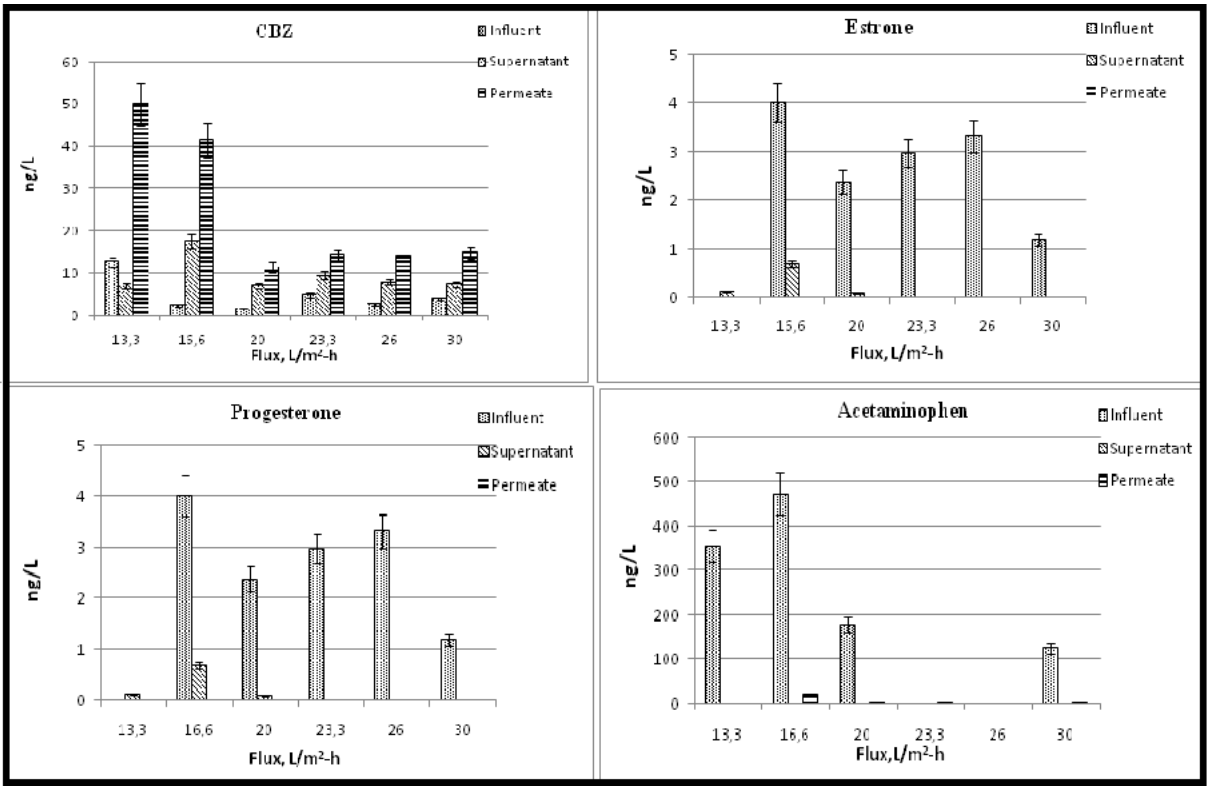

Figure 5. Removals of selected micropollutants in METU-Pilot MBR plant.

EDC Treatment in Conventional Biological Treatment Plants

Studies on activated sludge plants, CAS and BNRs, revealed a totally different picture where all five EDCs were almost entirely removed from effluents both by biodegradation and/or adsorption onto sludge. Carbamezapine is given here as example, which is not treatable in MBR plants, was perfectly treated in CAS plants as shown in Fig. 6 for a 700 000 m^3d^{-1} CAS (Ankara Tatlar) and a 100 000 m^3d^{-1} (Eskisehir) BNR plant. This behaviour immediately suggests differences in the nature of sludges. For example activated sludge might have been more hydrophobic due to selection pressure by the gravity settlers while MBR sludge being more hydrophilic in the absence of a selective pressure. This remains to be explored.

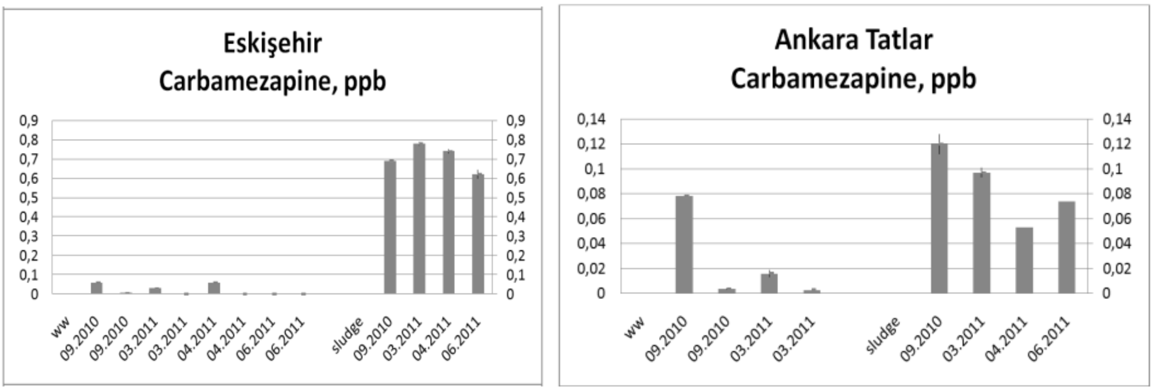

Figure 6. Carbamezapine removals in two activated sludge plants

(P29) Technical, economic and environmental evaluation of advanced tertiary treatments for micropollutants removal (oxidation and adsorption)

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Abstract

Two pilots for tertiary treatment, an advanced oxidation processes (AOP - O_3/UV/H_2O_2) pilot and a granular activated carbon pilot, were tested in three different wastewater treatment plants after a secondary treatment. A total of 64 micropollutants including drugs, pesticides, alkylphenols, PAHs and metals were analysed in the samples at the inlet and the outlet of the pilots. The tertiary treatments studied (ozone, AOP and activated carbon) were efficient for the removal of most of the compounds analysed in this study, except metals. The addition of hydrogen peroxide to ozone increased the number of substances well removed but it did not improve the removal of substances that readily react with ozone (such as betablockers or carbamazepine). The other AOP (ozone/H_2O_2 and UV/H_2O_2) did not improve the number of substances well removed in comparison with ozone alone. The granular activated carbon was still efficient (R>70%) after 6 months working 24/7 for most of the drugs and the urea and triazine pesticides. The 5 technologies studied were sized at full scale in order to calculate their cost for two sizes of WWTP. The implementation of a tertiary treatment on a 60 000 to 200 000 PE WWTP would increase the wastewater treatment cost by 1,5 to 17,6 euros cents per cubic meter treated according to the technology and the removal objective. Concerning the environmental impact, for the big WWTP, the activated carbon is more impacting than the other processes for most of the impacts calculated. The order of POA by increasing environmental impact is ozone < ozone/H_2O_2 < ozone/UV ~ UV/H_2O_2. For the medium size WWTP however, the activated carbon is comparable to the other solutions regarding environmental impact.

Keywords

Ozone; Advanced Oxidation Processes; Granular Activated Carbon; Micropollutants removal; Cost; Environmental impact

INTRODUCTION

One of the next major challenges of wastewater treatment is to reliably remove micropollutants and the related toxicity from treated water. Although they were not initially designed for this purpose, conventional wastewater treatment plants (WWTP) can eliminate part of the micropollutants by adsorption on sludge, biodegradation and/or volatilisation (Choubert *et al.*, 2010). However, some micropollutants remain in treated wastewater. Tertiary treatments can be implemented to help reaching concentration values compatible with a good status of the receiving water bodies.

This study was focused on two types of tertiary treatment investigated at pilot scale in three wastewater treatment plants. A pilot plant consisting in advanced oxidation processes (AOP) combining ozone, UV and hydrogen peroxide (Meier *et al.*, 2011) was tested in two plants with different upstream treatment processes: plant A, a membrane bioreactor; and plant B, a low load activated sludge followed by a sand filter. A granular activated carbon (GAC) filtration pilot was operated in plant C, a low load activated sludge followed by a sand filter and ozone for disinfection.

The objectives of the study were to evaluate and compare the performance of oxidation and adsorption for micropollutants removal, to assess the costs of these processes and their environmental impact.

MATERIAL AND METHODS

A total of 64 micropollutants were analysed in the samples of this study with several analytical techniques based on mass spectrometry. The selected substances and the analytical techniques are presented in table 1.

Table 1. Micropollutants analysed in this study and quantification methods.

Family of substances	Substances	Preparation/ Extraction	Analytical techniques	Limits of quantification (ng/L)
Betablockers (4)	Atenolol, metoprolol, propranolol, sotalol	SPE	HPLC/MS/MS	0.5 to 1
Antibiotics (10)	Sulfamethazine, sulfadimethazine, sulfamethoxazole, sulfadiazine, trimethoprim, erythromycin, roxithromycin, clindamycin, lincomycin, tylosin	SPE	HPLC/MS/MS	5 to 280
Other drugs (4)	Carbamazepine, diazepam, ibuprofen, diclofenac	SPE	HPLC/MS/MS	0.5 to 1
Herbicides, pesticides (2)	Glyphosate, AMPA	Derivation	HPLC/MS/MS	100
Herbicides, pesticides (4)	Atrazine, simazine, diuron, isoproturon	SPE	HPLC/MS/MS	5 to 15
Alkylphenols (6)	4-nonylphenol monoethoxylate, 4-nonylphenol diethoxylate, 4-nonylphenol, 4-ter octylphenol, 4-nonylphenoxyacetic acid, 4 ter butylphenol	SPE or SPME	LC/MS/MS and GC/MS	1 to 10
Polycyclic Aromatic Hydrocarbons (19)	Napthalene, dibenzothiophene, phenanthrene, anthracene, acenaphthylene, acenaphtene, fluorene, fluoranthene, pyrene, benzo(a)anthracene, chrysene + triphenylene, 2,1 benzo-naphtothiophene, benzo(b+j+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(c-d)pyrene, dibenzo(a,h + a,c)anthracene, benzo(ghi)perylene	SPME	GC/MS	0.1 to 1
Metals (15)	B, Ti, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Ba, Pb, U	-	ICP-MS	10 to 2000

MAJOR RESULTS AND CONCLUSIONS

Technical evaluation

Over 70% removal was obtained for 70% of the organic micropollutants studied by implementing ozone in optimized conditions (3 minutes contact time) and ozone dose (5 gO_3/m^3 ozone dose applied). Figure 1 displays the best results obtained according to the oxidation system.

Improvements resulting from AOPs concern:

- Compounds less reactive towards ozone: an addition of H_2O_2 to ozone increased the removal yield of pesticides by 5 to 50 %;
- Accordingly, removal yields of specific compounds were increased depending on operating conditions. For example, pesticides were better removed with the O_3/H_2O_2 solution with an excess of H_2O_2;
- Only the O_3/H_2O_2 system increased significantly the number of substances well removed (> 70%) in comparison with ozonation alone versus UV-AOPs.

However, the improvement’s extend may both depend on the conditions for AOP application and on the compound nature (aromatic rings, high electronic density functions...).

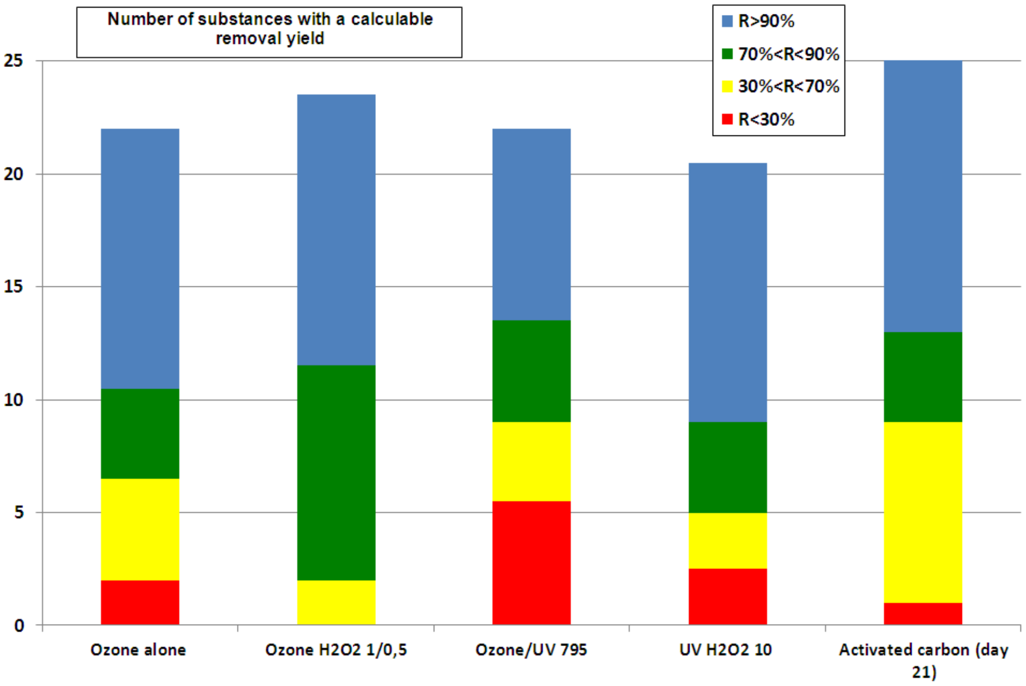

Figure 1. Number of organic substances with a calculable removal yield by categories for each of the advanced tertiary treatments applied in this study (under 30% red, between 30 and 70% yellow, between 70% and 90% green and over 90% blue).

The application of GAC filtration subsequent to ozone disinfection achieved high removal yields for drugs and pesticides, except glyphosate and AMPA. It is worth noting that the activated carbon treatment was still efficient for the removal of these molecules after 6 month operation. Some metals were also adsorbed by the activated carbon in particular at the beginning of the test (B, Cr, Zn, Pb) but the removal yield decreased over time. About 65% of the organic micropollutants studied were removed over 70% by GAC after 3 weeks functioning 24/7 (Figure 1). Removal yields of some of the organic compounds then decreased over time.

Economic evaluation

The investments and operations costs (CAPEX and OPEX) of the tertiary treatments studied were evaluated by extrapolating the results of the pilot trials to two hypothetical full scale wastewater treatment plants: a 200 000 PE WWTP and a 60 000 PE WWTP. The design of the full scale tertiary treatment was done considering an objective of at least 70% removal for 75% of the organic micropollutants analysed in this study.

As expected, treating the micropollutants may represent a significant specific additional cost:

- In proportion higher for a low/medium capacity of the plant than for a high capacity plant;
- Highly dependent on the technology;
- Additional treatment cost of 1.5 to 17.6 € cents per treated cubic meter of wastewater, corresponding to a bill of 1.3 to 16 € per inhabitant per year.

Environmental evaluation

The environmental impact of the tertiary treatment was assessed according to a Life Cycle Analysis methodology based on the operation of full scale treatments as defined in the economic study, allowing a comparison of the different technologies. However, the environmental impact evaluation is not a Life Cycle Analysis as only the operation phase was taken into account and not the construction phase.

For the 200 000 PE WWTP, the activated carbon is more impacting than the other processes for most of the impacts calculated (Figure 2), in particular for the impacts concerning land occupation, due to the activated carbon's end of life (in landfill in this study). The order of POA by increasing environmental impact is ozone < ozone/H_2O_2 < ozone/UV ~ UV/H_2O_2.

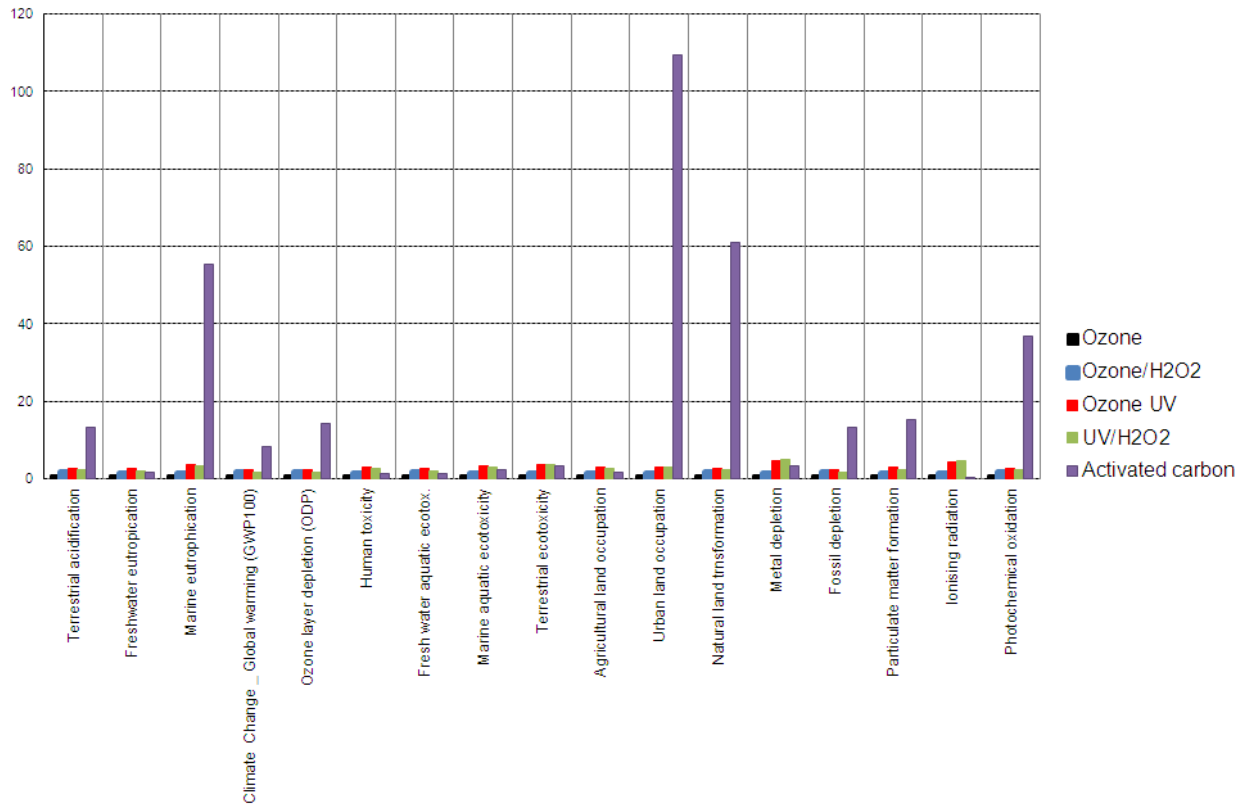

Figure 2. Normalised environmental impacts for the 200 000 PE WWTP

For 60 000 PE WWTP however, the activated carbon is comparable to the other solutions regarding environmental impact. The activated carbon is less impacting than AOPs concerning some impacts (ionising radiation, fresh water eutrophication and human toxicity) but it is more impacting for fossil depletion, particulate matter formation and land occupation impacts.

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(S26) Batch and continuous enzymatic reactors applied for the removal of bisphenol A by laccase

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Abstract

Removal of the endocrine disrupting compound (EDC) bisphenol A (BPA) by the enzyme laccase from *Trametes versicolor* was assessed in batch experiments in order to evaluate the effect of initial laccase concentration (500 and 1000 U/L) and pH (5, 6, 7) on the removal efficiency. The best conditions, pH 6 and 1000 U/L, were selected based on both enzymatic efficiency and percentage of BPA elimination after 1 h treatment. Then, an enzymatic membrane reactor (EMR) was applied to continuously remove BPA at the selected conditions. Different feed addition rates (43, 86 and 168 µg/L·h) were evaluated and a percentage of removal higher than 90% was attained. These results proved the viability of enzymatic reactors for the tertiary treatment of EDCs in real wastewaters.

Keywords
Laccase, Bisphenol A, Enzymatic membrane reactor

INTRODUCTION

During the last years, biological transformation of endocrine disrupting chemicals (EDCs) by ligninolytic enzymes has been developed as an attractive alternative to conventional oxidation processes due to the inherent advantages associated to these systems, e.g.: high oxidation potential of the enzymes, low energy requirements, simple control procedure and the non-toxic nature of the transformation products. Laccase (EC.1.10.3.2) is a multi-copper oxidase that catalyzes the one electron oxidation of substituted phenols, anilines and aromatic thiols to the corresponding radicals, with the concomitant reduction of molecular oxygen to water. A promising configuration for applying the free laccase as biocatalyst in a continuous operation mode consists of the use of an enzymatic membrane reactor (EMR). This system allows the separation of biocatalysts from products and/or other substrates by a semi permeable membrane that creates a selective physical/chemical barrier (L. Lloret et al., 2012).

In the present work, the enzyme laccase was proposed to perform the elimination of the phenolic EDC bisphenol A (BPA). Firstly, the effect of pH and initial laccase activity on the removal rate was evaluated in batch assays. Then, the most favorable conditions were selected to carry out the enzymatic transformation of BPA in a continuous EMR.

MATERIALS AND METHODS

BPA (99%), 2,2-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS) (98%) and laccase from *Trametes versicolor* were purchased from Sigma-Aldrich. Methanol (99.5%) and acetonitrile (99.8%) were purchased from J.T. Baker. Laccase activity was determined by the method described by Lloret at al. 2012.

Batch experiments for removing BPA by laccase were conducted in Erlenmeyer flasks in a final volume of 100 mL. The initial concentration of BPA was 10 mg/L and the reaction media contained 5% (v/v) methanol. Two different initial concentrations of laccase were assayed: 500 and 1000 U/L. Moreover, different pHs were evaluated: pH 5 by using 100 mM sodium acetate buffer and pH 6 and pH 7 by using 100 mM sodium phosphate buffer. BPA concentration in batch assays was quantified by HPLC.

Continuous removal of BPA was conducted in an EMR consisted of a stirred tank reactor (2 L, Biostat® MD, B. Braun-Biotech International) coupled to a nanofiltration membrane to permit the retention of the enzyme. Different feed addition rates (168, 86 and 43 µg/L·h) were assayed to investigate the effect of such parameter on the removal efficiency of BPA. BPA concentration in the effluent of the reactor was quantified by GC-MS.

RESULTS AND CONCLUSIONS

Initial laccase activity had a significant role on the removal rate of BPA and initial concentrations of 1000 U/L were necessary to achieve percentages of elimination higher than 95% after 1 h treatment (Table 1). The established criteria to choose the best conditions were, firstly, a percentage of oxidation higher than 95% and secondly the efficiency, defined as the ratio of the amount of BPA removed and the loss of enzyme activity. In this sense, although laccase stability was higher at neutral pH and the efficiency was also favored at pH 7, the percentage of elimination was considerably higher at pH 6: 96.3% versus 83.2% at neutral pH. The use of pH 5 was discarded due to the high enzyme deactivation. Therefore, pH 6 and 1000 U/L were the selected conditions to carry out the conversion of BPA in the continuous operation mode.

Table 1. Residual percentage of BPA and enzymatic efficiency after 1 h treatment by laccase at the different pHs and initial activities assayed.

	pH 5		pH 6		pH 7	
Laccase activity (U/L)	Residual BPA %	Efficiency (mg/U)	Residual BPA %	Efficiency (mg/U)	Residual BPA %	Efficiency (mg/U)
500	23.4±2.1	0.018±0.002	22.6±1.2	0.024±0.001	42.7±2.2	0.082±0.004
1000	4.1±1.2	0.013±0.003	**3.7±0.3**	**0.036±0.003**	16.8±1.2	0.046±0.002

In the EMR the highest removal rate was 121 µg/L·h of BPA and occurred for the feed addition rate of 168 µg/L·h. Nevertheless, the percentage of BPA removal was only 72%. The reduction of the addition rate to 86 µg/L·h led to an increase in the percentage of BPA removal above 79%, whereas the lowest feed addition rate, 43 µg/L·h, was required to attain removal percentages of BPA over 90%, which corresponded to a removal rate of 39 µg/L·h BPA. These results proved the viability of enzymatic reactors for the tertiary treatment of EDCs in real wastewaters.

ACKNOWLEDGEMENTS

This study was supported by the Spanish Ministry of Science and Innovation (MICINN, CTQ2010-20258) and by the Galician regional government (GRC-2010/37). Adriana Arca thanks the Spanish Ministry of Education for the FPU grant AP2010-2086.

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(S27) Electrochemical disinfection combined with micropollutant degradation using a boron-doped diamond electrode- On the way of a new eco-technology for advanced water treatment

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Abstract

The disinfection and micropollutant removalcapability of a boron-doped diamond electrode was evaluated in three different water matrices. The contaminated water contains *Pseudomonas aeruginosa*as indicator microorganisms and diclofenac as micropollutant.The applied current density was the most important parameter that affects the disinfection and diclofenac removal capacity.Nevertheless the composition of the water matrix also plays a significant role in the disinfection process and the disinfection by-product formation. A power requirements as low as 2kWh/m³ are enough to assure the complete disinfection of a contaminated model water.

Keywords
Electrochemical oxidation;disinfection;diclofenac; water reuse, energy demand

INTRODUCTION

With the increasing concern of decentralized treatment and reuse of domestic and industrial wastewater, an efficientoxidation and disinfection technology is a crucial point in ensuring a successful recycling loop.In recent years, effective electrochemical disinfection systems have been developed. Theycan achieve a satisfactory level of disinfection and micropollutants removal with economical and logistic advantages. The used anode material is the most important feature in the electrochemical disinfection. Among different anode materials, boron-doped diamond (BDD) electrodes are the most promising ones since they are known to achieve a high efficiency for the generation of different oxidants *in-situ* from water (Schmalz*et al.* 2009).The generated strong oxidising agents can be used to decontaminate water polluted with microorganisms or to sterilize surfaces and instruments in various applications. Simultaneously to the disinfection effect, an effective degradation of organic micropollutants is achievable. The objective of this research was to investigate the use of a BDD electrode for the removal of *Pseudomonas aeruginosa*as well as the micropollutant diclofenac (DCF)in different water matrixes and to evaluate the energy required for the process.

EXPERIMENTAL

Different water matrixes were spiked with *Pseudomonas aeruginosa*[N_0 = 5-7×10^{7-8} CFU/mL]and 50 µM DCF and were treated with a BDD electrode using a batch reactor system. The appliedwaters ranged in composition from deionized water to model waters I and II containing different concentrations of inorganic salts, *in particular*, increasing the chloride ion concentration from 20 to 250 mg/L in model water I and II, respectively. The inactivation of microorganisms was analyzed based after filtration according to ISO 16266 on selective agar. DCFconcentration was determined by LC-MS analysis. Measurements of residual ozone and free chlorine were done inparallel to the oxidation and inactivation experiments. Disinfection by-products, particularly chlorate and bromatewereanalysed as well. The energy consumption of the process was monitored and evaluated.

RESULTS

The current research showed that the efficiency for the removal of bacteria and DCFclearly depends on the applied current density and on the characteristic of the treated water. Generally, the higher the current density the faster the pollutant removal. The main factor affecting this behaviour is the electrical charge (Q/V) passing through the electrolyte solution.As shown in Figure 1A, at a Q/V-value of approx. 105 mAh/L, an inactivation level of almost 4-log unitswas reached applying a current density of 42 mA/cm² and 8-log unitsfor 167 mA/cm². However,considering the time to introduce the respective electrical charges, it quadruplicates moving from the lower to the higher current density (from 15 min to 60 min). This variation in the achieved inactivation level could be interpreted bearing in mind the measured ozone concentration during the experiments. Where a maximum ozone concentration of 0.9 mg/L was measured applying the higher current density, this was reduced to 0.03 mg/L applying the lower current density. The same tendency could be noticed for the oxidation of the micropollutant DCF.

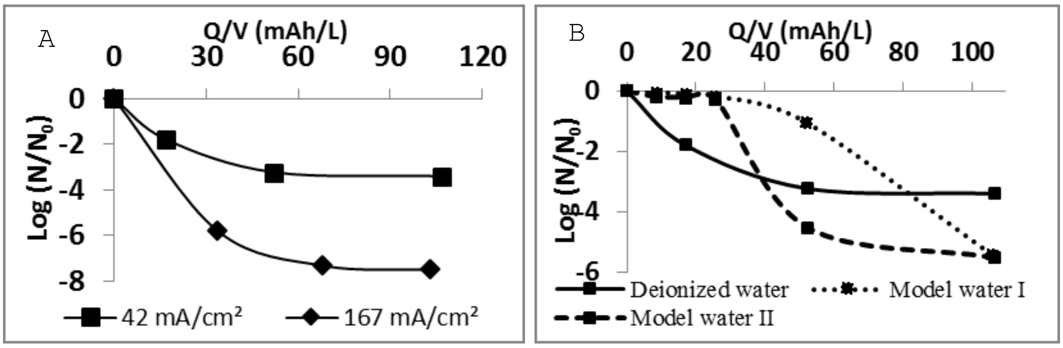

Figure. 1. Inactivation of *P.aeruginosa* as a function of applied chargein deionized water (A), and the effect of used water matrix at42 mA/cm²(B).

The presence of chloride ions in the water matrix also affects the disinfection process as further oxidants (free chlorine) are generated. Figure 1B shows the inactivation course comparing deionized water with two model waters.During the disinfection in both model waters, it appears that a delay period was required to produce a proper concentration of disinfectants.After this period the disinfection wasmore effective using the model water with high chloride contentin contrast to DCFremoval where higher salt concentrations lead to reduced removal rates. The application of higher current densities again accelerated the disinfection process. The energy consumption to achieve a disinfection level of 6-log units applying 167 mA/cm² in deionized water (6.03 kWh/m³) could be reduced to 2.03 kWh/m³ when applying the chloride-containing model waters.

Acknowledgement

This research was supported by the Federal Ministry of Education and Research (03X0087G).

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(P30) Influence of the organic loading rate on the removal of an azo-dye in aerobic and anaerobic submerged filters

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Abstract

Degradation of Direct Blue 2 begins with the cleavage of the two azo bonds producing two aromatic amines, benzidine and 4-aminobiphenyl, which are typical degradation by-products of the direct dyes. Although the microorganisms under anaerobic and aerobic conditions can degrade the azo dye as the sole substrate, the highest colour removal was obtained using a co-substrate. In this study it was shown that the dye degrades, first, in benzidine and 4-aminobiphenyl as products of the azo bond cleavage and then those aromatic amines are mineralized by the biofilm microorganisms under both aerobic and anaerobic conditions. The dye removal increases with increasing organic load. Under the organic loads of 3.4, 6.0 and 11.9 kgCOD/m^3·d, in the anaerobic filter, colour removal was 35, 56 and 61%, respectively and 33, 56 and 58%, respectively, in the aerobic filter.

Keywords

Biological filters, azo dyes, organic loading rate, aromatic amines

INTRODUCTION

Interest in the pollution potential of textile dyes has been primarily prompted by concern over their possible toxicity and carcinogenicity. This is mainly due to the fact that many dyes are made from known carcinogens, such as benzidine and other aromatic compounds (Banat *et al*., 1996).

Fixed-film treatment processes have been shown to be more amenable to the removal of xenobiotics than suspended growth systems. Aerobic biofilms have a number of potential advantages for the treatment of xenobiotics in general, and azo dyes in particular. They offer higher solids retention times necessary to prevent washout of adapted organisms. Films also provide a diffusion barrier against high, inhibitory concentrations of pollutants (Jiang and Bishop, 1994). Banat *et al*. (1996) suggest that the advantages of mixed cultures, normally found in biofilms, can collectively perform complex biodegradation tasks that no individual strain can achieve.

In some cases, the azo dye cleavage produces metabolites more toxic than the original molecule (Solis *et al*., 2012; Van der Zee and Villaverde, 2005). Degradation of Direct Blue 2 (DB2) begins with the cleavage of both -N=N- bonds producing two aromatic amines, benzidine and 4-aminobiphenyl which are common by-products of direct dyes degradation. Considering the work made by Işik and Sponza (2007) and Sponza and Işik (2005) this work proposes that the Direct Blue 2 azo bonds will be broken by microorganisms as shown in figure 1. The main objective of this work was to evaluate the influence of the organic loading rate on the Direct Blue 2 degradation using anaerobic and aerobic biofilms growing on small lava stones.

MATERIALS AND METHOD

The two identical filters consisted of a vertical PVC pipe with an internal diameter of 15 cm filled with lava stones. The effluent was placed 10 cm above the upper stone layers and a diffuser was placed under the lava stones at the bottom to supply high pressure air for backwashing (and to supply air in the aerobic filter). The main characteristics of the filters and filter media are shown in tables 1 and 2.

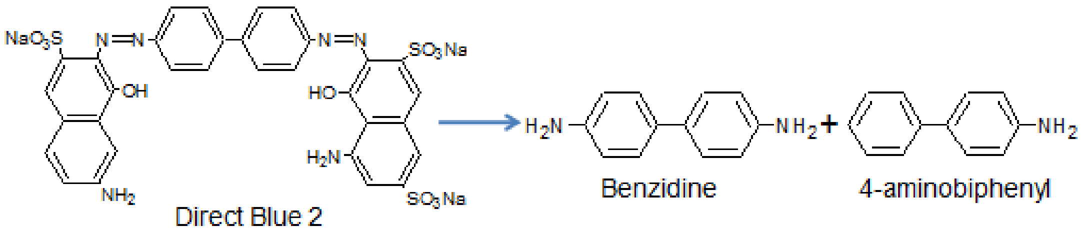

Figure 1. Direct Blue 2 and degradation by-products

Table 1. Biological filters characteristics

Total height	1.9 m
Filter media depth	1.0 m
Total volume	17.0 L
Effective volume	9.0 L

Table 2. Filter media characteristics (stones)

Average diameter	4.7 mm
Specific area	1,952 m^2/m^3
Apparent porosity	54 %
Bulk density	710 kg/m^3
Lava stones density	1,921 kg/m^3

Experimental work was carried out in two stages: First, the azo dye (λ=598 nm) was fed to the submerged biofilters with a concentration of 50 mg/L mixed with synthetic wastewater (carbon source: maltodextrin and hydrolysed vegetable protein) under three different organic loading rates (OLR) of 3.4, 6.1 and 11.9 $kgCOD/m^3 \cdot d$ (OLR was controlled modifying COD; the wastewater flow rate was held constant). In the second stage, only the azo dye was fed as sole carbon source to the microorganisms (50 mg/L). The azo dye quantification was made using a spectrophotometer and HPLC. Profiles of the azo dye concentration and aromatic amines were made using HPLC.

RESULTS

Both anaerobic and aerobic filters were operated under constant hydraulic retention time of 3 h and at room temperature (23.7 °C). The anaerobic filter was operated during 512 days and the aerobic filter was operated during 642 days with an average dissolved oxygen concentration of 6.2 mg/L. Backwashing of both filters was performed daily mainly to distribute the biomass homogeneously along the filter depth and, as consequence, to avoid microbial stratification. Because the lava stones are heavy to achieve a bed expansion with conventional procedures, backwashing was performed using pulsing conditions as described by Humby and Fitzpatrick (1996).

Start-up of both biological filters was carried out with synthetic wastewater (Cobos-Becerra and González-Martínez, 2013), without the azo dye, to promote the microorganisms adherence and growth to the filter media. In the anaerobic filter the DB2 feed began 78 days after start-up and, in the aerobic filter, the DB2 feed started after 208 days. Both filters were operated at the same OLR of 3.4 $kgCOD/m^3 \cdot d$. Figures 2 and 3 shows the DB2 concentrations during the experimental time according to the applied OLR.

Under the 3.4, 6.1 and 11.9 $kgCOD/m^3 \cdot d$ OLR, in both filters, it was observed that, with increasing OLR, the colour removal increased. Several authors suggest that the degradation of azo dyes proceeds easily when an organic co-substrate acts as electron donor and they also suggest that, with increasing azo dye/co-substrate relation, the colour removal increases (Solís *et al.*, 2012; van der Zee and Villaverde, 2005). When DB2 was fed as sole carbon source, the OLR decreased to 0.57 $kgCOD/m^3 \cdot d$ and the colour removal dropped dramatically; however, after a few days the colour removal increased steadily to reach values of approximately 40 %. The colour removal for both filters is shown in table 3.

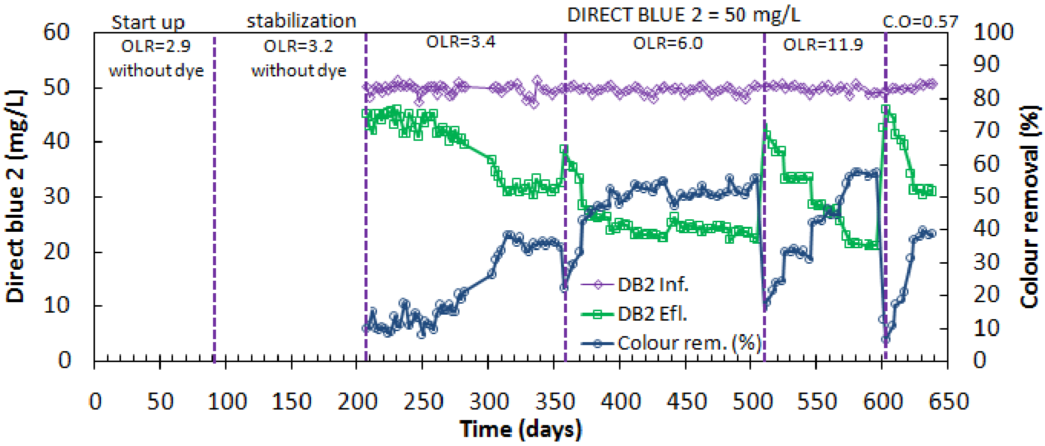

Figure 2. DB2 removal in the aerobic filter

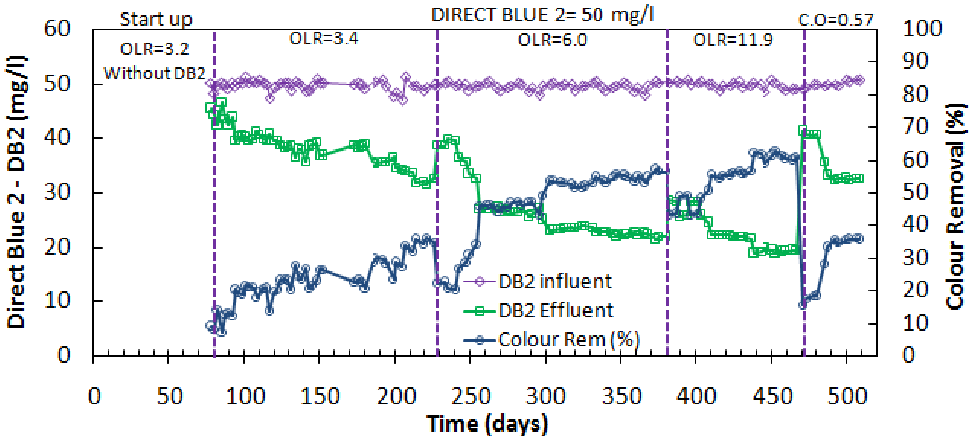

Figure 3. DB2 removal in the anaerobic filter

Table 3. Colour removal in both anaerobic and aerobic filters at the end of every experimental phase.

Experimental phase	OLR (kgCOD/m^3·d)	Colour removal (%)		COD removal (%)	
		Aerobic filter	*Anaerobic filter*	*Aerobic filter*	*Anaerobic filter*
DB2 + synthetic wastewater	3.4	35	35	91	76
	6.0	56	56	93	83
	11.9	58	61	75	80
DB2	0.57	39	36	38	31

Figures 5 and 6 show DB2 and benzidine concentration, and COD profiles in both aerobic and anaerobic filters. For every organic load, in each experimental phase, COD and dye removal increases. The highest benzidine concentration was obtained under the organic load of 3.4 kgCOD/m^3·d. In the anaerobic filter, the highest benzidine concentration was 5.3 mg/L at 60 cm height, reaching the top of the filter bed at 2.8 mg/L. In the aerobic filter, the highest benzidine concentration was 3.5 mg/L at 40 cm height and then decreasing rapidly indicating that benzidine is consumed by the microorganisms. The highest 4-aminobiphenyl concentrations (not shown in this abstract) were observed with the highest organic load in both biofilters.

CONCLUSIONS

The dye removal increased with the organic load. For OLR of 3.4 , 6.0 and 11.9 kgCOD/m^3·d, in the anaerobic filter, the colour removal were 35, 56 and 61 %, respectively; and in the aerobic filter, colour removals were 33, 56 and 58 %, respectively. When the dye was the sole carbon source colour removal was 36 % in the anaerobic filter and 39 % in the aerobic one.

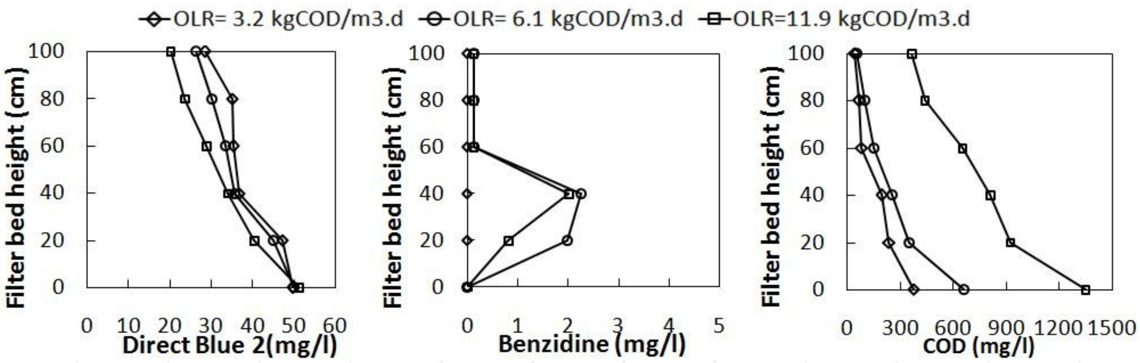

Figure 5. DB2, benzidine and COD profiles in the aerobic filter.

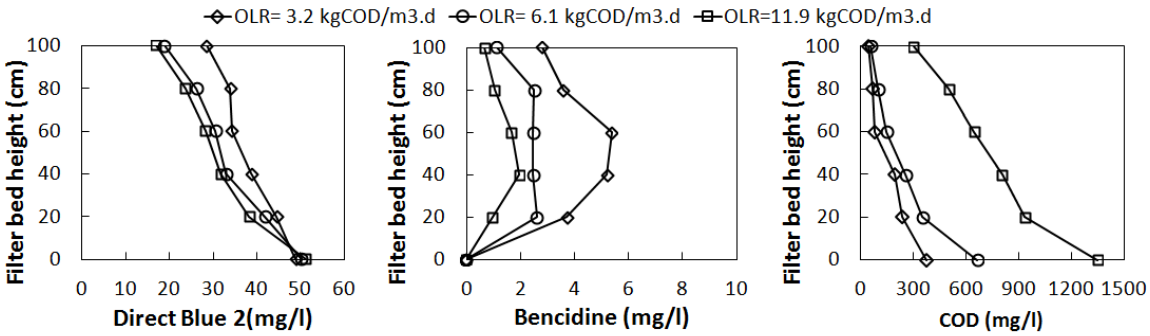

Figure 6. DB2, benzidine and COD profiles in the anaerobic filter.

Under both anaerobic and aerobic conditions the microorganisms attached to the lava stones can degrade the dye as sole substrate; nevertheless, better colour removal was obtained in the presence of a co-substrate (electron donor). As a result of the azo bond breaking, benzidine and 4-aminobiphenyl were formed and then mineralized by the biofilm microorganisms under both aerobic and anaerobic conditions. COD was removed better under lower organic loading rates (lower organic substrate concentration). Independently of the anaerobic or aerobic condition of the filters and of the time required for every experimental phase (months), until the loading rate was changed, the colour removal increased with time steadily without reaching a stable value and COD reached a constant removal rate after several weeks (not shown in this abstract).

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(P31) Sustainability of urban wastewater treatment plants' discharges: control of disinfection by-products and comparison of applicative systems

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Abstract

The study aims to present the control of the discharges of the public owned wastewater treatment plants (WWTPs) for microbiological parameters and dangerous substances control with particular reference to the by-products of disinfection systems (DBPs). The ban of chlorine and its compounds by Veneto region (Northern Italy) since December 2012, according to the *Water Protection Plan* (Regional Council Deliberation n. 107/2009), determines the need to develop valid alternatives but also to verify the microbiological abatement efficiencies and the effective presence of DBPs and their levels in the final discharges. The study focuses on contamination in the wastewaters of WWTPs with potentiality higher than 10,000 Population Equivalents (PE) in the province of Venice (Veneto region). The available data produced by the Veneto Regional Environmental Prevention and Protection Agency (ARPAV) in the period 2005-2012 for institutional control activity have been elaborated, presented and discussed. Abatement efficiencies in the chosen set of plants for disinfections systems with Sodium hypochlorite, Peracetic acid, Ozone, UV rays and Performic acid have been assessed with data produced by the three chosen plants' managers.

Keywords
Microbiological pollution, Chlorine, Ozone, Per-acetic and Per-formic acid, disinfection by-products (DBPs), Trihalomethanes (THMs), Escherichia coli.

INTRODUCTION

The need of disinfection systems for wastewaters to achieve sanitary and environmental objectives is a fundamental issue for political as well for technical Authorities to improve and apply effective regulations and at the same to guarantee the use of resources and the reduction of chemical by-products. Water protection is one of the priority objectives of environmental policies in Europe, as ratified in the Water Framework Directive (WFD) 2000/60/EC (EC 2000). The Directive requires the achievement of a Good chemical status for surface water within pre-established dates. Disinfection is needed to achieve compulsory microbial limit values (in Italy *Escherichia coli* - EC) is imposed by law with a maximum limit value of 5,000 cfu/100 mL for wastewater), according to the use of the receiving water body.

In general, wastewater disinfection due to the presence of organic and inorganic materials can produce by-products, where dangerous substances can be found too. The ban of chlorine and its compounds by Veneto region (North Italy) since December 2012 according to the Water Protection Plan (Deliberation n. 107/2009, Veneto Region 2009), as well as in other Italian regions, determines the need of alternative disinfection techniques but also to verify the microbiological abatement efficiencies and the effective presence of disinfection by-products and their levels. The disinfections systems with Sodium hypochlorite, Peracetic acid, Ozone, UV rays have been investigated. Moreover a new system with Performic acid (PFA) has been experimented by one of the selected plant manager (Ragazzo *et al.* 2013) and the last full scale experimental phase on the plant has been followed in this research to investigate DBPs.

The study aims to investigate: the level of microbiological pollution; the disinfection efficiency and dangerous substances levels in discharges (where possible priority and priority hazardous too, according to the European list - EC, 2008 as emended in 2013), in order to satisfy Environmental Quality Standards (EQSs) in the receiving water body. A set of n. 15 WWTPs (> 10,000 PE) with different disinfection systems has been analysed. Among these plants a subset of n. 7 plants was chosen for the assessment of the microbiological abatement using plants' managers data (not for all the assessment was possible). A comparison of the different disinfection systems has been produced.

The chosen set of WWTPs: The set of WWTPs with different disinfection systems, considered in this study and for which abatement efficiency was assessed, is detailed in table 1, according to the served area and the plant manager. The other WWTPs, considered in the province of Venice as microbiological sources with direct impact on the sea quality and assessed in this research are reported in table 2.

Table 1. Set of WWTPs analysed in the study with localization and plants' managers

WWT Plant	**SIRAV Code***	**Management society**	**Location**	**PE max (actual)^**	**Final discharge**	**Disinfection system**	**Period of activation**
Caorle	4148	First company	Via Traghete	120,000	Traghete/Saetta channels	NaClO/PFA**	15/03-30/09
Eraclea Mare	4869	First company	Via dei Pioppi	32,000	Primo channel	NaClO/PFA**	15/03-30/09
Jesolo	4155	First company	Via Aleardi	185,000	Sile river	PAA/PFA**	15/03-30/09
San Donà di Piave	4165	First company	Via Tronco	45,000	Tabina channel	NaClO/PFA**	15/03-30/09
Musile di Piave	4157	First company	Via Rovigo	10,000	Piave river	NaClO/PFA**	15/03-30/09
Fusina-Venezia	4140	Second company	Fusina, via dei Cantieri	330,000	Venice lagoon	UV	whole year
Paese	3733	Third company	Via Brondi	45,000	Irrigation channel	Ozone	whole year

*Code of the Veneto Regional Environmental Informative System (regional cadasters).

^ Source: Province of Venice.
** PFA since 8th March 2013 (date of effective chlorine and products' prohibition according to the Water Protection Plan of Veneto region).

Table 2. Set of WWTPs in the province of Venice considered in the study

WWT Plant	**SIRAV Code ***	**Location**	**PE max (actual)^**	**Final discharge**	**Disinfection system**	**Period of activation**
Chioggia	4139	Val da Rio	160,000	Brenta river	UV	15/03-30/09
Campalto	4141	Via Brigadiere Scantamburlo	130,000	Osellino Channel/Lagoon	UV	whole year
Lido di Venezia	4143	Via Galba	60,000	Adriatic sea 4 km far from the beach	NaClO/PAA **	15/03-30/09
Cavallino	4167	Via Fausta	105,000	Adriatic sea 4 km far from the beach	NaClO/PAA **	15/03-30/09
Quarto d'Altino	4164	Via Marconi	30,000	Sile river	PAA	15/03-30/09
S. Stino di Livenza	4158	Via Canaletta	10,000	Malgher channel/Lemene river	PAA	15/03-30/09
Portogruaro	4162	Destra Reghena	8,400	Reghena river	PAA	whole year
Bibione	4161	Via Parenzo	150,000	Maestro ch./Tagliamento river	NaClO/PFA **	15/03-30/09

*Code of the Veneto Regional Environmental Informative System (regional cadasters)
^ Source: Province of Venice
** PAA/PFA since 8th March 2013 (date of effective chlorine and products' prohibition according to the Water Protection Plan of Veneto region).

METHODS

Sampling and analytical methods

Official sampling and analytical methods adopted in Italy were applied during this study: *Analytical methods* (APAT, 2003) used since 2004; where analytical methods were lacking in the Italian national legal framework International official methods were also used (i.e. APHA *et al.*, 2005). For the research of *Escherichia coli* ARPAV Laboratories (Venice and Treviso) followed the Italian Official methods (APAT, 2003) with instantaneous sampling (samples of 500 mL of WW were collected), method n. 7030 F membrane filtration according to APHA *et al.* (2005) and AOAC (1995) and expressed as cfu/100 mL, with culture terrain TBX (Tryptone Bile X Glucuronide Agar). For the control of chemical parameters the samples were taken with the following official procedures: mean-composite sampling every 24 hours (instantaneous withdrawal at a fixed time over a period of 24 hours according to Directive 271/91/EEC for a sample representative of the real WWTP behaviour) according to the official Italian method (APAT 2003). The limits of quantification (LOQs) are defined in accordance with Hubaux & Vos, 1970 and with Vanatta & Colemann, 1997; ARPAV laboratories satisfies periodical inter-calibrations (Schmidt 2003) and are certified ISO 17045.

RESULTS AND DISCUSSION

For space reason only some exemplificative cases from the assessment performed are reported in the following.

Sodium hypochloride (HYPO) and Peracetic acid (PAA) - Jesolo WWTP: The abatement efficiency is reported for year 2011 in table 3 (HYPO disinfection, while in 2006 PAA was used). For Jesolo plant disinfection efficiency increased passing from PAA (2006) to HYPO (2011). Disinfection is considered always in the high season period.

Table 3. Jesolo WWTP - Abatement efficiency with HYPO - EC

DATE	Escherichia Coli_IN cfu/100mL	Escherichia Coli_OUT cfu/100mL	EC_IN Log	EC_OUT Log	EC ABAT Log	% EC ABAT
24/05/11	36000	9	**4.6**	**1.0**	**3.6**	**99.98**
31/05/11	37000	50	**4.6**	**1.7**	**2.9**	**99.86**
07/06/11	1400000	10	**6.2**	**1.0**	**5.2**	**100.00**
14/06/11	42000	9	**4.6**	**1.0**	**3.7**	**99.98**
21/06/11	30000	58	**4.5**	**1.8**	**2.7**	**99.81**
28/06/11	28000	57	**4.5**	**1.8**	**2.7**	**99.80**
05/07/11	91000	110	**5.0**	**2.0**	**2.9**	**99.88**
12/07/11	83000	220	**4.9**	**2.3**	**2.6**	**99.73**
19/07/11	55000	21	**4.7**	**1.3**	**3.4**	**99.96**
26/07/11	64000	160	**4.8**	**2.2**	**2.6**	**99.75**
02/08/11	34000	63	**4.5**	**1.8**	**2.7**	**99.81**
09/08/11	56000	5	**4.8**	**0.7**	**4.1**	**99.99**
16/08/11	410000	210	**5.6**	**2.3**	**3.3**	**99.95**
23/08/11	110000	83	**5.0**	**1.9**	**3.1**	**99.92**
30/08/11	19000	2	**4.3**	**0.3**	**4.0**	**99.99**
06/09/11	88000	18	**4.9**	**1.3**	**3.7**	**99.98**
13/09/11	58000	2300	**4.8**	**3.4**	**1.4**	**96.03**

Performic Acid (PFA) - Eraclea mare WWTP: During 2011 the disinfection of Eraclea mare plant was performed with PFA; abatement data are reported in table 4.

Table 4. Eraclea mare WWTP - Abatement efficiency with PFA- EC

DATE	Escherichia Coli_IN cfu/100mL	Escherichia Coli_OUT cfu/100mL	EC_IN Log	EC_OUT Log	EC ABAT Log	% EC ABAT
09/05/11	12000	2	**4.1**	**0.3**	**3.8**	**99.98**

16/05/11	9800	8	**4.0**	**0.9**	**3.1**	**99.92**
30/05/11	31000	280	**4.5**	**2.5**	**2.0**	**99.10**
13/06/11	220000	14	**5.3**	**1.2**	**4.2**	**99.99**
20/06/11	9900	5	**4.0**	**0.7**	**3.3**	**99.95**
27/06/11	42000	23	**4.6**	**1.4**	**3.3**	**99.95**
04/07/11	55000	270	**4.7**	**2.4**	**2.3**	**99.51**
18/07/11	62000	360	**4.8**	**2.6**	**2.2**	**99.42**
01/08/11	36000	35	**4.6**	**1.5**	**3.0**	**99.90**
08/08/11	62000	45	**4.8**	**1.7**	**3.1**	**99.93**
16/08/11	370000	410	**5.6**	**2.6**	**3.0**	**99.89**
22/08/11	63000	290	**4.8**	**2.5**	**2.3**	**99.54**
29/08/11	10000	37	**4.0**	**1.6**	**2.4**	**99.63**
05/09/11	41000	12	**4.6**	**1.1**	**3.5**	**99.97**

DBPs (according to performed test list) higher than LOQ have been considered, assessed and listed for each plant (here not reported for space reasons).

CONCLUSIONS

Disinfection is necessary to reduce or stop the pathogen microorganisms' growth (bacteria, virus, protozoa, etc.) and to sensibly reduce the diffusion of diseases. The choice of the disinfection system must be based on the effective need according to the use of the receiving water body and its level of microbiological contamination; bathing waters appear to be particularly sensitive to microbiological pollution due to sanitary risk. In the choice of a specific disinfection system different factors must be considered beyond the water quality objectives: plant costs, operative costs, residual toxicity of DBPs. In this study the WWTPs of the province of Venice with potentiality higher than 10,000 PE and with different disinfection systems (with the addition of a WWTP from Treviso Province as it is equipped with ozone disinfection) have been considered; the discharge control data produced by the Veneto Environmental Regional Protection Agency (ARPAV) have been recovered and assessed for the period 2005-2012 for microbiological pollution and for DBPs research. A specific set of WWTPs (n. 7 plants) of the total set has been selected: for these plants the managers' data have been used to determine the abatement efficiencies; from the assessment of the disinfection systems performed in this study it can be said that, with differences among the WWTPs, the abatement efficiencies were good and that satisfactory results have been achieved except for ozone (probably caused by technical and management problems).

The DBPs have been investigated according to the analytical panel normally executed by ARPAV with routinary methods (classes of Chlorophnols, Organohalogenated compounds comprehensive of Trihalomethanes-THMs). THMs have been found at values higher than LOQs especially for chlorine disinfection systems, but the values detected appeared to be always at values lower than discharge limit values but also lower than quality standards for wastewater reuse standards. It must be observed that many classes of emerging pollutants (Halonitromethanes, Haloacetic acids, Haloaldehydes, Haloketones, etc.) are not yet investigated neither regulations give specific indication on limit or standard values.

Due to the prohibition of chlorine and compounds (defined in 2004 and effective since December 2012) by the Veneto region, the same plant manager experimented since 2005 the Performic acid (PFA) in wastewater disinfection. ARPAV took part to the experimentation with integrative samples for DBPs identification during 2012. The analyses were quantitative for the main classes of DBPs, while for other classes only qualitative. No evidence of particular DBPs have been pointed out. PFA appears very interesting: high efficiency and low level of by-products. More sperimentation is in any case necessary on the mid to long-time scale.

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(P32) Photocatalytic porcelain gres tiles with micro-sized TiO_2: tests of degradation of dyes in water

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Abstract

Some particular drawbacks due to the industrial use of nano-sized TiO_2 (safety, recovery) can be closed with the choice of micro-sized TiO_2 in the anatase form as photocatalytic powder. Good photocatalytic performance in the degradation of three organic dyes in water phase were obtained. Furthermore, tests on industrially prepared photocatalytic tiles, having the surface of porcelain tiles hot-coated with micro-sized TiO_2, were also performed. The obtained results can represent a good alternative to TiO_2 suspensions and pave the way for the fully industrial use of photocatalysis in environmental remediation.

Keywords

Photocatalysis; TiO2; micro-sized anatase; porcelain gres tiles; organic dyes

INTRODUCTION

Titanium dioxide (TiO_2) is worldwide considered as one of the best semiconductor to be used as photocatalyst for pollutants degradation. Exposition under UV light promotes redox reactions and charges separation that lead to oxidative processes as reported by Razavi et al.[1]. TiO_2 is often used in powdery form as nano-sized particles with high surface area, so as to enhance its photoactivity. According to Carneiro et al.[2] organic dyes are more and more considered an important source of contamination for water streams, because of their extensive use in many industries and nano-sized TiO_2-based photocatalytic systems are considered a valid technique for the removal of this kind of contaminants[3].

However, some recent papers have underlined the possible side-effects on human health due to both use and exposure to nanoparticles[4], as the ultra-small particles can penetrate inside human body from skin and nose especially when they are used in products like paints or simply cold-coated on materials surfaces for air purification and a loss of photoactive powder cannot be neglected.

Problems can be observed in liquid phase as well, where nano-sized powder can affect the catalyst recovering at the end of the reaction, hindering an industrial use of TiO_2 nanopowders, due to the extreme difficulty in the final filtering necessary to separate photocatalytic powder and the cleaned solution, as reported by Schulze et al.[5].

On this basis, a great attention is focused on the potential of TiO_2 micro-sized powders to be used as photocatalyst for the degradation of organic contaminants. Recent results for both NOx and VOC degradation in gas phase seem to be very promising[6] but no data are available for the degradation of pollutants in liquid phase yet.

Main target of the present work is to investigate the performance of a commercial micro-sized TiO_2 (1077 by Kronos) used as photocatalyst in the degradation of three different dyes (Rhodamine B, Crystal Violet and Methylene Blue) in water. Micro-sized sample was used as received, so to compare the obtained results with the classical nano-sized commercial P25 by Evonik,

Previously Marcos et al.[7] reported a good activity of nano-sized TiO_2 photocatalytic layers on glazed ceramic tiles in the degradation of Orange II dye. In the present case, micro-sized 1077 was industrially hot-coated at the surface of a porcelain tile (Orosei Active^{TM}). Tests using photoactive tiles were carried out to verify the efficacy of the coated catalyst to degrade dyes in water media in order to obtain a stable and very easy way to separate the photocatalyst from the solution at the end of the reaction.

Rhodamine B (RhB, dye content ~95%), Methylene Blue (MB, dye content ≥97%) and Crystal Violet (CV, dye content ≥90%) were used as organic pollutant. Each dye (Sigma Aldrich) was used without further purification treatment.

Two different dye concentrations were used in the present paper: $1x10^{-4}$ M and $1x10^{-5}$ M, depending on the reaction set-up. The most concentrated solution was used to verify the efficiency in the photodegradation of organic molecules in water of powdered micro-sized TiO_2 in stressing conditions. These results were compared to the results already obtained by P25 by several authors in the past and reconfirmed in the present operative conditions as reported in this text. The less concentrated solution, however higher than the one reported by Marcos et al.[8], were used to test the performance of Orosei Active^{TM} tiles.

The solutions were prepared by dissolving the dye in distilled water and without any pH adjustment, but leaving them at their spontaneous values.

PHOTOCATALYTIC TEST USING POWDERED NANO AND MICRO-TIO2 CATALYSTS

Dyes degradation in water media was performed in a slurry reactor (Fig. 1a) of 0,5 L volume. Irradiation was allowed by the use of an external UV lamp (500W, Jelosil®, HG500, halide lamp), emitting in the range 315-400 nm and with a emitting power evaluated in the middle of the reactor by a radiometer instrument (Delta OHM, model HD2102.2) of 75 W/m^2. The reactor was equipped by an internal refrigerating serpentine system.

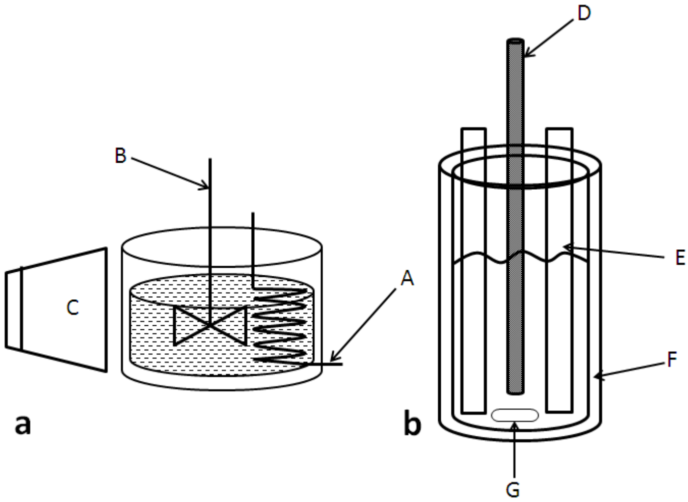

Figure 1. a: Continuous stirred slurry reactor. A: refrigerating serpentine system; B: Dye solution; C: Stirrer; D: UV lamp. b: Cylindrical batch reactor used for photocatalytic experiments. A: UV lamp; B: Orosei Active® tiles; C: Cooling jacket; D: Magnetic stirrer; E: Dye solution

Dye adsorption tests have been carried out in the dark using a catalyst amount of 1 g/L at four different dyes solution (concentration ranged between 10^{-6}-10^{-4}M) for six hours.

Photolysis tests have been performed for six hours; the same for photocatalysis performed using fresh 0,1 g/L TiO_2 in powder form. Dyes degradation was checked every 60 min. Analytic determination of the dyes concentrations in water solution was performed by a UV-vis spectrophotometer analyzer (T60 UV-vis PG LTD instruments), using water as the reference.

PHOTOCATALYTIC TEST USING PHOTOACTIVE TIO_2 TILES

A cylindrical batch reactor of 1 L volume was used for dye degradation tests in presence of ten photoactive tiles (0.03 m^2 total surface photoactive area) immersed into the liquid solution, as schematically shown in Fig.1b. Refrigeration was allowed by a cooling jacket. Two different lamps directly immersed into the dye solution were used with this setup: a typical germicidal 9 W UV lamp (Philips TUV BL-S, model AEPL-7913 mercury vapor low pressure), with an UV-A illuminance at the tiles surface of 1 W/m^2 and a 125 W UV-A lamp (Jelosil, mercury vapor low pressure), with an illuminance of 65 W/m^2.

The same batch of Orosei Active^{TM} tiles was used for all the tests reported in the present paper; after each test the tiles were simply washed using deionized water and acetone and then left in deionized water all night long.

Adsorption tests were carried out by dipping the tiles into the dyes solutions in dark conditions for six hours. To avoid any alteration of both irradiating conditions and fluid dynamic of the system, photolysis was performed with the tiles still inside the reactor but with the active faces turned towards the dark side of the reactor, thus preventing the photoactivation of the TiO_2 catalyst. During photocatalytic tests the TiO_2 active faces of the tiles were turned towards the UV light.

The same dyes solution described in the above section were used in the present setup at a concentration of $1x10^{-5}$ M. Kinetics were monitored by UV-vis spectrophotometric analysis.

RESULTS

Photocatalytic tests show good results in dyes abatement with photocatalysts in powder form. Nano-sized powder shows the best results for all the considered dyes achieving the complete decolorizing of the water solution in 6 hours, but also micro-sized sample are able to degrade the pollutants with a good efficiency (ranging from 48 to 58% depending on the dye in six hours).

According to the previous results obtained by the use of micro-sized TiO_2 catalyst, the activity of 1077 industrially hot-coated onto porcelain tiles was evaluated in another experimental setup verifying the material efficiency with two different UV lamps immersed inside the dyes solution.

Control experiments of photolysis and adsorption of dyes on the tiles were carried out. Dark tests shown a 25% adsorption of CV and MB, while RhB adsorption is on the contrary almost negligible. However, dyes were exclusively fixed in the backside and lateral sides of the ceramic pieces, i.e. in the surfaces uncovered by the photocatalytic layer.

Results obtained by photocatalytic tests, carried out by using the coated micro-TiO_2 catalyst onto the tiles surface are showed in Fig. 2 for 9W lamp.

Degradation of dyes is improved by the use of the photoactive tiles; in fact after a six hours reaction, the percentage degradation value obtained is 78% for CV, 88% for MB, and the 30% for RhB, revealing an increase of about 15% of degradation on all dyes in comparison to the simply photolysis tests.

Tests with the 125W UV-A lamp lead to the complete degradation of CV (Fig. 2) and MB in less than three hours and the disappearance of 71% RhB in 6 h.

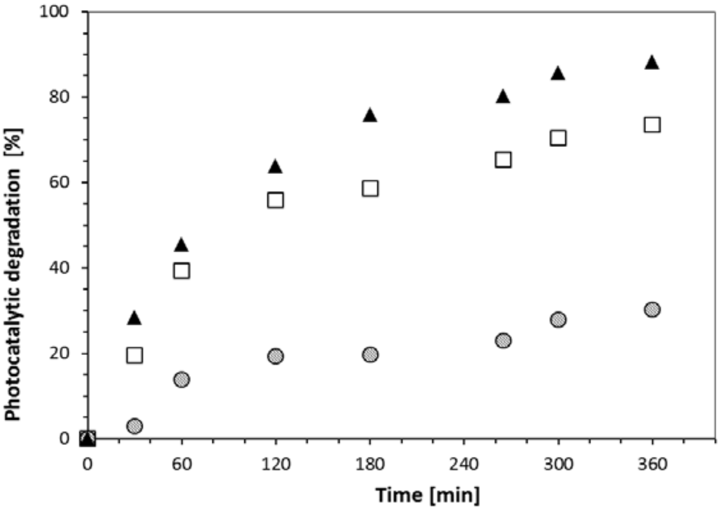

Figure 2. Photocatalysis with OroseiTM Active tiles and UV-light irradiation (9W immersion UV lamp); Crystal Violet; Methylene Blue; Rhodamine B.

The obtained results have to be considered with great importance as using micro-sized TiO_2 the health risks related to nano-sized particles can be avoided; moreover such a micro-sized powder can be easily filtered and recovered, in order to be immediately reused for further photodegradation reactions, opening the way of a fully industrial use of photocatalysis in environmental remediation. Moreover, these new industrial ceramic materials are surely an interesting alternative to TiO_2 suspensions, for example in photocatalytic applications avoiding the removal of the particles at the end of the process.

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(S28) Optimization of photocatalytic degradation of chloramphenicol by chemical and biological analysis

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Abstract

Chloramphenicol (CAP) is a broad-spectrum antibiotic exhibiting activity against both Gram-positive and Gram-negative bacteria, as well as other groups of microorganisms. Due to its incomplete removal during conventional wastewater treatment processes, residual parts with metabolites get into the surface water and ground water. The present work deals with the photocatalytic degradation of CAP using TiO_2 as photocatalyst. The variation of TiO_2 amount and the initial CAP concentration on the reaction rate were systematically investigated using the experimental design methodology. A single polynomial expression modelling the reaction was also obtained. A set of bioassays (*D. magna*, *P. subcapitata* and *C.dubia*) was performed to assess the potential detoxification of CAP and its oxidation by-products in order to evaluate how agree are chemical test and biological assay. Besides, the formation of ammonia and chlorides during photocatalysis was monitored as a function of irradiation time.

Keywords
Ceriodaphnia dubia, Chloramphenicol, *Daphnia magna,* photocatalysis, *Pseudokirchneriella subcapitata*

INTRODUCTION

Among a number of emerging contaminants continually discharged into the aquatic environment without any restriction, threating the ecosystem and the public health, pharmaceuticals have been increasingly detected in sewage water, natural water, surface water and ground water (Chatzitakis et al., 2008; Fatta-Kassinos et al., 2011).

Due to their continuous input and persistence into the aquatic ecosystem, antibiotics are recognized as one of the most urgent environmental questions, primarily due to the potential for the development of antimicrobial resistance.

Several studies have shown their incomplete removal during conventional wastewater treatment processes (Joss et al., 2006) and, therefore, the application of new and improved wastewater treatment technologies, including advanced oxidation processes (AOPs), is a necessary task (Rizzo et al., 2009; Lofrano et al., 2014). Although it is very difficult to make a complete classification of the advanced oxidation processes for the diverse combinations that are presented among them, AOPs are all based on the production and utilization of hydroxyl radicals which are very powerful oxidants that quickly and unselectively oxidize a broad range of organic compounds. Since during the oxidation process some by-products (intermediates) are formed and the effluent may become more toxic than the untreated solutions or the parent compounds respectively, the overall efficiency of the treatment process for this class of chemical pollutants strictly depends on the toxicity and estrogenic potency assays of treated effluents. Therefore, the use of bioassays to optimize AOPs when applied to treat toxic effluents or compounds is considered crucial to assess the applicability of these processes (Rizzo et al., 2009).

The present work deals with the photocatalytic degradation of CAP using TiO_2 as photocatalyst. The variation of TiO_2 amount and the initial CAP concentration on the reaction rate were systematically investigated. The experimental design methodology (response surface methodology, RSM) allowed to fit the optimal values of the parameters leading to the degradation of the pollutant. A single polynomial expression modelling the reaction was finally obtained. A set of bioassays (*Daphnia magna*, *Pseudokirchneriella subcapitata* and *Ceriodaphnia dubia*) was performed to compare the results of chemical analysis and biological assays. Besides, the formation of ammonia, nitrate, nitrite and chlorides during photocatalysis was monitored as a function of irradiation time.

MATERIALS AND METHODS

Reagents

Photocatalytic degradation experiments were carried out using TiO_2 Degussa P-25. CAP ($C_{11}H_{12}O_5N_2Cl_2$, m.w. 322.96, Figure 1), HPLC grade water and methanol were supplied from Sigma Aldrich. The compounds were separated using as mobile phase a mixture of methanol/ultrapure water (35%/65%) at flow rate of 1mL min^{-1}.

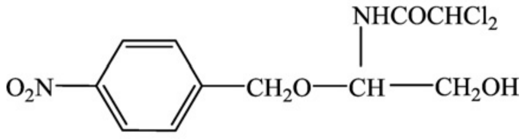

Fig. 1 Structure of chloramphenicol (CAS 56-75-3).

Experimental set-up

Photolysis experiments were carried out at room temperature in a 250 mL stirred cylindrical Pyrex vessel filled with 200 mL aqueous solution at different TiO_2 and CAP concentrations. The vessel was placed in a chamber and illuminated for certain periods with a xenon arc lamp (450 W, LotOriel Group, Italy) equipped with special glass filters restricting the transmission of wavelengths below 300 nm. The light intensity as determined by the potassium ferrioxalate actinometry was found to be 4.5×10^{-7} Einstein s^{-1} (Hatchard, 1956).

Analytical procedures

Chemical analysis

Changes in the concentration of CAP were monitored by HPLC-UV (Finnigan Surveyer) equipped with a reversed phase C18 analytical column (Vydac, 5µm, 150mm ×3.0 mm).

Multivariate experimental design

An experimental factorial design of the reaction system was performed to find the optimal conditions of CAP degradation during the photocatalytic treatment. Multivariate design was performed according to the methodology of response surface (RSM). The use of factorial design allows finding with minimum number of experiments the optimal experimental conditions for the degradation of a pollutant. The initial CAP concentration range was considered between 5 and 25 mg L^{-1} while TiO_2 concentration range varied from 0.5 to 1.75 mg L^{-1}. The residual CAP concentration obtained after 30 min of illumination during the photocatalytic treatment procedure were selected as the response factor (Y).

Toxicity

The toxicity of untreated and treated CAP solutions through bioassays was monitored in samples collected during the oxidation process.

Daphnia Magna

Newborn daphnids (<24 h old) were exposed to samples according to the ISO 6341 method (ISO, 2013). Daphnids were grown at 20 ± 1◦C under a light source of 1000 lux using cool lamps and control tests were carried out at the same temperature without light emission. They were fed with *P. subcapitata* (300,000 cellsmL^{-1}). In each quadruplicate treatment schedule, 20 daphnids were scored according to their immobilization frequency in 10mL sample volume.

Ceriodaphnia dubia

The chronic toxic bioassay with *C. dubia* was carried out according to ISO 20665 (ISO, 2008) *C. dubia* less than 24 h old were exposed in a synthetic reconstituted aerated hard ISO medium. Ten replicates were incubated at 25◦ C and tested a 16 h:8 h light:dark cycle (500 lux). The start time of the bioassay was recorded after the transfer of the crustacean. Every 24 h, the organisms were transferred into a new series of beakers containing solutions and fresh food prepared according to the same guidelines followed for the preparation of the bioassay. During the transfer operations, the dead animals were recorded and removed, and the newborns were counted and then discarded.

Pseudokirchneriella subcapitata

Weekly transplanted algae in exponential growth were cultured in a salt solution dissolved in ultrapure water (ISO, 2012). Cultures were kept in Erlenmeyer flasks at the same conditions of *D. magna*. The toxicity tests were initiated from an algal concentration of 3000 cellsmL^{-1} and conducted in six replicates using 25mL sample volume. The endpoint consisted of cell growth inhibition, which was measured after 72 h in a Burker cell counting chamber and calculated by dividing the difference of the number of control and sample cells to the number of control cells.

RESULTS AND DISCUSSION

Preliminary experiments

Preliminary experiments on 25 mg L^{-1} CAP were carried out under dark conditions and with UV to evaluate the extent of adsorption and photolysis processes on the antibiotic transformation. However after 120 min no significant removal could be observed in the maximum peak of CAP as effect of both processes. Consequently, degradation of the CAP subjected to TiO_2 photocatalysis was mainly due to the active species produced during the photocatalytic oxidation process (e.g. hydroxyl radical, holes and reactive oxygen species (ROS)). On the other hand the degradation rate of CAP increased when the concentration of TiO_2 increased till to a maximum value, after that showed a decreasing tendency. A certain concentration increase can enhance the hydroxyl radical produced from irradiated. However, higher concentration of TiO_2 particles becomes much easier to aggregate and impedes further penetration of light in the reactor. In any given application, this optimum TiO_2 concentration must be determined to avoid superfluous and ensure total absorption of radiation photons for efficient degradation. Another important parameter is the initial concentration of CAP in the degradation process, since it influences the initial rate of disappearance of CAP. According to our results the degradation rate of CAP decreased with the increase of CAP concentration.

Construction of polynomial expression and 3D response surface

The use of factorial design yields optimized parameters from a minimum set of experiments. Using codified values of the variables under study it is possible to obtain a polynomial expression that empirically describes the reaction yield (Calza et al., 2006). Since the different input variables presented different dimensional units, these variables can only be compared if they are normalized to a common unit. Therefore, coded variables were a need during the modelling procedure. Solving the matrix a second grade polynomial was obtained. This mathematical expression describes the photocatalytic degradation of cloramphenicol under given conditions which are not valid for a different type of pollutant or different set of conditions.

According to our results the degradation rate of CAP gradually increased with both TiO_2 concentration and CAP initial concentration increasing, however, the trend of CAP degradation rate decreased under the higher level of TiO_2 concentration and CAP initial concentration. This lead to conclusion that the CAP degradation rate significantly decreased when TiO_2 concentration and CAP initial concentrations are too high or too low, both of TiO_2 concentration and CAP initial concentration have the respective optimal levels. HPLC results showed as CAP was effectively removed by photocatlaysis (>85%). Chlorides, nitrate and ammonia in the solution were also measured.

Toxicity

D. magna, *C. dubia* and *P. subcapitata* were affected by exposure of untreated and treated CAP aqueous solutions. The initial concentration of CAP influenced toxicity much since the formation of oxidation by products was higher at higher initial CAP concentrations. This trend was attributed to an higher formation of by products (Rizzo et al., 2009; Lofrano et al.,2014)

Further ammonia and chlorides were not suspected to cause the toxicity at oxidation pH and occurred concentrations (Lofrano et al. 2014)

CONCLUSIONS

Results obtained by the adsorption in the dark and direct photolysis for a time period of 120 min proved that both adsorption and photochemical processes were scarcely responsible for the observed fast transformations when the solution of CAP was irradiated in the presence of TiO_2.

The experimental design methodology (RSM) allowed to fit the optimal values of the parameters leading to the degradation of the pollutant. All specie tested resulted in different of response curves, however, almost complete removal of toxicity to all species tested was provided at the end oxidation at optimal process conditions.

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(S29) Analysis of Industrial Effluents with a Battery of Rapid Ecotoxicity Assays

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Abstract

The aim of the present study was to investigate the response of a selected battery of rapid ecotoxicity assays to treated effluent samples from different tank truck cleaning (TTC) companies. The battery of tests consisted of (1) the *Vibrio fischeri* bioluminescence inhibition test, (2) a rapid photosynthesis inhibition test using extracted photosynthetic enzyme complexes (LuminoTox PECs), (3) a rapid photosynthesis inhibition test using whole algal cells (LuminoTox SAPS), and (4) an enzymatic inhibition test with *Artemia* nauplii (Fluotox). We found that the results from (routine) chemical analyses did not correlate with the ecotoxicity assays, and that a single toxicity test, such as the widely used bacterial bioluminescence inhibition test, may not cover all the possible toxic modes of action effected by complex effluent samples.

Keywords
industrial wastewater; rapid ecotoxicity assay; tank truck cleaning; whole effluent toxicity

INTRODUCTION

Discharge limits for treated industrial wastewater are currently mostly based on chemical analyses. The European Water Framework Directive however requires that receiving water bodies attain not only a good chemical, but also a good *biological* water quality. Several studies suggest that results from both routine and advanved chemical (waste)water analyses are not able to predict the ecological impact potentially present in treated effluents. A battery of ecotoxicity tests is therefore necessary for the assessment of effluent toxicity (OSPAR 2003, De Schepper *et al*. 2010).

In addition, operators from industrial wastewater treatment plants should react quickly to the appearance of ecotoxicity in the effluent before it is discharged, e.g. by diverting the water stream to an advanced post treatment stage. Classical acute ecotoxicity assays (e.g. OECD guidelines) however are not appropriate for this kind of process control as these tests not only require long incubation times but also costly specific equipment and trained personnel.

In view of this discussion, there is clearly a need for rapid cost-effective, easy-to-operate and sensitive toxicity assays that can routinely be used by wastewater treatment plant operators. The aim of the present study was to investigate the response of a selected battery of rapid ecotoxicity assays to treated effluent samples from different tank truck cleaning (TTC) companies. Wastewater originating from TTC activities is characterized by a high degree of variability in composition and degradability, and is therefore a very appropriate test case (De Schepper *et al*. 2010).

MATERIALS AND METHODS

We collected treated effluent samples from four different Belgian TTC companies (labelled A to D). The wastewater treatment consisted of a succession of physical-chemical and biological treatment processes. Tertiary treatment (dissolved air flotation, sand filtration and/or activated carbon filtration) was applied in some cases. All samples were taken before the activated carbon filter. Five grab samples were collected during one week for every location, and stored in the fridge (4°C) until analysis. The following chemical analyses were performed: pH, conductivity, turbidity and COD.

The battery of ecotoxicity tests consisted of four assays: (1) the 30min bacterial bioluminescence inhibition test (according to ISO 11348-1:1998 using *Vibrio fischeri* NRRL B-11177), (2) a rapid photosynthesis inhibition test using the LuminoTox PECs test kit based on extracted photosynthetic enzyme complexes (Lab_Bell Inc., Canada), (3) a rapid photosynthesis inhibition test using the LuminoTox SAPS test kit based on whole algal cells (Lab_Bell Inc., Canada), and (4) the 1h enzymatic inhibition test (Fluotox) with *Artemia* nauplii (Espiritu *et al*. 1995). The wastewater concentration applied in the assay was 50 vol% for the bioluminescence inhibition test, and near 100% for the other assays.

RESULTS AND DISCUSSION

The selected inhibition assays were relatively inexpensive, rapid (exposure and response in less than 2h) and easy to operate.

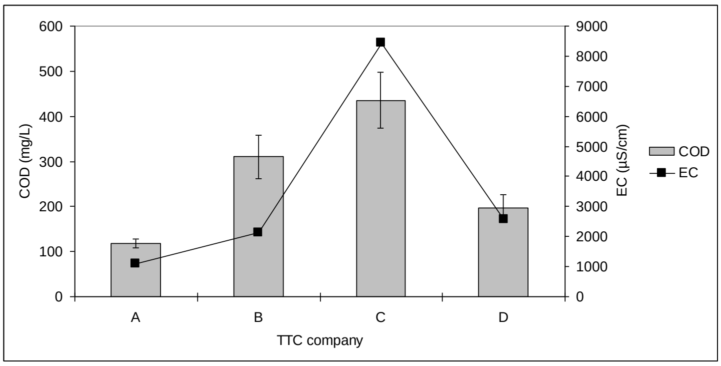

Figure 1. Average COD and conductivity values of the TTC effluent samples.

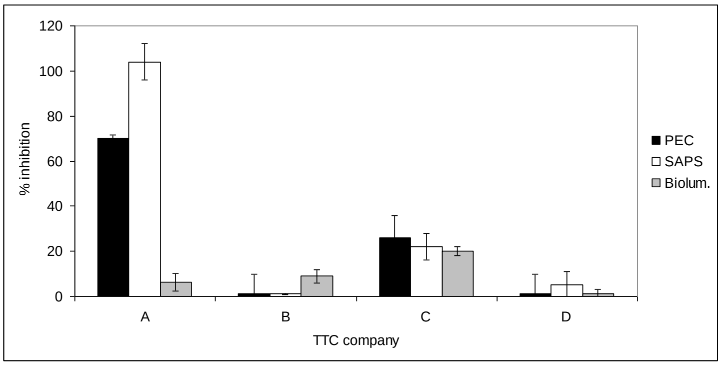

Figure 2. Average inhibition of the photosynthesis activity and the bacterial bioluminescence by the TTC effluent samples.

The lowest COD, turbidity and conductivity were observed in the effluent from company A (Fig. 1). In contrast, this effluent caused a significantly higher inhibition of the photosynthesis activity than the effluents from the other TTC companies (Fig. 2).

Bacterial bioluminescence inhibition was not significant in any sample (Fig. 2), while the results from the Fluotox assay were highly variable and difficult to replicate (results not shown).

CONCLUSION

The assessment of the ecological impact of treated industrial wastewater requires the use of a battery of ecotoxicity tests, because (1) the results from (routine) chemical analyses did not correlate with the ecotoxicity assays, and (2) a single toxicity test, such as the widely used bacterial bioluminescence inhibition test, may not cover all the possible toxic modes of action effected by complex effluent samples.

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(S30) Novel pre-polymerized coagulant agents used for the treatment of industrial wastewaters

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Abstract

Coagulation is widely used for water or wastewater treatment, in order to remove mainly suspended solids (SS), colloidal particles, natural organic matter (NOM) and other soluble compounds, such as phosphate ions. However, many industrial and food process waste streams are inherently high in *o*-phosphates content. The aim of this study was the investigation of alternative composite inorganic coagulants (polyaluminum ferric silicate chloride) for the treatment of representative industrial wastewaters, such as those from tanneries, or from yeast-production (fermentation) plants, The coagulants proved to be quite effective, depending upon the specific properties; therefore, the addition of 80-100 mg/L of $PSiFAC_{1.5:10:15}$ in yeast wastewater resulted to a reduction of COD between 22-56%, of turbidity 14-40%, of UV_{254nm} absorbance 15-25% and of phosphates 38-43%, respectively, but higher removal rates were obtained in tannery wastewater (COD 67%, turbidity 96%, phosphates 62%, UV_{254nm} 10%).

Keywords

Coagulation; composite inorganic coagulants; phosphates removal

INTRODUCTION

Colloids are very small “particles” (0.01-1.0 μm), which cannot be removed from wastewater by simple sedimentation, forming rather stable suspensions in aqueous media. The colloids carry the same (usually negative) surface charge and they are stabilized by development of electrostatic repulsion forces, acting between the particles, hence preventing the coalition between them. To remove effectively the colloids from water, this repulsion forces must be eliminated, permitting the colloids to close each other, interacting, becoming unstable and finally, agglomerating (Kivisaari, 2009, Metcalf and Eddy, 2003).

The Coagulation/Flocculation (C/F) process is a core environmental protection technology, which finds a wide range of several (and diverse) applications in water and/or wastewater treatment facilities. In particular, coagulation is regarded as a viable option for the treatment of surface waters, or wastewaters aiming to remove mainly suspended solids (SS), colloidal particles, natural organic matter (NOM) and other soluble, mostly inorganic compounds, such as phosphate ions, metals etc. Several research efforts suggested also that the coagulation process can be effectively utilized as a pre- or post-treatment method for hazardous wastewater treatment. The combination of coagulation with other appropriate physicochemical or biological treatment processes, such as submerged biological filters (bioreactors), results in the enhancement of treatment efficiency, especially when treating refractory wastewaters. The coagulation process by the addition of coagulants (inorganic reagents) can involve the following (subsequent) steps: (1) the destabilization of suspended and colloidal particulate matter, (2) the (partly) adsorption of colloidal and dissolved organic matter onto the surface of the destabilized particles, and (3) the aggregation of destabilized particles and the subsequent creation of flocs, which enmesh suspended, colloidal and dissolved material, as they settle (Zouboulis *et al.*, 2009a).

Domestic and industrial wastewater can contain rather high concentrations of phosphorous, nitrogen and other carbonaceous contaminants that are essential nutrients for the growth of organisms. However, many industrial and food process waste streams are inherently high in nutrients content, causing severe eutrophication problems. Very important is considered the case of phosphorous (usually in the form of orthophosphates), which has to be removed efficiently from wastewaters (Kelley and Handley, 2011). Phosphorus can be removed from waters/wastewaters either biologically or chemically. At many wastewater treatment plants, chemical addition is required to meet the respective strict requirements, regarding the discharge (final permissible concentrations) of phosphorus. Membrane filtration is an attractive option for removing the chemically precipitated phosphorus, but that process can be impeded by the usual fouling of membrane, mainly due to the presence of effluent organic matter (EfOM) (Kim *et al.*, 2008).

The application of conventional activated sludge treatment typically reduces the total phosphorus (TP) concentrations in the treated effluent down to 1–2 mg/L, whereas the "enhanced" biological phosphorus removal processes can lower further that value to 0.1–0.2 mg/L, although under rather ideal conditions (Blackall *et al.*, 2002). Nevertheless, in practice supplemental additions of chemical agents, such as Al or Fe(III) salts, poly-aluminum chloride (PACl) and/or lime, are often required to maintain acceptable effluent TP concentrations. More recently, composite polymeric aluminum products, such as PASiC (aluminum-silicate polymer composite), or PAC (hydroxylated polyaluminum chloride) have been also tested in laboratory experiments, as well as in full-scale applications (Gao *et al.*, 2002b, Zouboulis *et al.*, 2008, 2009b). Alternatively, an MBR treatment system can be also effectively applied. The major problem during the operation of any MBR system is membrane fouling. Thus, the continuous control of membrane fouling is a common pre-requirement in the MBR process efficiency. There are several methods available to control the fouling of membranes, such as the appropriate pre-treatment of wastewaters, the physical and/or chemical cleaning, the inhibition of concentration polarization by increasing the turbulence/aeration near the surface of membrane, or by reducing the respective flux, and the mixed-liquor modification by the addition of appropriate chemicals, such as coagulants or adsorbent-type reagents (e.g. powdered activated carbon). The pre-treatment of feed wastewater is considered nowadays as a necessity for all MBR systems (Radjenović *et al.*, 2008).

This study is part of a research project that aims to find the optimal operating conditions and the efficient composite coagulants to control fouling in membrane bioreactors (MBRs). For this purpose it has been developed a pilot-scale unit with fully automatic operation, where the introduction of selected coagulants was also predicted for the pre-treatment of feed wastewater (*Gkotsis et al., 201*3). Among the major scopes of this study was the investigation of alternative composite inorganic coagulants, such as PSiFAC - polyaluminum ferric silicate chloride (Tolkou *et al.*, 2013a, b) initially for the treatment of representative industrial wastewaters (e.g. tanneries, or yeast-production/fermentation plants), in order to be used latter, as the appropriate and effective coagulant, applied to the developed hybrid MBR system for the control of membrane fouling.

MATERIALS AND METHODS

All used chemical reagents were of analytical grade. De-ionized water (with conductivity lower than 0.5 μS/cm) was used to prepare all solutions, while de-ionized carbonate free water was used for the preparation of stock solutions of the coagulants used.

Synthesis of poly-aluminum-ferric-silicate-chloride coagulants

Composite coagulants (PSiFAC-polyaluminum ferric silicate chloride) were produced in this work at room temperature, according to a procedure proposed by Tolkou *et al.*, 2013a, under various experimental conditions, and using different ratios of components and (inorganic) polymerization modes. The used initial solutions were 0.5 M $AlCl_3 \cdot 6H_2O$ (Merck), 0.5 M $FeCl_3.6H_2O$ (Merck), 0.5 M NaOH (Merck) - as the added base - and the prepared polysilicic acid solution (pSi), according to Tzoupanos *et al.*, 2009. In particular, appropriate amount of ferric chloride solution is added to a solution of aluminum chloride, under vigorous stirring at the desired ratios of Al/Fe and in the formed solution is added the pSi at desired ratios of Al+Fe/Si, followed by the polymerization of the Al with the slowly (under magnetic stirring) addition of the appropriate amount of NaOH solution.

Jar tests

Jar tests were used for the examination of coagulants' efficiency. A jar-test apparatus (Aqualytic) equipped with six paddles was used, employing 1 L glass beakers. Three different industrial wastewater samples were examined: (1) a tannery wastewater; (2) a yeast manufacturing wastewater, subjected to preliminary anaerobic treatment; (3) the latter sample, but after subsequent aerobic treatment as well. The properties of all samples are given in the following Table 1, while the conditions used in the jar-test runs are shown in Table 2. It is worth noting that during these experiments the common polyelectrolyte addition was not applied.

Table 1. Major physico-chemical properties of initial wastewater samples.

Type of wastewater to be treated	Turbidity (NTU)	Absorbance $UV_{254\ nm}$	COD (mg/L)	Phosphates (mg/L)
Tannery Wastewater	668	2.981	6800	1.76
Yeast wastewater (after anaerobic treatment)	418	3.748	11455	3.49
Yeast wastewater (the previous, but after post-aerobic treatment, as well)	143	3.307	4590	2.40

Table 2. Experimental conditions of coagulation experiments for the aforementioned wastewater samples, according to Moussas et al., 2012.

	Rapid mixing period		Slow mixing period		Sedimentation
Type of treatment	Duration (min)	Mixing rate (rpm)	Duration (min)	Mixing rate (rpm)	(min)
Wastewater samples	3	200	30	40	45

Water samples were collected from the supernatant of each beaker and were analyzed for the determination of: turbidity, absorption at UV_{254nm} that provides an indication of the amount of natural organic matter (NOM) existing in the water samples, COD and phosphates.

RESULTS AND DESCUSSION

Physicochemical properties of prepared coagulant

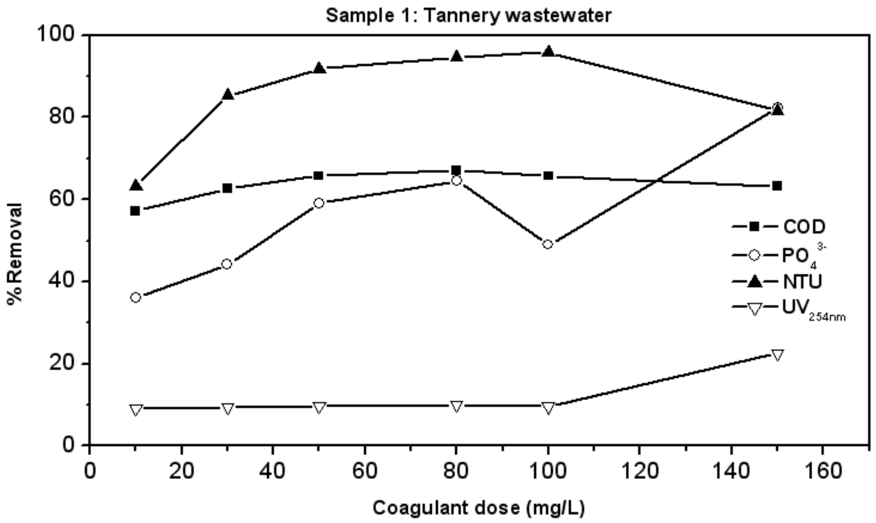
The most effective coagulant obtained during preliminary experiments (Tolkou *et al.*, 2013a, b), i.e. $PSiFAC_{1.5:10:15}$, was applied for the treatment of the aforementioned wastewater samples to evaluate its coagulation efficiency against these (considered as) relatively high-strength industrial wastewaters. Table 3 displays the major physicochemical properties of laboratory prepared composite inorganic coagulant.

Table 3. Properties of laboratory prepared coagulant.

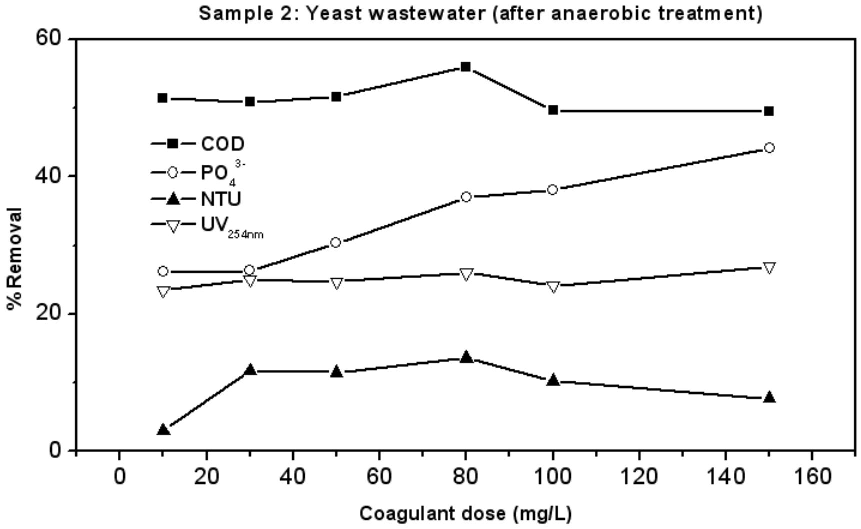
Coagulant type	[OH]/[Al]	[Al]/[Fe]	[Al+Fe]/[Si]	pH	Turbidity (NTU)	Conductivity (mS/cm)
$PSiFAC_{1.5:10:15}$	1.5	10	15	3.	218.0	26.0

The results of coagulation experiments for (%) turbidity, absorption at UV_{254nm}, COD and phosphates removals of wastewater samples are given in Figure 1; the experimental results indicated that, the addition of 80-100 mg/L of *$PSiFAC_{1.5:10:15}$* in yeast wastewater resulted to a reduction of COD 56%, of turbidity 40%, of UV_{254nm} absorbance 25% and of phosphates 43%; and to a reduction of COD 22%, of turbidity 14%, of UV_{254nm} absorbance 15% and of phosphates 38% respectively to samples 2 and 3.

However, higher removal rates were obtained by the same *$PSiFAC_{1.5:10:15}$* dose in tannery wastewater, resulting to a reduction of COD 67%, and 96% for turbidity and 62% for phosphates. Although regarding the UV absorbance at 254 nm, the rates were found to be rather small (10%), as the wastewater sample was not subjected to any pre-treatment stage this is a highly contaminated sample, but coagulation was beneficial to the improvement of its quality.



a)



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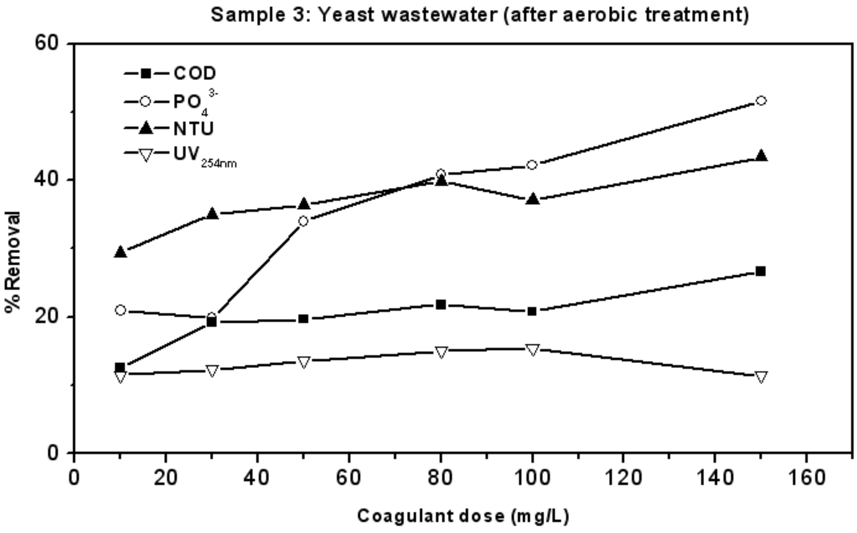

c)

Figure 1. Coagulation experiments for (a) tannery wastewater; (b) yeast manufacturing wastewater, subjected to preliminary anaerobic treatment; and (c) yeast latter sample additionally subjected (subsequently) to aerobic treatment.

This study is part of a research project that aims finding the optimal operating conditions and efficient composite coagulants to control fouling in membrane bioreactors, whereas membrane fouling is the major problem during the MBR process. The aim of this study was the investigation of alternative composite coagulants (such as $PSiFAC_{1.5:10:15}$ - polyaluminum ferric silicate chloride) for the treatment of representative industrial wastewaters samples, such as those from tanneries, or from yeast-production (fermentation) industries, in order to be used latter as the appropriate coagulant to prevent/control fouling, applied in a hybrid treatment system (MBR + coagulation) that has been developed in laboratory and in pilot-scale, with fully automatic operation.

CONCLUSIONS

The preliminary results of coagulation experiments, regarding the removals of turbidity, of absorption at UV_{254nm}, of COD and of phosphates of the 3 wastewater samples examined, showed that this composite coagulant proved to be quite effective, depending upon the specific wastewater properties; therefore, the addition of 80-100 mg/L of $PSiFAC_{1.5:10:15}$ in yeast wastewater resulted to a reduction of COD between 22-56%, of turbidity 14-40%, of $UV_{254\ nm}$ absorbance 15-25% and of phosphates 38-43%, respectively to the aforementioned yeast samples. However, higher removal rates were obtained by the same coagulant ($PSiFAC_{1.5:10:15}$) addition regarding the treatment of tannery wastewater, resulting to a reduction of COD 67%, of turbidity 96%, of phosphates 62%, but only 10% of $UV_{254\ nm}$ absorbance.

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(S31) Degradation of an endocrine disrupting chemical (EDC) using different Advanced Oxidation Processes

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Abstract

Advanced oxidation processes (AOPs) are considered as potential technologies for treating wastewater contaminated with persistent and recalcitrant compounds such as pharmaceutical products, especially endocrine disrupting substances. These compounds are contaminants found, although usually at low concentrations, at the time of inspection of water quality in many treatment plants, which shows that conventional treatments used to purify sewage are not 100% effective.That is why it is necessary to find new alternatives, such as AOPs, for the removal of these compounds. In this paper is studied the application of O_3/UV, O_3/H_2O_2 and UV/H_2O_2 processes for degradation of a commercial hormone. High removals were obtained, around 85% when were used the treatments O_3/UV and O_3/H_2O_2 for removing of Depo-Provera for an initial concentration of 150 mg/L.

Keywords

Advanced oxidation processes, endocrine disrupting chemical, pharmaceutical compounds, wastewater

INTRODUCTION

There are a large number of pharmaceutical compounds such as anti-inflammatories, antibiotics, antidepressants, contraceptives, psychoactives, etc. (Al-ahmad&Mersch-sundermann, 2000), which have become in potential contaminants, since due to the similarity of their behavior physicochemical with xenobiotics and their low biodegradability, are persistent in aquatic environments touching off adverse effects on the ecosystem. Such is the case of contraceptives dumping to water bodies that disrupt the hormonal control of the development of aquatic organisms. These hormones are considered exogenous substances that alter the function of the endocrine system and consequently cause adverse health effects of organisms, their progeny and all population of the same that coming in contact with these (Esplugas et al., 2007). Hormones affect mainly on animals and humans bringing about feminization of male fish, changes in reproductive and immune system of fish, reptiles, birds and mammals; reducing the quantity and quality of sperm, trend of increasing breast, testicular cancer and prostate, among others (Commission of the European Communities, 2001). At present have been identified three ways of entry of these compounds in the environment, such are hospital effluents, and animal and human excretions. Conventional treatments used in the WWTP to remove these kinds of pollutants are not enough, so it becomes necessary combine them with other treatmentslike the advanced oxidation processes, being effective to guarantee a correct degradation and transformation of these compounds of difficult treatability (Verlicchi et al., 2012). AOPs are processes able to increase the biodegradability of compounds present in the water by means of redox reactions. These processes can be the ozonation, UV irradiation, hydrogen peroxide application and processes based on the attack of hydroxyl radicals • OH (Gültekin&Ince, 2007). By all previously mentioned, the objective of this paper is to evaluate the effectiveness of the application of three different combinations of advanced oxidation processes (O_3/UV, O_3/H_2O_2 y UV/H_2O_2) to remove a disruptor substance of endocrine system, shaped like contraceptive (Medroxy-Progesterone Acetate) of a water sample.

MATERIALS AND METHODS

Materials

As study compound was used progesterone hormone Depo-Provera in commercial presentation, kind ampoule of 3ml that containing 150mg Medroxy-progesterone acetate per ampoule. Different dilutions of the compound were prepared in water and were made absorbance measurements using a UV-VIS, Hach Model DR 5000 spectrophotometer. By scanning in the wavelength range between 200 and 500nm was determined that the wavelength for maximum absorption of the compound is in the 254nm. This value is used to make monitoring the compound during treatment.

The reactor is a glass vessel borosilicate of 550 mm length, 100 mm in outside diameter, with a volume of 1414 ml, which has a mercury UV lamp of low pressure in the center, as seen in Figure 1. Ozone is generated externally by a machine Microzone 300P 120V/60HZ trademark Clearwater Tech, LLC, with a production ozone of 237mg O_3/h which is distributed in the reactor through a porous plate on the bottom that has an average pore size.

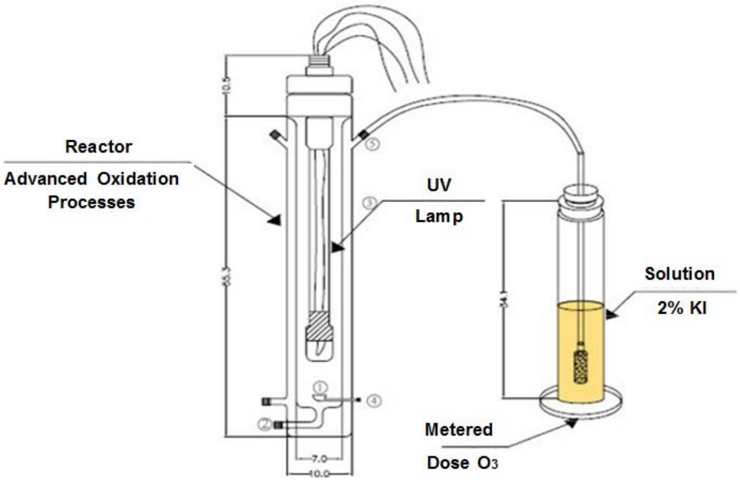

Figure 1.Ozone/UV reactor

General procedure

Three different solutions of Depo-proverawere preparedadding 1 L of distilled water per vial of the drug, in each of solutions was controlled the volume of water to obtain the optimum concentration to facilitate the analysis in the spectrophotometer. Before and after the treatment of advanced oxidation, the pH value measurement was performed to the sample, which remained in all cases 1 hour in the reactor. During this time UV measurements were made on liquid samples (3 ml) every 15 minutes to monitor the decay of the drug concentration. Also, COD measurements were made before and after the AOP. The reaction time in each AOP began with the activation of the elements that provide the oxidizing agents, usually started when the UV lamp and ozone producer were connected to the reactor interacting with hydrogen peroxide, added previously.

RESULTS AND DISCUSSION

Firstly, Characterization of Depo-provera solutions was made and it is shown in Table 1.

Table 1. Characterization of Depo-provera solutions.

Parameter	*Unit*	*Time*	*Sample AOP*		
			O_3/UV	*O_3/H_2O_2*	*UV/H_2O_2*
pH	-	Initial	6.26	6.60	6.22
		Final	3.82	3.86	8.24
COD	mg/L	Initial	530	530	530
		Final	202	297	217
TOC	mg/L	Initial	448	448	448
		Final	68	74	70

After of doing the characterization of Depo-Provera solutions proceeded to apply selected advanced oxidation processes to each solution, these were exposed for 1 hour in the reactor to oxidizing agents. The absorbance values obtained in time are presented in Table 2. Based on the absorbance value obtained, was calculated the removal percent (%) from the initial value.

Table 2. Absorbance and removal percentage of Depo-provera for AOPs applied.

ADVANCED OXIDATION PROCESSES								
O3/H2O2			***O3/UV***			***UV/H2O2***		
Time (min)	*Absorbance (cm^{-1})*	*Removal (%)*	*Time (min)*	*Absorbance (cm^{-1})*	*Removal (%)*	*Time (min)*	*Absorbance (cm^{-1})*	*Removal (%)*
0	0.623	-	0	0.623	-	0	0.634	-
15	0.323	48.2	15	0.325	47.83	15	0.609	3.9
30	0.122	80.4	30	0.149	76.08	30	0.594	6.3
45	0.100	83.9	45	0.102	83.63	45	0.574	9.5
60	0.083	86.7	60	0.102	83.63	60	0.359	43.4

As seen in Table 2, the measured absorbance value decreased significantly from 0 minutes to 60 minutes in each of the AOPs applied, this suggests an elimination or removal of the pharmaceutical compound due to decay in their concentration. At the end of the implementation of the three advanced oxidation processes was obtained a Depo-provera removal of 86% when was applied O_3/H_2O_2, suggesting that this treatment is the best for drug redox. However, the other 2 treatments also showed very satisfactory results.Although AOPs are not 100% effective in removing the contaminant compound, the application of these treatments generates further degradation of the compound by any biological process.At presently, tests are being conducted to determine the improvement in the biodegradability of Depo-Provera hormone after application of AOPs.

CONCLUSIONS

The removal of the hormone Depo-provera by advanced oxidation processes in aqueous solution was studied in this paper. From applying of O_3/UV, UV/ H_2O_2, O_3/H_2O_2 in the removal of the hormone, was obtained that an aqueous solution treated with O_3/UV and O_3/H_2O_2 is highly effective because a removal of almost 85% for both based in an initial concentration of 150mg / L.

ACKNOWLEDGEMENTS

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(S32) Removal of heavy metals using Advanced Oxidation technology

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Abstract

With the rapid increase in population, developmental works and industries, the environment is bound to get polluted, if timely steps are not taken for proper treatment of the pollutants, before allowing their mixing in the raw form with the main components of the environment i.e. air, food and water, earth, forests etc. which are the life sustaining resources available in the environment. The need of the hour is to adopt necessary steps for proper treatment of all types of wastes that are generated in the society due to our own day to day activities. The electroplating of a metallic product is done to prevent it from corrosion and to give a decorative and smooth finish. This paper deals with Characterization, quantification and treatment of electroplating Industry wastewater. The wastewater was treated using Advance Oxidation technology with Fenton's reagent for the removal of heavy metals. The results indicated an increase in the percentage reduction of heavy metals with an increasing dose of Fenton's reagent. Hydrogen peroxide alone was not effective in the removal of heavy metals. However, hydrogen peroxide in combination with ferrous Sulphate (Fenton's reagent) was effective in the removal of heavy metals.

Keywords
Characterization, treatment, electroplating, heavy metals, sustainable environment.

Materials and methods:

Source of Waste Water for analysis:

The Waste water was obtained from M/s Sigma Electroplating Industry, Anoopshahr Road, Aligarh (U.P.), India which is a sister concern of M/s Link Locks (P) Ltd, Industrial Estate, Aligarh (U.P.). The Wastewater samples were analyzed in the Environmental Engineering Labs at Aligarh Muslim University, Aligarh(U.P.)

Addition of Fenton's reagent:

In this step the Fenton's reagent was added in four different amounts in the Wastewater (kept in four jars of the jar test apparatus). The mixing of the reagent was done by the stirring device, at an agitation rate of 300 rpm for 5 minutes.

Results and Discussion:

The effect of various doses of Fenton's reagent on the removal of Cr, Cu and Ni without adjusting the pH of the wastewater is presented in Table 1, Table 2 and Table 3 respectively. The results indicate an increase in the Cr, Cu and Ni removal with an increasing Fenton's reagent dose. A 53.15 % removal of Cr, 48.53 % removal of Cu and 26.46 % removal of Ni is observed at the Fenton's reagent dose containing 20 ml of H_2O_2. This is due to the increase in the production of hydroxyl radicals at higher doses of hydrogen peroxide. The effect of various doses of Fenton's reagent on Cr, Cu and Ni removal with pH adjustment is presented in Table 4, Table 5 and Table 6 respectively. The results indicate an increase in the percentage reduction of heavy metals with an increasing dose of Fenton's reagent .A 60.00 % reduction of Cr is observed at a Fenton's reagent dose containing 20 ml of hydrogen peroxide with 1.0 g of ferrous sulphate.A 59.81 % reduction of Cu is observed at a Fenton's reagent dose containing 20 ml of hydrogen peroxide with 1.0 g of ferrous sulphate and a 48.79 % reduction of Ni is observed at the same dose of Fenton's reagent as in case of Cu. It is also observed that for each dose of the Fenton's reagent the percentage reduction efficiency which is obtained after the pH adjustment is higher than that without adjusting the pH. This might be due to the generation of $Fe(OH)^2+$, which is generating the OH radicals in the pH of 4.0.

Conclusions:

- Hydrogen peroxide alone was not effective in the removal of heavy metals.
- However, hydrogen peroxide in combination with ferrous Sulphate (Fenton's reagent) was effective in the removal of heavy metals the removal efficiency increases with increase in hydrogen peroxide concentration.
- The removal efficiency of heavy metals increases by adjusting the pH of the solution to 4.0.
- The results show that about 60% of Cr, 60% Cu and 50% of Ni can be removed from an electroplating effluent by advanced oxidation process using Fenton's reagent at acidic pH of 4.0.

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Environmental and Economic Assessment - GHG emissions

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(K7) Lessons learnt from N_2O production during extremely high nitrogen streams treatment

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Abstract

High influent NH_4^+, mixed liquor NO_2^- concentration and low BOD/N ratio are defined as the main parameters for N_2O formation.Partial nitritation (PN)-anammox processes are applied to treat high nitrogen and low BOD/N ratio streams. PN process is the main N_2O source linked with ammonium oxidizing bacteria (AOB) activity. When operating PN-anammox in one singlestep, N_2O production was lower as well as NO_2^-. However, AOB activity and N_2O production were also reduced at extremeNO_2^- concentration. In two reactors configuration, AOB activity can be partially inhibited by high NH_3 and HNO_2 concentrations as well as HCO_3^- limitation which would reduce aerobic N_2O formation during the PN process. The application of anoxic feedings resulted in heterotrophic community structure highly adapted and low diverse when treating wastewaters with high N and heterogeneous COD. Competence for electrons was observedcausing N_2O accumulation. In this context, heterotrophic denitrification should be avoided.

Keywords
Nitrous oxide; partial nitritation; ammonia oxidizing bacteria; denitrification; high N load;

INTRODUCTION

N_2O is a greenhouse gas with a global warming potential300 times higher than CO_2. Biological nitrification-denitrification process is responsible for the majority of anthropogenic N_2O emission from wastewater infrastructures. To establish their contribution, severalstudies have monitored N_2Oin conventional biological nutrient removal (BNR) and partial nitritation (PN)–anammox processes(Foley et al. 2010, Kampschreur et al. 2008). Experimental results between studies vary largely due to the different operational conditions, and up to date there is no consensus on their extent.However, the fundamental research carried out in recent years has allowed understandingthe main conditions leading to N_2Oaccumulation and later emission. On one hand, aerobic N_2O production is mainly caused by ammonia oxidizing bacteria (AOB) activity by two metabolic pathways: hydroxylamine oxidation and autotrophic denitrification. The main parameters that affected N_2O production by AOB are high NO_2^- concentrations, high influent NH_4^+loads and low dissolved oxygen (DO) concentrations (< 1 mg O_2 L^{-1})among others(Kampschreur et al. 2008). On the other hand, anoxic N_2O production can be linked totwo main pathways. During anoxic conditions both autotrophic and heterotrophic denitrification occurs. Heterotrophic denitrifiers can reduce NO_3^- to N_2 in four steps ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) using biodegradable organic matter (BOD) as electron donor.Low BOD/N ratio and electron competence between denitrification enzymes are defined as key parameters for N_2Oproduction(Pan et al. 2013). Also, AOB can autotrophically denitrify NO_2^- to NO (Yu et al. 2010) which would be available for further heterotrophic denitrification.

Wastewaters containing high nitrogen concentration and low BOD/N ratio can be treated by PN-anammox process as a more sustainable alternative than conventional nitrification-denitrification. PN-anammox can be performed in one single reactor or in two reactors. Given the oxygen inhibition of anammox bacteria, operation in a single step has to ensure low DO levels (<1 mg O_2 L^{-1}) which favors N_2O production(Desloover et al. 2011). Since both processes occur in the same tank, low concentrations of NO_2^- and $NH_4^+$are achieved(<10 mg N L^{-1}), causing low N_2O production (Joss et al. 2009). On the other hand, aerobic process (PN) and the anoxic process (anammox) can be decoupled in two reactors in a two-stage PN-anammox configuration. Since anammox pathway does not produce N_2O(Desloover et al. 2011), the PN reactor -the preparatory step for an anammox reactor where about half of the NH_4^+ is partially oxidized to NO_2^-- would be the main source of N_2Odue to the high NH_4^+ and NO_2^- concentrations in the mixed liquor. Additionally, anoxic feedings can be included to oxidize the BOD while consuming NO_2^-heterotrophically. This would reduce the nitrogen load for the subsequent anammox reactor, as well as aeration requirements for BOD oxidation in aerobic conditions.

In this contribution we discuss themain findings of our work on N_2O emissions from partial nitritation reactors treating high nitrogen loads, comparing them with state-of-the-art literature.

N_2O PRODUCTION AT HIGH NITROGEN LOADS

LEQUIA has developed the Panammox®technology to treat mature landfill leachate. Panammox® is a two-step PN-anammox process in SBR configuration. Its successful treatment of leachate has been already demonstrated (Anfruns et al. 2013, Ganigué et al. 2009, Ruscalleda et al. 2008). The first step of Panammox® is a PN-SBR operated at high temperatures -25°C and 35°C; (Gabarró et al. 2012)-, which objective is to produce a suitable effluent to feed the subsequent anammox reactor. However, landfill leachates have high COD concentration. This COD is heterogeneous in terms of biodegradability, with a larger proportion of non-biodegradable recalcitrant compounds, another part of slowly biodegradable COD (BOD_u) and low easily biodegradable COD (BOD_5) content.Anoxic feedings were included in the PN-SBR cycle configuration to promote heterotrophic denitrification via NO_2^-. This would reduce both nitrogen loading for the subsequent anammox reactor and removal of BOD_5 without energy consumption (aeration).

The PN-SBR treated mature landfill leachate combining anoxic feedings with aerobic reactions. Stable performance was achieved at a nitrogen loading rate (NLR) of 1.5 kg N m^{-3} d^{-1}, producing a suitable and stable effluent to feed a subsequent anammox reactor (1000 mg N-NH_4^+ L^{-1} and 1000 mgN-NO_2^- L^{-1} approx.). According to the literature, these stringent conditions should lead to very high N_2O production (Kampschreur et al. 2008). However, the overall PN-SBR N_2O production was 3.6 ±0.4% of the total influent nitrogen, in a similar range of other studies with lower concentrations and treating lower loads. Looking at the contribution of the different phases, anoxic phases were responsible of 60% of the total N_2O production while aerobic phases accounted for 40% of the total N_2O production (Gabarró et al. 2014).The contribution of anoxic pathways was far greater than the aerobic if we take into account that anoxic time represented only 20% of the total cycle time.These observations are in contradiction to the findings of Ahn and co-workers (2010), who reported that aerobic treatment has a larger N_2O productionthan anoxic processes. However, this study was conducted in a conventional wastewater treatment and differences in wastewater type and processes could explain differences.

Comparing the emission factor of the PN with other similar studies in literature, reactors at lab scale treating synthetic wastewater (500 mg N-NH_4^+ L^{-1}) had N_2O emission of1.5 ± 0.2% of the NLR(Kong et al. 2013). Values ranging from 0.6 to 2.6% were reported for systems treating black water (1000-1500 mgN-NH_4^+ L^{-1}; (de Graaff et al. 2010)). Regarding full scale measurements in two stages PN-anammox systems, Desloover et al reported an N_2O emission factor of 5.1-6.6% from a reactor treating industrial potato digestate (264mg N-NH_4^+ L^{-1}; (Desloover et al. 2011)) and 2.3% as N_2O was emitted from a system treating digester liquor (1500 mg N-NH_4^+ L^{-1}; (Kampschreur et al. 2008)). Both studies attributed their critical parameters for N_2O production to DO, high NH_4^+ and NO_2^- concentrations.Nevertheless, the aerobic N_2O production during the treatment of mature leachate in the PN-SBR (1.4%) was lower than the expected N_2O production values at high NO_2^- concentration, high NLR and high influent nitrogen concentration.

Finally, it is important to bear in mind that the previously reported studies were conducted using synthetic media or were focused on the treatment of digestate liquor. In this respect, fully aerobic conditions were applied, and the present results on N_2O emissions from anoxic phases cannot be compared. Nevertheless, from the results of this study, the anoxic-aerobic strategy to promote heterotrophic denitrification had high N_2O production (2.2% of the total NLR), and should be avoided due to the competence for electrons of the different denitrification enzymes as the heterotrophic community is highly specialized and adapted to stringent conditions (Gabarró et al. 2013).

N_2O PRODUCTION PATHWAYS TREATING HIGH NITROGEN STREAMS

Based on the experimental results, the main nitrogen bio-transformation pathways in the PN-SBR are presented in Figure 1. AOB is the only aerobic N_2O source and its production exponentially correlates with their activity(Law et al. 2012). Nevertheless, experimental results showed that aerobic production was moderate (1.5% of the NLR). This is because PN-SBR treating mature leachate operated at very low NH_4^+ oxidation rates(20 mgN-NH_4^+ $gVSS^{-1}$ h^{-1}; (Gabarró et al. 2014) due to the free ammonia (FA) and free nitrous acid (FNA) activity inhibition, as well as the HCO_3^-substrate limitation(Gabarró et al. 2012).This is in agreement with the confounding effect of NO_2^-, reported by Law et al. (2013),: In their study, they observed that at high NO_2^-concentrations (up to 1000 mg N NO_2^- L^{-1}) the N_2O production was reduced.

Regarding the anoxic pathways,AOB can denitrifyNO_2^- during anoxic conditions but producing NO as the end-product (Yu et al. 2010) which could be reduced to N_2O by heterotrophic bacteria. On the other hand, in heterotrophic denitrificationNO_2^- is sequentially reduced to NO, N_2O and finally N_2using BOD_5 and BOD_u from feeding phases as the electron donor.Experimental results showed significant N_2O generation in anoxic conditions. This could be due to several reasons. Some authors pointed out that N_2O reducing enzyme (*nosZ*) can be inhibited by FNA(Zhou et al. 2008). In this light, the genetic potential of the PN-SBR community to denitrify N_2O was low because *Bacteroidetes* sequenced from mixed liquor samplesdid not have the *nosZ*gene(Gabarró et al. 2013). In this context, a small part of the microbial community (*Alphaproteobacteria*and *Betaproteobacteria*) would be able to denitrify N_2O (Gabarró et al. 2013). Denitrifying batch tests were conducted to verify this and results were in agreement with Pan et al. (2013) who reported a competence between denitrification enzymes for electrons which causes N_2O accumulation in the mixed liquor(Gabarró et al. 2014). This hypothesis would make sense if the same bacterial group is responsible for the full denitrification. Based on these findings we propose an ecological equilibriummodel (Figure 1) where *Baceroidetes*, which are specialized on the oxidation of BOD_u(Gabarró et al. 2013), would not significantly denitrify NO_2^- while heterotrophic *Alphaproteobacteria*and *Betaproteobacteria* would be the responsible for NO_2^-, NO and N_2O denitrification with the BOD_5.

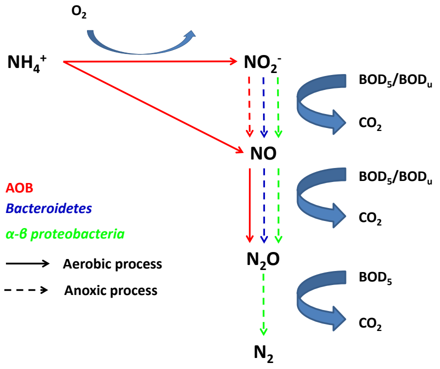

Figure 1. Possible biological pathways for nitrogen transformations in the PN-SBR. Different colors are used to separate biological pathways. Ammonia oxidizing bacteria (AOB) pathway is in red, *Bacteroidetes* in blue and *alpha* and *betaproteobacteria* in green. Aerobic processes are marked by solid lines and anoxic processes by dashed lines.

CONCLUSIONS

Anoxic phases should be avoided when treating wastewaters containing high recalcitrant and heterogeneous COD to reduce N_2O production.

Aerobic N_2O production from PN reactor treating high N concentrations was moderate due to the reduced AOB activity due to the FA and FNA inhibition and the bicarbonate substrate limitation.

Heterotrophic denitrification should be avoided because at low BOD/Nratios, the high electron competence between denitrification enzymes causes N_2O accumulation.

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(P33) Monitoring of the oxygen transfer efficiency and greenhouse gas emissions in the oxidation tank of San Colombano WWTP

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Abstract

This paper shows the results of a monitoring campaign of the oxygen transfer efficiency and of the greenhouse gas emissions, in a large urban wastewater treatment plant (600000 P.E.) located in Tuscany (Italy). Different measurements techniques were compared for GHGs emission monitoring. Off-gas tests were successfully carried out showing high-performance of the aeration system. The ammonia-DO cascade controller recently installed guaranteed an oxygen transfer efficiency higher than the one registered in a previous off-gas test campaign carried out when the air-flow rate control was based only on the DO concentration. Wastewater treatment processes actually produce GHGs (nitrous oxide, methane and carbon dioxide), which can be successfully monitored using the off-gas test device. The different sampling techniques gave similar results, but the daily variability of the N_2O production requires continuous sampling of the off-gas. The present results are in accordance with literature data both in terms of emission concentrations and of the ratio between the N_2O emissions and the inlet total nitrogen load.

Keywords
Off-gas method; nitrification; N_2O emissions; greenhouse gas; oxygen transfer efficiency; wastewater treatment plant.

INTRODUCTION

During the last 200 years, the atmospheric concentrations of greenhouse gases (GHGs) have been increasing. The interest for greenhouse gases (GHGs) emissions from wastewater treatment plants (WWTPs) has considerably increased in the recent years. The major GHGs, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) can all be produced in wastewater treatment operations and a quantification of GHGs is necessary to improve the sustainability of WWTPs.

Nitrous oxide (N_2O) emissions from WWTPs vary substantially between plants, ranging from negligible to substantial because of different designs and operating conditions. Based on recent field-scale measurements, the biological nitrogen removal processes could emit up to 7% of the influent nitrogen load as gaseous nitrous oxide (N_2O) and nitric oxide (NO) (Kampschreur et al., 2008). Since the first published data by Czepiel (Czepiel et al. 1995) reporting N_2O emissions from a WWTP, awareness of N_2O emissions during wastewater treatment has grown significantly. Such emissions are deleterious to the environment. The greenhouse equivalence of N_2O is about 300 times that of carbon dioxide, it is very persistent (lifetime of 114 years) and is currently the single most important ozone-depleting gas (Ravishankara et al., 2009). In general, N_2O emissions primarily occur in aerated zones owing to active stripping, and ammonia-oxidizing bacteria, rather than heterotrophic denitrifiers, are the main contributors. N_2O and NO are known intermediates in heterotrophic denitrification and autotrophic nitrification and denitrification. However, the detailed mechanisms have not been fully elucidated. Additionally, there is a real scarcity of systematic protocols that enable collection of N_2O emission fluxes from open-surface activated sludge bioreactors using consistent methodology. Owing to the complexity involved in measuring N_2O emissions from full-scale plants and the lack of standardized measurement methods, the N_2O emissions for the wastewater sector have been often estimated on the basis of models, without the input of measured data.

Moreover, economic and environmental benefits can be reached by optimizing the aeration distribution system. As a matter of fact, energy saving plays a key role in reducing operating costs and CO_2 emissions WWTPs (Libra et al, 2002). Since in a conventional activated sludge plant energy demand is largely dominated by the aeration (Rosso and Stenstrom, 2005), considerable savings are possible by optimizing its design and operation. Fine bubble aeration system offer numerous advantages, including energy savings by about 50%, compared to the coarse bubble aeration systems. However, due to the chemical nature and morphology of the membrane materials, they are subject to fouling and scaling which can affect their operation and reduce the benefits of their utilization in the long term.

This study presents the results of an off-gas test campaign carried out to monitor the oxygen transfer efficiency in the oxidation tank of a conventional urban WWTP. Results obtained with the recently installed control system have been compared with the ones obtained with the previous air flow control strategy.

Moreover, this study shows the results of the continuously monitoring of the off-gas emissions from the oxidation tank, aimed at obtaining a complete data set about the emissions during a day. Different monitoring procedures were compared.

In order to collect the off-gas produced in the oxidation tank, the off-gas test hood was used.

MATERIALS AND METHODS

The off-gas measurement campaign has been carried out in the oxidation tank of the San Colombano WWTP which is a municipal conventional activated sludge WWTP (managed by Publiacqua SpA) with denitrification-nitrification processes, which treats about 60,000,000 m^3/y. The aeration tank is provided with fine bubble diffusers (ABS, PIK300) with EPDM membranes. The air flow rate is automatically regulated through a cascade ammonia-DO controller with an ammonia set point in the range of 0,5 - 1,5 mg/l. This system guaranteed a significant decrease of the energy consumption with respect to the previous controller based only on the DO concentration.

The oxygen transfer efficiency (OTE) aeration systems under process conditions (αSOTE) has been assessed through off-gas tests according to the method developed by Redmon et al. (1988), based on the comparison between the oxygen content in the atmosphere (Ref) and in the off-gas (OG) withdrawn from above the process tank.

The instrument is equipped with a combustible chamber that makes it possible to measure the oxygen content in the gas flows, a column (h=0.255 m, d=0.025 m) for absorbing the CO_2 and the water vapour present in the gas flows, a hot wire anemometer for measuring the off-gas uptake captured by the hood, and a valve for choosing between sending the ambient air and the off-gas into the test circuit. The signals coming from the oxymeter and the anemometer are automatically acquired every 0.05 seconds using an acquisition data card (National Instruments, sbRIO-9632). In order to collect the oxidation tank off-gas, a rectangular PVC hood was used with a 0.7 m^2 capturing surface, fitted with a hose with a 0.038 m diameter that allows for conveying the off-gas towards the analyser. The hood was placed in the first part of the aeration tank.

The following parameters are continuously measured during the analysis: the OG flow-rate captured by the hood (also used for mass flow rate of GHGs), the oxygen concentration in the gas phase, the dissolved oxygen concentration in the liquid phase (DO), the atmospheric pressure, and the temperature of the gas and liquid flows. The recorded data allow to calculate the oxygen transfer efficiency under process conditions (OTE) and in standard conditions in process wastewater.

In this case, the system used for off-gas monitoring, was also equipped and used for monitoring the nitrous oxide, the carbon dioxide and the methane produced in the aeration tank.

Tests have been carried out continuously for 24 hours, in order to evaluate the emissions during the day and the night. Different procedures have been implemented in order to measure, both in the gaseous and in the liquid phase, the nitrous oxide, the carbon dioxide and the methane. A continuous gas monitoring system (InfraRed-Photoacustic Multigas Monitor) and two different discrete gas monitoring systems were used: tedlar sampling bags (26 bags, 10 l capacity each) and AT575 passive sampler (10 samplers).

The gas collected in the bags and the gas desorbed from the passive gas samplers were analyzed with the gas chromatograph - Electron Capture Detector (GC-ECD) and the gas chromatograph - Flame Ionization Detector (GC-FID).

In order to measure the nitrous oxide in the liquid phase, the mixed liquor has been sampled from the nitrifying tank in sample vials. The gas has been extracted from the head space and the nitrous oxide has been measured trough GC-ECD.

In order to correlate the GHGs emissions with the organic and the nitrogen load of the WWTP influent, a 24-hour monitoring was carried out of COD and nitrogen compounds in the inlet and in the outlet of the oxidation tank.

RESULTS AND DISCUSSION

Results of the off-gas tests showed a high performance of the aeration system, with OTE of 29 % and αSOTE of 29.5% on average during the test. These values were higher than those registered in a previous off-gas test campaign carried out when the air-flow rate control was based only on the DO concentration. Economic and environmental benefits of the new controller will be presented in the full paper. During the test, DO ranged between 0,2 e 1,2 mg/l with the exception of a very short period (30 min) with values between 1,2 and 2,2 mg/l. The low values of DO registered in the tank, while are beneficial for the energy saving, could significantly affect the GHGs production.

As far as the GHGs emission is concerned, experimental results showed that the nitrous oxide concentration trend in the off-gas of the aeration tank is variable during the day. The results obtained with the three different monitoring procedures show a similar trend: lower values during the morning and the night, and higher values during the afternoon. The nitrous oxide trend follows that of $N\text{-}NH_4$ and N_{tot} concentration in the influent. In accordance with the literature data, the N_2O concentration was higher for lower values of the dissolved oxygen in the oxidation tank.

Moreover, not only the trends were similar, but also the values obtained with the different procedures were in the same range (differences lower than 0.5 ppm were always registered). Table 1 shows the nitrous oxide concentrations in the gaseous phase, obtained with the different measurement techniques. The values obtained are in accordance with the literature data (Rosso et al., 2011). The value of the nitrous oxide concentration in the ambient air during the monitored day varied between 0.2 and 0.4 ppm.

Table 1. Nitrous oxide concentration in the gaseous phase

Nitrous oxide concentration (ppm)	Tedlar bag sampling	IR monitoring	AT575 passive sampler
Maximum	5.18	6.26	5.11
Minimum	2.79	2.81	2.13
Average	3.73 (n=26)	3.39	3.15 (n=10)

Considering the off-gas flow rate, the average nitrous oxide production was 8900 mg/h, while the maximum and the minimum values were 22950 and 4450 mg/h.

On average, nitrogen emitted as N_2O from the oxidation tank represents the 0.025% of the inlet total nitrogen. This value is in accordance with the literature data (Lotito et al., 2012).

The nitrous oxide concentration in the mixed liquor varied during the day. Values were negligible

(<0.5 mg/l) during the early morning and the night, and higher in the afternoon when the nitrous oxide concentration reached the highest values. Table 2 shows the average values of the nitrous oxide concentration in the gaseous and in the liquid phase during the afternoon.

Table 2. Nitrous oxide concentration in the gaseous and in the liquid phase

Nitrous oxide concentration	gaseous phase (ppm)	liquid phase(mg/l)
14:30-16:00	5.11	0.032
16:00-17:30	4.68	0.016
17:30-19:00	4.81	0.026

Table 3 shows the CO_2 and the CH_4 concentrations measured in the off-gas. The average concentration of CO_2 and CH_4 in the atmosphere during the monitored day were 635 ppm and 1.77 ppm.

Table 3. CO_2 and CH_4 concentrations measured in the off-gas

	CO_2 (ppm)	CH_4 (ppm)
maximum	22129	4.03
minimum	19364	0.61
average	20889	2.61

Considering the off gas flow rate, the average methane production was 2.42 kg CH_4/h. The influent COD was 133.24 kgCOD/h. Therefore, this leads to an emission factor (kgCH_4/kgCOD) of 1.82%. This value is in accordance with the literature data (Daelman et al., 2013).

According to our experimental study we can conclude that off-gas test was successfully carried out showing high-performance of the aeration system. The ammonia-DO cascade controller guaranteed an higher oxygen transfer efficiency than the one registered in a previous off-gas test campaign carried out when the air-flow rate control was based only on the DO concentration.

Moreover we can assess that wastewater treatment processes actually produce greenhouse gases, which can be successfully monitored using the off-gas test device. The different sampling techniques gave similar results, but the daily variability of the N_2O production requires continuous sampling of the off-gas. The present results are in accordance with literature data, both in terms of emission concentrations and of the ratio between the N_2O emissions and the inlet total nitrogen load.

An economic and environmental analysis has been carried out to assess the optimal control strategy for reducing the energy consumption without increasing too much the GHGs emissions: the results will be shown in the full paper.

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(P34) Identification and Characterization of Process Scenarios Leading to Peak CH_4 and N_2O Emissions in a Full-Scale Wastewater Treatment Plant

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Abstract
As a result of the importance of methane (CH_4) and nitrous oxide (N_2O) on the global climate, emissions from any industrial process should be understood, quantified and minimized. Relevant amounts of these gases have been found to be emitted during wastewater treatment, but the process parameters and events affecting gas emissions need to be identified and characterized. In this study, CH_4 and N_2O emission dynamics were studied during normal wastewater treatment operation in a conventional, full-scale activated sludge system during 60 days. Within this period, peak emission events occurred and were correlated with real-scale process scenarios. Aeration drop, nitrification instability and reject wastewater influxes were identified as major triggers of N_2O and/or CH_4 peak emissions. Identifying these process scenarios and their impact on green-house gases emission creates awareness among plant operators, and minimization strategies can be suggested and implemented.

Keywords
Methane; nitrous oxide; green-house gas emissions; full-scale activated sludge; wastewater treatment

INTRODUCTION

Carbon dioxide (CO_2), CH_4 and N_2O are the most important green-house gases related to wastewater treatment processes. CH_4 and N_2O have a global warming potential which is about 25 and 300 times larger than the one attributed to CO_2 respectively, in a 100-years scope. In this study, only CH_4 and N_2O emissions were on focus due to their importance, and because their dynamics in wastewater treatment systems are to a large extent unknown. Furthermore, there is very limited data on CH_4 and N_2O emissions from full-scale wastewater treatment plants (WWTPs), and the process conditions that trigger gas production and emission are still to be identified.

In wastewater treatment systems, CH_4 is produced as a consequence of anaerobic processes, such as sludge digestion. Sewer systems have also been proven to be a source CH_4 from which it can be distributed and released (Guisasola *et al*. 2008). Agitation and aeration during wastewater treatment processing facilitates CH_4 stripping to the atmosphere. On the other hand, N_2O production is generally attributed to nitrification and denitrification processes, with the first one being considered the source of the majority of emissions in WWTPs (Colliver and Stephenson, 2000). Green-house gas emissions reported to date in full-scale studies are highly variable and strongly bounded to specific operating conditions. The objective of this study was to identify and analyse the particular process scenarios or events that presented the largest impact on CH_4 and N_2O emissions in a full-scale activated sludge bioreactor.

MATERIALS AND METHODS

The monitoring site chosen in this study was the WWTP of the city of Granollers, near Barcelona (Spain). This plant treats the domestic wastewater of 112.000 person equivalents (P.E). Also, industrial effluents are occasionally discharged at the inlet of the plant. After primary treatment and settling, the wastewater is treated biologically in two parallel activated sludge plug-flow reactors where chemical oxygen demand (COD) and nitrogen removal are performed. Then, the wastewater flows into a secondary settler before being released into the environment. Sludge in excess is treated in an anaerobic digester in order to produce biogas for electricity generation. A flow of reject wastewater (anaerobic sludge digestion liquor) is periodically released at the inlet of the plant for its treatment.

Only one of the activated sludge reactor lanes was characterized in terms of CH_4 and N_2O emissions. It was divided in 6 different sampling sites: Site 1 (anoxic 1.A), site 2 (anoxic 1.B), site 3 (oxic 1), site 4 (oxic 2), site 5 (anoxic 2) and site 6 (oxic 3). Gas emissions were monitored on-line during up to 72 hours in each site during two months, using a gas collection hood connected to a commercial gas analyser (VA-3000, Horiba, Japan). Liquid-phase CH_4 and N_2O patterns were followed along the treatment process (at the inlet, primary and secondary settlers and in each bioreactor sampling site). Dissolved CH_4 concentration was characterized by means of gas chromatography and dissolved N_2O was measured with a microsensor with data logging (Unisense A/S. Aarhus, Denmark). Dissolved oxygen (DO) and temperature were continuously recorded and grab samples for the determination of chemical oxygen demand (COD), ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) concentrations were regularly taken with an automatic sampler. On-line data of the aeration flow at each of the sampling points and additional information were acquired from the SCADA system of the WWTP.

RESULTS AND DISCUSSION

Sources and spatial distribution of CH_4 and N_2O emissions

Most of the dissolved CH_4 found at Granollers WWTP was measured in grab samples taken from wastewater before it reached the aerated areas of the bioreactor, specially at the inlet of the plant (0.05 mg CH_4 /L) and in samples of reject wastewater (0.7 mg CH_4/L) (Fig. 1A). These were assumed to be the main sources of CH_4 flowing into the bioreactor, as shown previously in other studies (Guisasola *et al*. 2008; Daelman *et al*. 2012). In terms of dissolved N_2O, both primary and secondary settlers, as well as the first anoxic zone (site 1) of the bioreactor, presented similar average values (~0.1 mg N-N_2O/L). The largest concentration of N_2O was found in the second anoxic zone (site 5) with over 0.3 mg N-N_2O/L. Aerated parts of the bioreactor presented nearly undetectable levels of dissolved N_2O, with the exception of the third aerated area (site 6) in which these levels exceeded 0.15 mg N-N_2O/L (Fig. 1A) probably due to production in site 5 (anox 2). This finding is supported by previous research pointing at anoxic zones as the main areas where N_2O is produced as a result of the nitrifying denitrification process (Colliver and Stephenson, 2000).

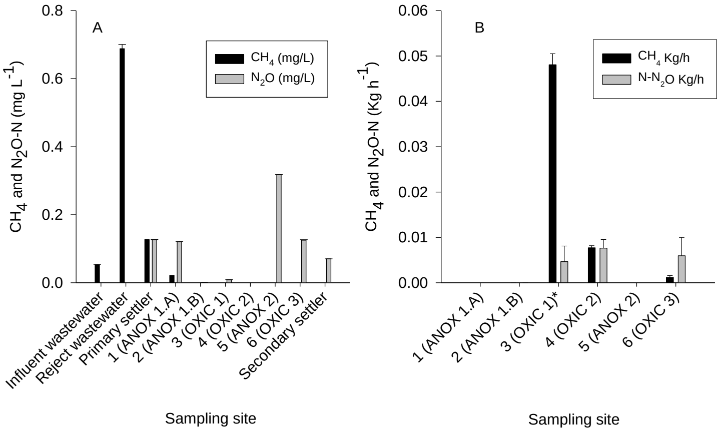

Figure 1 (A) Spatial distribution of average dissolved CH_4 and N_2O in different sites along the WWTP of Granollers and (B) average CH_4 and N_2O emissions from the different sites of the bioreactor lane under study, during the experimental period. Error bars correspond to the standard error of the means.

Average emissions of CH_4 and N_2O are shown in figure 1B. In general, the anoxic zones of the bioreactor presented nearly 0 emissions of both gases. The largest emissions of CH_4 were registered in the first aerated area (site 3) of the bioreactor (~0.05 Kg CH_4/h) sharply decreasing in the following sites to levels well below 0.01 Kg CH_4/h. On the contrary, N_2O emissions were very similar in all aerated zones, ranging from 0.004 (site 3) to 0.007 Kg N/h (site 4), as shown in figure 1B. N_2O emissions were irregular and presented large variations within sites, even on different days during the same week.

Process scenarios triggering CH_4 and N_2O peak emissions

During the measurement campaign, several events of CH_4 and N_2O peak emissions were recorded. These events were correlated with different process scenarios occurring at the WWTP, as described and discussed below.

Release of reject wastewater. CH_4 presented a regular periodic emission pattern in the aerated zones of the bioreactor (Fig. 2.A), with daily peaks and valleys separated by similar time spans (~12h). The curve described by the CH_4 emission was highly correlated with the one showed by the influent wastewater flow rate, but independent from the aeration flow or DO. As mentioned before, reject wastewater was regularly mixed with influent wastewater. It could therefore be asserted that the daily CH_4 peak emissions were given as a result of reject wastewater release flowing into the bioreactor. A recent study by Daelman *et al.* (2012) reported similar conclusions about the impact of reject wastewater on CH_4 emissions.

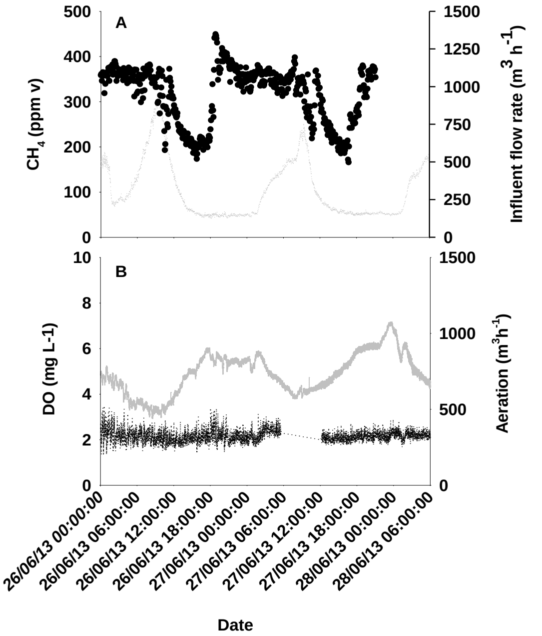

Figure 2 Dynamics of (A) CH_4 emissions (grey dotted-line) and influent wastewater flow (black dots), and (B) DO (black-dotted line) and aeration flow (grey line) during a 54h-period measured in sampling site 3.

Irregular aeration and aeration drop. Figure 3A.1 shows the N_2O emission pattern together with the concentration of NH_4^+, NO_2^- and NO_3^- during three consecutive days in which the aeration flow and the DO levels were heavily modified (Fig. 3A.2). Generally, in terms of aeration and DO, there were two differentiated periods: The first 36 h (aeration of 500-1000 m^3/h and DO 0.5-1.5 mg/L) and the rest of the period (aeration up to 1700 m^3/h and DO around 2 mg/L). N_2O emissions presented a very low and stable profile (nearly 0 ppm v) and seemed to be unaffected by irregular aeration or DO levels. However, there were three isolated N_2O peaks ranging from around 10 to over 40 ppm v (Fig. 3.A1). These, were registered right after three episodes of ~2h aeration drops (no aeration, 0 mg/L DO) occurring along the experimental profiling (Fig. 3A.2). When aeration was re-started after each 2h-period and DO was recovered, N_2O peak emissions were released. In general terms, both NH_4^+ and NO_3^- concentrations showed a decreasing trend along this three-day period of irregular aeration and

DO, and NO_2^- was not accumulated. However, NH_4^+ peaks of different level (2.5-12 ppm v) were observed in parallel with the N_2O peaks mentioned before. Production of N_2O during transient DO conditions has previously been reported in literature (Yu *et al.* 2010) and could explain N_2O peaks after periods of aeration stop.

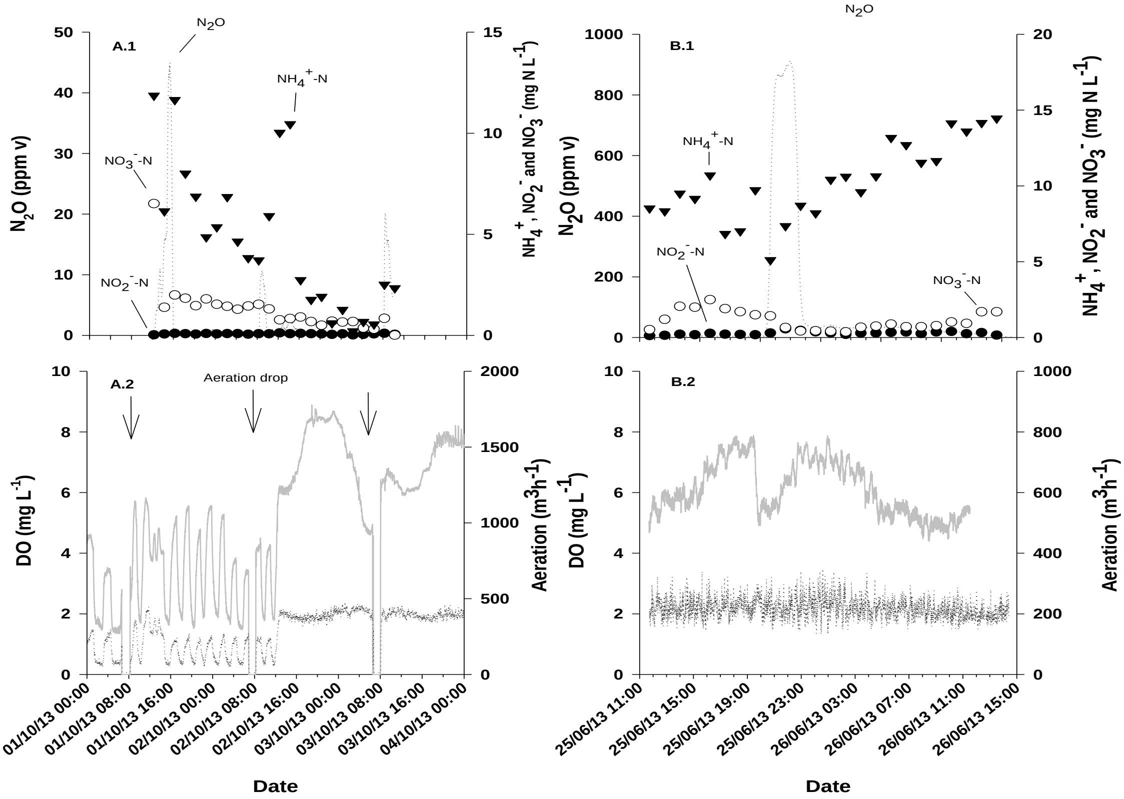

Figure 3 Dynamics of (A1 & B1) N_2O, NH_4^+-N, NO_2^--N and NO_3^--N and (A2 & B2) DO (black-dotted line) and aeration flow (grey line) during (A1 & A2) a period of different DO levels and aeration drops (marked with arrows) and (B1 & B2) a period of nitrification instability measured in sampling site 3.

Nitrification instability. Figure 3 (B1 & B2) represents a 28h-period in which the concentration of NH_4^+ tended to accumulate in sampling site 3 of the bioreactor, showing an increasing trend from around 5-10 mg N/L in the beginning of the period to 15 mg N/L in the end. NO_2^- and NO_3^- values were in general steady and remained low (Fig. 3.B1). During this time, the N_2O emissions described a large peak of around 900 ppm v simultaneously to the moment in which NH_4^+ started to accumulate significantly. This N_2O peak lasted for around 3h before it decreased to lower levels (~1-2 ppm v) for the rest of the period. The curve described by the aeration flow presented a valley (from 800 decreasing to 500 m^3/h) during the same time in which N_2O emissions peaked, but the DO level was regular during the whole period, always around 2 mg/L as shown in figure 3.B2. This large peak of N_2O was probably due to a failure in the nitrification process which led to incomplete NH_4^+ oxidation and N_2O production (Butler *et al.* 2009). The exact cause of this episode of nitrification instability remains unknown, although toxicity from industrial effluents may be suggested.

CONCLUSIONS

CH_4 emissions in the plug-flow reactor presented a regular pattern with peak emissions released as a result of the regular discharge of reject wastewater at the inlet of the plant. On the other hand, N_2O emission dynamics were highly variable and mainly related with the instability of the nitrification process occurring in the reactor and/or with aeration drops leading to transient DO conditions. These process scenarios could be avoided in order to minimize green-house gases peak emissions. Future studies are needed in order to suggest and design emission minimization strategies.

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(P35) Plume Measurements For Quantifying CH_4 And N_2O Emissions from Three Wastewater Treatment Plants

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Abstract
Many municipal wastewater treatment plants are significant sources of the greenhouse gasses nitrous oxide and methane. The plume dispersion method can be used for determine hot-spots and total emissions of nitrous oxide and methane at uncovered wastewater treatment plants. Plume measurements at three Swedish wastewater treatment plants were performed in this study. It was revealed that nitrifying trickling filters were a significant source of nitrous oxide. Also, stored sludge was an important source for nitrous oxide, as well as for methane. At Sjölunda Wastewater Treatment Plant the nitrous oxide emissions corresponded to 5.8% of the nitrogen load and the methane emissions was 0.11 kg CH_4 kg^{-1} $COD_{influent}$.

Keywords
Methane; nitrous oxide; plume measurements; wastewater treatment

INTRODUCTION

Municipal wastewater treatment plants (WWTPs) are highlighted as a significant source of the greenhouse gasses (GHGs) methane and nitrous oxide in the reports of the United Nation Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2006) However, the suggested emission factors for direct nitrous oxide and methane emissions have been observed to be too low and the emissions are very variable (Kampschreur *et al*., 2009; Daelman *et al*. 2012). The carbon footprint of WWTPs is strongly reflected by direct nitrous oxide and methane emissions (Gustavsson & Tumlin, 2013). Total GHG emissions from covered WWTPs can easily be measured in ventilation air systems (Kosonen *et al*., 2013; Daelman *et al*., 2012). However, most WWTP are uncovered. Several studies with spot measurements of GHG emissions at WWTPs have been performed with different techniques, such as static and dynamic flux chambers (Chandran, 2011; Desloover *et al*., 2011). Downwind plume concentration measurements (plume dispersion method), using one or two supporting trace gases and a highly sensitive mobile instrument, have previously been used to identify and quantify hot-spots of emissions and to quantify total methane emissions from landfills (Scheutz *et al*., 2011). Similar plume measurements of emissions can be used to estimate the total GHG emissions from an uncovered WWTP (Yoshida *et al.,* 2013). The aim of this study was to identify individual methane and nitrous oxide sources and to quantify these emissions at three different WWTPs in Sweden. The WWTPs were chosen to enable an evaluation of different measurement challenges for the plume dispersion method, given by the different WWTP process configurations and geographical location.

METHOD

Plume measurements

By releasing a tracer gas at a known rate near a methane emission source and measure the downwind plumes of methane and tracer gas, the emission rate methane can be calculated using the following equation,

$$E_{CH4} = R_{tracer} \times (A_{CH4}/A_{tracer}) \times (M_{CH4}/M_{tracer}),$$

where E_{CH4} is the methane emission rate, R_{tracer} is the tracer gas release rate, A_{CH4}/A_{tracer} is the ratio of the integrated plume areas above background concentrations and M_{CH4} and M_{tracer} are the molar weights. The plume dispersion method requires access to areas downwind from the emission source and fairly stable atmospheric conditions, and can with the right configuration identify and quantify the individual emission sources (Mønster *et al.*, 2013). The method also requires mobile measurements of gas difference in concentrations down to low ppb level with a high time resolution. Previously, such measurements were best done by Fourier transform infrared spectroscopy instruments (Galle *et al.*, 2001), but recent instrument development has enabled the production of cavity ring-down spectroscopy (CRDS) instruments targeting specific gasses. This development has made it possible to also measure nitrous oxide sufficiently fast and precise, and thereby enable identification and quantification measurements from fugitive nitrous oxide sources such as WWTPs. The measurements in this study were done by two CRDS instruments from Picarro Inc. First instrument was able to measure methane and acetylene (used as tracer gas) and the second measured nitrous oxide and ammonia. By doing initial whole site screenings at the WWTPs, the hot-spots of methane and nitrous oxide emissions can be identified which enable an accurate placing of the tracer gas (Mønster *et al.*, 2013).

Wastewater treatment plants

The first measurement campaign was performed at Sjölunda WWTP in Malmö, Sweden (load ≈ 260,000 population equivalents (P.E.)). The COD and enhanced nitrogen removal at Sjölunda are separated with a high-loaded activated sludge (HLAS) plant for COD removal and subsequent nitrification in trickling filters (NTFs) and post-denitrification in moving-bed biofilm reactors (MBBRs) with methanol dosage (Hanner *et al.*, 2003). The produced sludge is anaerobically digested, and stored at least six month at the plant. The sludge liquor is treated either in a sequencing batch reactor (SBR) with nitritation only, with sodium hydroxide dosage, or in a MBBR with nitritation-anammox. One half of the HLAS also receives some nitrate-rich NTF effluent for pre-denitrification, while the second half of the HLAS only receives the very low flow of treated sludge liquor. Plume measurements at Klagshamn WWTP (load ≈ 50,000 P.E.) will be performed early in 2014. Klagshamn WWTP has also post-denitrification in MBBRs (ethanol) and mesophilic digestion, but a nitrifying activated sludge plant, and some post-denitrification in a dual-media sand filter. Measurement campaigns will also be performed at a plant with a conventional activated sludge with pre-denitrification and nitrification.

Figure 1. An aerial photo of Sjölunda WWTP with marked positions of important process steps.

RESULTS AND DISCUSSION

The initial screening at Sjölunda WWTP (July 2nd, 2013), showed different sources of methane and nitrous oxide emissions (Figure 2). The highest methane concentrations were detected downwind open piles of dewatered digested sludge and downwind the uncovered storage tank for newly digested sludge in the sludge treatment area. The highest nitrous oxide concentrations were measured downwind the NTFs, the piles of digested sludge, and to some extent, from the sludge liquor treatment area.

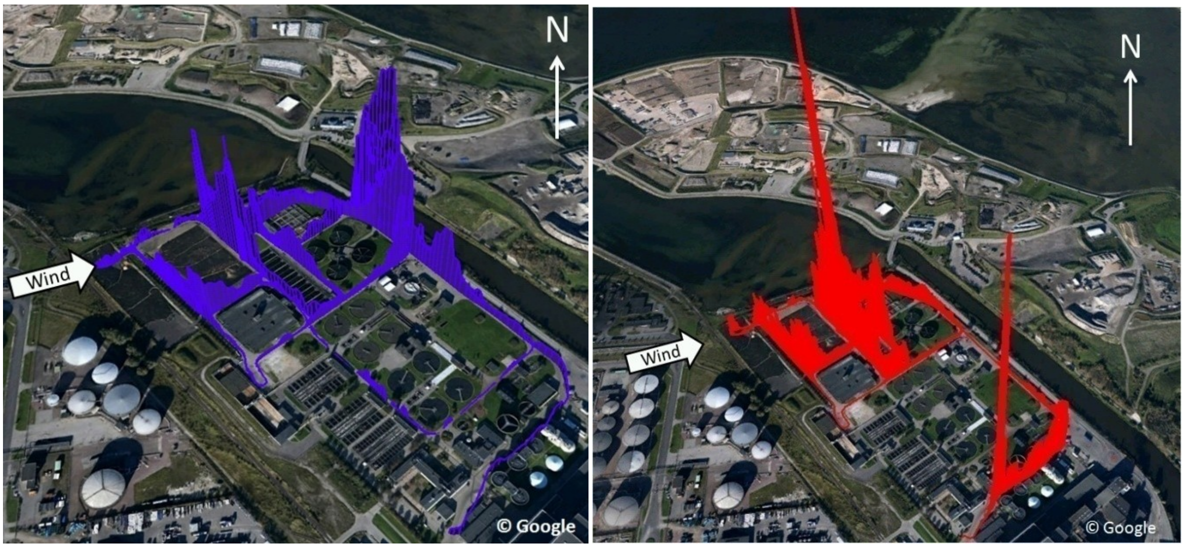

Figure 2. Nitrous oxide (left) and methane (right) screenings at Sjölunda WWTP.

The same day as the screening (2nd July, 2013), a tracer gas (acetylene) source was placed on the west side of the piles of digested sludge, and the plume transect measurements were performed during one hour on a road situated west of the treatment plant and downwind a landfill (Figure 3). The total nitrous oxide emission was 5.8% (SD = ± 3.5%) of the nitrogen load or 8.9% of the denitrified nitrogen, which is a very high emission compared to estimates based on measurements found in the literature (e.g. Kampschreur *et al.*, 2009), However, no study in the literature, known by the authors of this study, has included sludge storage or nitrifying trickling filters. It was not possible to determine the specific hot-spot of the emissions at the prevailing wind conditions at the specific road. Gustavsson & la Cour Jansen (2011) detected nitrous oxide emissions from the nitritation SBR in the sludge liquor area that corresponded to 0.62% of the nitrogen load to Sjölunda WWTP. Consequently, the emissions from the NTFs and the sludge piles seem to be the dominating sources.

The disturbance of methane emissions from the landfill was subtracted from the estimated methane emissions from Sjölunda WWTP (method described in (Mønster *et al.*, 2013)). For example, a hot-spot of methane emission on the landfill was detected, area C in Figure 3. Again, it was shown that two areas at the WWTP dominated the methane emissions, the sludge treatment area and the sludge pile area (Figure 3). The total methane emissions corresponded to 0.11 kg CH_4 kg^{-1} $COD_{influent}$ (SD = ± 0.05) of which 78% originated from the sludge treatment area. The detected methane emissions at Sjölunda WWTP are tenfold higher than found in other studies (Daelman *et al.*, 2012).

CONCLUSIONS

At Sjölunda WWTP, the plume dispersion method revealed hot spots of emissions of nitrous oxide and methane. Nitrous oxide is mainly emitted from the stored sludge and the nitrification process. Methane is mainly emitted from the sludge treatment area and from stored sludge. The plume measurements revealed total nitrous oxide emission of 5.8% of the nitrogen load and total methane emissions of 0.11 kg CH_4 kg^{-1} $COD_{influent}$ at Sjölunda WWTP.

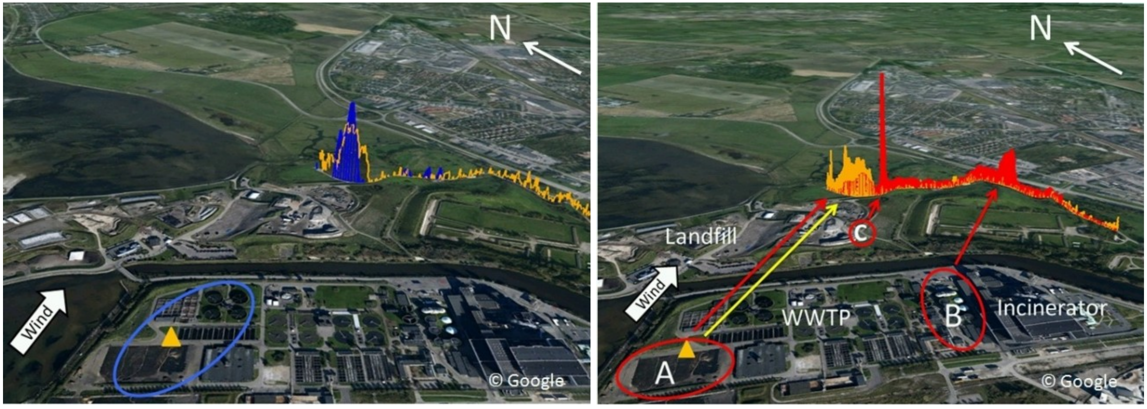

Figure 3. Nitrous oxide (left) and methane (right) plume measurements at Sjölunda WWTP.

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(P36) Effect of nitrite on the N_2O and NO production on the nitrification of low strength ammonium wastewater

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Abstract

The effect of nitrite on N_2O and NO emission was assessed in a nitrifying lab-scale reactor fed with a synthetic low strength ammonium wastewater (50 mg NH_4^+-N.L^{-1}). The effect of nitrite pulse additions (0 to 100 mg NO_2^--N.L^{-1} reactor concentration) and of step-wise increase nitrite concentrations (0 to 240 mg NO_2^--N.L^{-1}) was studied. For the pulse addition experiments, an increase in the N_2O and NO emission was observed when adding the pulses, decreasing until original levels when the nitrite was consumed. Higher pick emissions were detected at nitrite concentrations higher than 50 mg NO_2^--N.L^{-1}. For the step-wise nitrite increase tests (constant nitrite concentration in the reactor), it was found that the N_2O-N/NH_4^+-N converted increased linearly from 0.16% (in the absence of nitrite) to 2.8% (for 240 NO_2^--N.L^{-1}). NO emissions were substantially affected at nitrite concentrations higher than 50 mg NO_2^--N.L^{-1}, reaching 5.0% NO-N/ NH_4^+-N converted at the highest concentration tested (240 mg NO_2^--N.L^{-1}). The results show that nitrite is an important influencing factor concerning the N_2O and NO emissions, having a stronger effect on the NO emissions than on the N_2O emissions at higher concentrations.

Keywords

Low strength ammonium wastewater; nitric oxide; nitrifying system; nitrite; nitrous oxide

INTRODUCTION

Ammonium oxidizing bacteria (AOB) are one of the main responsible for nitrous oxide (N_2O) and nitric oxide (NO) emissions during wastewater treatment (Kampschreur et al., 2008; Wunderlin et al., 2012). Known pathways for the production of N_2O and NO by AOB are the reduction of nitrite (nitrifier denitrification), which takes place mainly under limited oxygen concentrations, and the oxidation of hydroxylamine. The emission of these gases causes adverse environmental effects. N_2O is a significant greenhouse gas which may contribute significantly to the carbon footprint of wastewater treatment plants (WWTP), while NO is involved in chemical reactions that cause ozone layer depletion. Therefore, the study of the factors affecting the emission and production of N_2O and NO is highly important. Nitrite was reported as one of the major influencing agents in the production of N_2O and NO (Colliver and Stephenson, 2000). This study addresses the impact of the nitrite concentration on the production and emission of N_2O and NO in a nitrifying system treating low strength ammonium synthetic municipal wastewater.

MATERIALS AND METHODS

A sequencing batch reactor (SBR) of 8L was inoculated with activated sludge from the WWTP of Girona (Spain) and was operated during 4.5 months obtaining a nitrifying mixed bacterial culture. The SBR was operated in 6-h cycles: 240 min of continuous feeding and aeration, settling during 100 min and 20 min for decanting. Each cycle, 4 L of synthetic wastewater was fed, resulting in a hydraulic retention time (HRT) of 12 h. To mimic the conditions of municipal wastewater, the ammonium concentration in the influent was set low (50 mg NH_4^+-N.L^{-1}) and no temperature control was established in the reactor. Dissolved oxygen (DO) was controlled with a programmable logic controller (PLC) between 2.0 and 2.5 mg O_2.L^{-1} by adding air and nitrogen gas at a constant gas flow rate of 3.5 L.min^{-1}. The pH was controlled between 6.7 and 7.0 by adding 1 M $NaHCO_3$.

Three months after start-up, batch tests were performed in the SBR to assess the influence of nitrite on the production of N_2O and NO. A first series of experiments consisted of the addition of different nitrite pulses leading to reactor concentrations of 5 to 100 mg NO_2^--N.L^{-1}. Triplicates were done for the 5 and 10 mg NO_2^--N.L^{-1} pulses. The added nitrite was oxidized to nitrate due to the activity of nitrite oxidizing bacteria (NOB) present in the SBR. In a second series of experiments the nitrite concentration in the reactor was increased in step-wise mode from 0 to 240 mg NO_2^--N.L^{-1}. This was achieved by adding nitrite to the SBR until the desired concentration and maintaining this concentration by adding nitrite continuously to the reactor at the same rate as it was being consumed by the NOB. Gaseous N_2O and NO were continuously analysed during the batch tests using commercial analysers. N_2O was analysed with the infrared gas analyser Servomex 4900 (Servomex) and NO was measured via the chemiluminescence gas analyser CLD64 (Eco Physics).

RESULTS AND DISCUSSION

The batch tests were conducted when the SBR was enriched with a mixture of AOB and NOB and all the incoming ammonium was converted to nitrate without the accumulation of ammonium or nitrite. The N_2O and NO emissions during normal operation were very low (0.16% and 0.001% of the ammonium converted being emitted as N_2O and NO respectively).

Effect of pulse nitrite addition on NO and N_2O production

Pulse additions of nitrite resulted in an increase of N_2O emissions, which decreased to initial values as soon as nitrite was completely oxidized to nitrate (Fig. 1A). Similar maximum emissions (≈ 0.21% N_2O/NH_4^+-N converted) were found among the tests with nitrite pulses in the range of 5 to 40 mg NO_2^--N.L^{-1} (Fig. 1B). When higher concentrations of nitrite were added in pulses, the N_2O emissions slightly increase to a mean value of 0.81%.

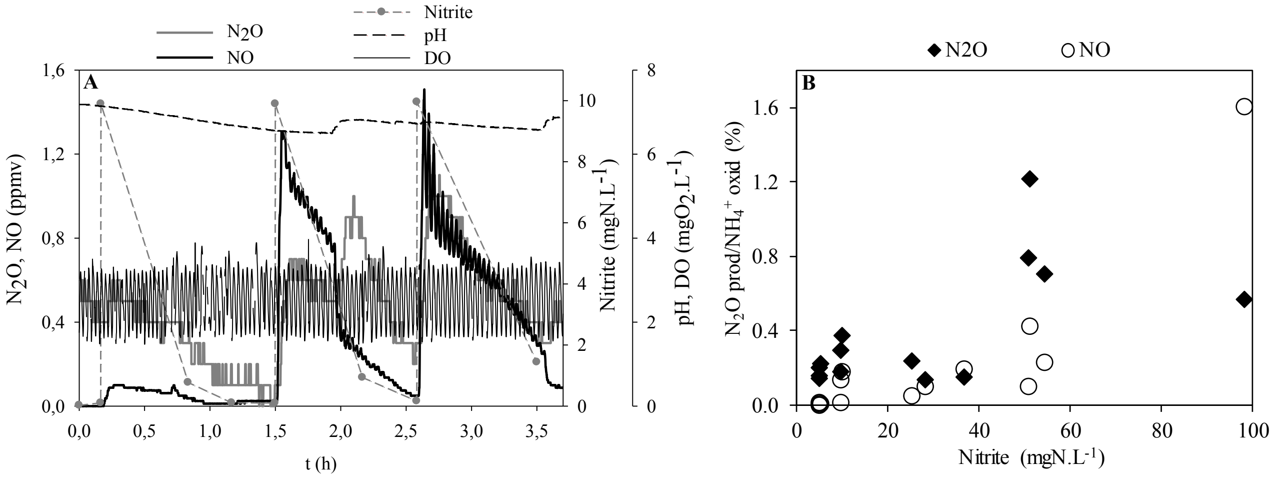

Figure 5. Effect of the nitrite added in pulses on the N_2O and NO production: A) Example of a test performed with 3 pulses of 10 mg NO_2^--L^{-1} (reactor concentration) (*Note: the emissions of N_2O for this test were very close to the lower detection limit of the analyser);* B) N_2O and NO emissions per NH_4^+-N converted in terms of the reactor nitrite concentration.

NO emissions also increased in response to the addition of nitrite pulses (Fig. 1B). The increase was practically constant until the addition of 50 mg NO_2^--N.L^{-1} (0.11%), while a maximum emission of 1.6% was observed with a pulse of 100 mg NO_2^--N.L^{-1}. Interestingly the emission of NO was substantially larger during the second nitrite pulse added compared with the emission detected during the first addition of nitrite at the same concentration (Fig. 1A), behaviour observed during all the tests with the repetition of pulses at the same concentration, but not for the N_2O.

Effect of step-wise increase nitrite concentration on N_2O and NO production

The N_2O production per NH_4^+ converted increased with increasing nitrite concentration in the reactor (Fig. 2B). These results differ from the study of Law et al. (2013) where an increase on nitrite concentrations from 50 to 500 mg NO_2^--N.L^{-1} resulted in a gradual decrease in N_2O emissions in an enriched AOB culture treating reject wastewater and always exposed to high levels of nitrite. This highlights the capability of AOB to adapt to different environments (high nitrite vs. low nitrite concentrations) responding differently in terms of emissions when being exposed to the same nitrite concentration.

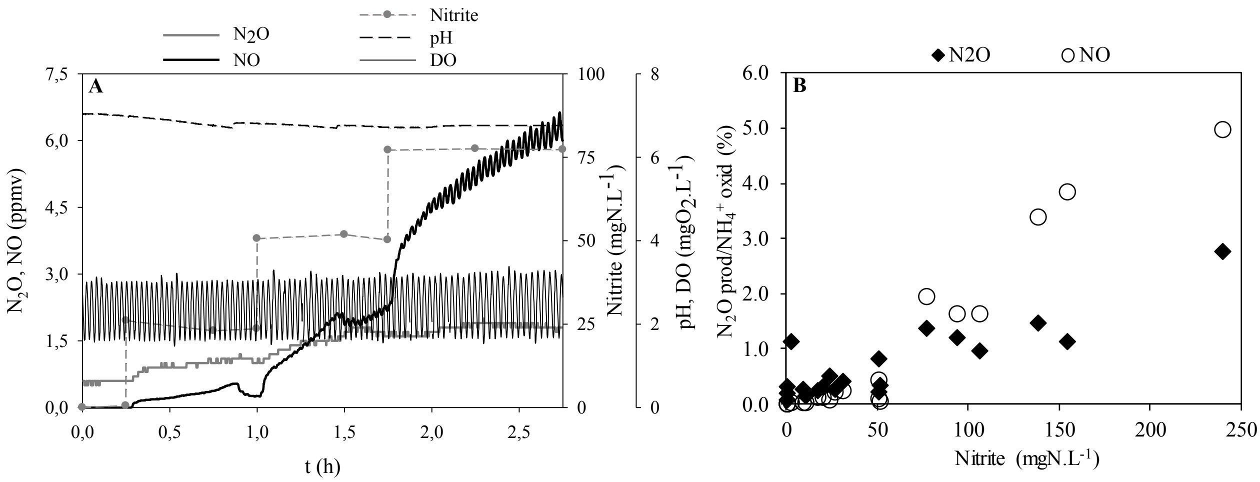

Figure 6. Effect of the stepwise increase of the nitrite concentration on the N_2O and NO emissions: A) Example of a test performed from 25_50_75 mg NO_2^--N.L^{-1}; B) N_2O and NO production per NH_4^+-N converted in terms of the reactor nitrite concentration

An increasing nitrite concentration in the SBR also resulted in increasing on NO emissions (Fig. 2B). These emissions substantially increased when nitrite concentration was higher than 50 mg NO_2^--N.L^{-1} resulting in higher emissions for NO than for N_2O in those tests. However, the NO emission profile differed from the N_2O emission profile on the fact that NO not only increased during an increase on the nitrite concentration but also during the exposition time at the same nitrite concentration (Fig. 2A).

CONCLUSIONS

- Nitrite pulses in a nitrification reactor resulted in an increase in N_2O and NO emissions. These emissions decreased to original levels when nitrite was completely oxidized to nitrate.
- Step-wise addition of nitrite during ammonium oxidation caused a proportional increase on the N_2O and NO emissions factors (N_2O or NO emitted/NH_4^+-N converted).
- NO emissions were higher than those of N_2O when biomass was exposed to constant nitrite concentrations higher than 50 mg N/L.

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(P37) Optimisation and stability of biofiltration of methane diffuse emissions using a low-cost organic carrier

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Abstract

This work was focussed on the long term operation and optimization of a biofilter treating gaseous streams containing diffuse methane concentrations in terms of empty bed residence times (EBRT) and inlet loads applied. A mixture of bark chips, compost and perlite was used as a conventional and low-cost packaging. The influence of the nitrogen source and the limitations of the system were studied in order to increase biofiltration performance. EBRT were varied from 2 to 10 minutes and inlet loads from 9.7 to 109 g CH_4 $m^{-3}h^{-1}$ were applied. Highest removal efficiencies obtained were 36.2 % corresponding to 4.9 g CH_4 $m^{-3}h^{-1}$ of elimination capacity (EC) with 7 minutes of EBRT and 13.6 g CH_4 $m^{-3}h^{-1}$ of inlet load. Packed material was stable with no significant pressure drop increases. The selection of the nitrogen source appears to be a significant issue, since the results obtained with ammonia were slightly higher but at long term stability may be affected by potential acidification. On the other hand, the results obtained with nitrate were not so high, but a more stable operation was maintained.

Keywords

Methane, biofiltration, diffuse emissions, optimization biofilter, empty bed residence times, inlet loads.

INTRODUCTION

Methane is the second most important anthropogenic greenhouse gas (GHG) present in the atmosphere. The concentration of this gas has increased 2.4 times from pre-industrial time to 2005 (Boucher et al., 2009). The main emissions of this GHG are present in the form of large flows and diffuse concentrations (< 0.5%). In order to deal with this challenge, biological alternatives such as biofiltration or biotrickling filters appear to be an interesting option, especially in terms of economic and environmental sustainability (Cooper & Alley, 1986; Datta and Allen, 2005). But also the use of this kind of biological technologies has been supported from the perspective of Life Cycle Management (Alfonsín et al., 2013), due to its simplicity, flexible design and low capital costs involved (Datta and Allen, 2005).

The aim of this work is to characterise the influence of the nitrogen source, EBRT and inlet loads (IL) on the biofiltration of an air stream containing diffuse methane emissions (0.2%), using a conventional low-cost packaging containing bark chips, compost and perlite.

MATERIALS AND METHODS

The biofilter (BF) used in this work is made of glass and has a total volume of 13.4 L, an inner diameter of 0.1 m and a length of 1.7 m with sampling points at different heights. The BF was packed with 5.7 L of a mixture of wood pine bark, perlite and compost which is equally distributed on three independent modules

Biomass containing methanotrophic bacteria was used as inoculum, which was obtained from the aerobic chamber of an innovative wastewater treatment plant comprising three stages: anaerobic, aerobic and membrane compartments. The biomass collected was mixed with the packaging material and then placed inside the biofilter, where an air stream containing a diffuse methane concentration (0.2 %) was supplied. Nutrients and water were supplied through the recirculation of a liquid phase being the mineral medium employed the one proposed by Cornish et al. (1984) with the difference in the composition of the N-source solution, which was initially composed by 50 g NH_4Cl L^{-1}.

The influent gas fed to the reactor was obtained mixing a pure methane stream (supplied by Carburos Metalicos, Spain) with an air stream, being the mixture controlled by means of mass flow controllers (Bronkhorst High-Tech BBV, The Netherlands). The inlet flow applied corresponded initially to an EBRT of 4.4 min. The inlet concentrations were maintained in a range of 2000 to 2050 ppmv CH_4, corresponding to IL from 16.8 to 17.3 g CH_4 $m^{-3}h^{-1}$. This inlet concentration is quite low in comparison with other studies (López et al., 2013)

RESULTS AND DISCUSSION

Start-up and stable operation. Influence of nitrogen source.

After start-up, the biofilter was operated during 248 days under different periods of operation: a) Period 1 (P1) in which ammonia (0.5 g $N\text{-}NH_4^{+}L^{-1}$) was used as N-source, b) Period 2 (P2) in which nitrate was used, c) Period 3 (P3), when the EBRT and the IL were optimised, and d) Period 4 (P4) in which steady-state was again restored.

Figure 7 indicates that during P1 the start-up was quite fast, with the maximum methane elimination capacities (EC around 6 g CH_4 $m^{-3}h^{-1}$) and removal efficiencies achieved after 1 month of operation. However, instability occurred due to the appearance of acidification processes (pH values of 3.5 - 4 were detected in the leachate), which took place inside the biofilter and lowered the EC down to 4-5 g CH_4 $m^{-3}h^{-1}$. In order to solve these problems, nitrate (0.2 g $N\text{-}NO_3^{-}$ L^{-1}) was used in the nutrient solution (P2), which led to a stable operation (no acidification was detected). Nevertheless the efficiency of the process was not improved as expected, EC was ranged 3.5 – 4.5 g CH_4 $m^{-3}h^{-1}$ (25 % of RE).

Short-term optimization tests

During days 129 to 161 (P3), EBRT and IL were varied in order to test their influence on methane removal.

EBRT

Five residence times were applied: 2, 4, 6, 8 and 10 minutes, being maintained each one along 24 hours. Operating at an influent concentration of 2000 ppm of CH_4 (0.2 %), the best results (RE of 34.1 %) were obtained at residence times above 7 minutes. On the opposite, EBRT lower than 4 minutes imply smaller removal efficiencies. Moreover, the use of a very high EBRT does not imply a better removal efficiency, as indicated when operating beyond 9 minutes.

Inlet Load

A wide range of inlet loads were applied to the biofilter: 9.7, 10.6, 10.8, 17.2, 26.0, 48.3, 85.4 and 109.6 g CH_4 $m^{-3}h^{-1}$, each one during 1 day of operation. In terms of RE, an optimum was found when applying 17.2 g CH_4 $m^{-3}h^{-1}$ with RE of 30% (5.2 g CH_4 $m^{-3}h^{-1}$ of EC). At higher IL the removal efficiencies drop in the range 18-24%, although the EC is always higher due to the increase of the IL applied.

As a conclusion of this period, the biofilter was again operated under steady conditions for the following 3 months (P4) under those optimal conditions: EBRT of 7 min and an IL between 11 - 18 g CH_4 $m^{-3}h^{-1}$. After a short time of adaptation RE values increased slightly with maximum values of 36.2 % (4.9 g CH_4 $m^{-3}h^{-1}$).

Limitations of the system

This work shows that the operation of biofiltration at diffuse methane concentrations (0.2%) imply a low potential elimination capacity of this system. It is because the concentrations of methane expected in the liquid phase (around 0.045 mg L^{-1}, according to Henry's law) is in the lowest limit of the affinity constants range reported for methanotrophs (0.014 and 1.06 mg L^{-1}**)** (Arcangeli and Arvin, 1999; Dunfield et al., 1999). In this sense the application of higher ILs (by increasing of inlet methane concentration and maintaining the flow) should lead to higher ECs as showed in this work, although the microbial biomass present in the biofilter was not able to increase the removal efficiency during the short period of testing (24 h). However previous reports show methane elimination capacities in biofiltration processes in a wide range of 17- 50 g CH_4 $m^{-3}h^{-1}$ although most of them were carried out at higher inlet concentrations and inlet loads which mean more favourable conditions for the microbiological oxidation process.

In this work, the use of a concentration of 0.2 % methane was selected to be representative of diffuse emissions usually occurring in facilities like STP. Moreover, our tests have indicated that this level implies a compromise between the EC (higher at higher methane concentration) and RE (higher at lower methane concentration) since the range tested (0.05 – 1.2 % in gas phase) corresponds to liquid concentration of 0.01 – 0.27 mg CH_4 L^{-1} again close to the lowest affinity constant reported.

CONCLUSIONS

The biofiltration of diffuse methane emissions (0.2 %) was maintained during a long-term operation (248 days), with the maximum removal efficiencies achieved in the range of 36.2 % when the optimal values of EBRT and IL were applied (7 minutes and 11-18 g CH_4 $m^{-3}h^{-1}$, respectively).

Two nitrogen sources were tested (0.5 g N-$NH_4^+L^{-1}$ to 0.2 g N-$NO_3^-L^{-1}$) and nitrate gave the most stable operation, since the use of ammonia led to the appearance of acidification inside the biofilter. The use of a conventional low-cost packing comprised by bark chips, compost and perlite was adequate since no significant drop pressure was observed and humidity packaging were maintained stable during the whole study.

Methane concentration in liquid phase corresponding to the gas content of 0.2 % (0.045 mg L^{-1}) represents an important kinetic limitation if reported affinity constants are considered (0.014 – 1.06 mg L^{-1}). Although the increase of IL applied would lead to higher EC, RE will not follow that trend, being 0.2 % a suitable compromise between both variables.

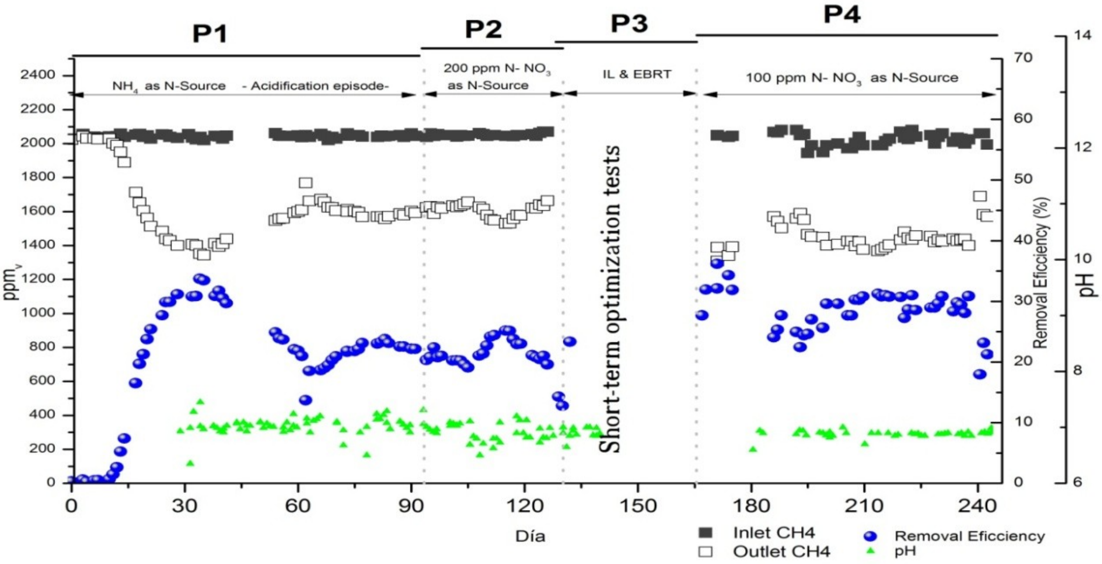

Figure 7 Evolution inlet and outlet concentration, removal efficiency and pH during the whole study

ACKNOWLEDGEMENTS

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(P38) Wastewater treatment processes impact on energy savings and greenhouse gas emissions

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Abstract

The objective of this work is to collect data on WWTP energy consumption, to develop a mathematical model to evaluate both onsite and off-site GHG emissions and to propose energy savings strategies that can be implemented to reduce both energy consumption and GHG emissions in Greece. Operating and electricity consumption data from ten WWTPs in Greece were collected. These WWTP with a treatment capacity ranging from 10,000 – 4,000,000 population equivalents (p.e.), employed various treatment schemes that included conventional activated sludge systems with anaerobic sludge digestion, extended aeration nutrient removal activated sludge systems and nutrient removal activated sludge systems with anaerobic sludge digestion. According to the findings of the survey average daily energy consumption ranged from 0.075 to 0.154 kWh/p.e. The higher energy consumer in all systems studied was the aeration system accounting for 40% to 70% of the total plant energy requirements. The average daily GHG emissions varied significantly according to the treatment schemes employed and ranged from 0.18 kgCO_2/p.e. to 0.40 kgCO_2/p.e. The highest values of CO_2 emissions were obtained in extended aeration systems and the lowest in conventional activated sludge systems employing biogas recovery for gas production. Key strategies that wastewater industry could adopt to mitigate GHG emissions are identified and discussed. Optimizing energy intensive wastewater treatment processes such as activated sludge aeration, mixing and pumping may significantly reduce power demand and GHG emissions. In addition energy savings through biogas utilization to produce biogas and heat is evaluated. A case study for Psyttalia WWTP is presented to demonstrate potential energy savings and GHG emission reduction.

Keywords
Wastewater treatment, energy consumption, energy efficiency optimization, minimizing carbon footprint.

INTRODUCTION

Traditional municipal waste management in many European countries is mostly addressing public health and environmental issues related to waste storage, treatment and disposal. As a result, in many cases municipal wastewater management has been practiced in a non sustainable way, employing treatment schemes that exert a high energy demand, have a large carbon footprint and contribute significantly to climate change. In the USA average annual energy consumption in WWTPs is approximately 29 kWh/population equivalent (pe), ranging from 16 to 71 kWh/pe (Stillwell et al., 2010). Similarly in Europe annual energy consumption from WWTPs ranges from 20 kWh/pe to 54 kWh/pe. As reported by Jonasson (2010) annual energy consumption from WWTPs in the UK, Sweden and Austria is approximately 38 kWh/pe, 42 kWh/pe and 23 kWh/pe, respectively (Jonasson, 2010; UK Environmental Agency, 2009). These values are comparable to the German energy manual, MURL (1999), that sets an objective for energy optimization of approximately 20 – 30 kWh/pe, depending on the size of the WWTP. In most medium and large WWTPs that employ activated sludge systems for secondary treatment, aeration typically accounts for approximately 50-60% of all electricity consumption followed by sludge treatment (15-25%) and secondary sedimentation including recirculation pumps (15%).

WWTPs directly produce carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) as a result of the treatment units and additionally contribute to CO_2 and CH_4 emissions through energy consumption. Reported values of GHG emissions from conventional activated sludge WWTPs with nutrient removal range from 0.9 to 2.2 $kgCO_{2e}/m^3$ (Flores-Alsina et al., 2011).

The objectives of this work are to collect data on WWTPs energy consumption, to develop a mathematical model to evaluate both onsite and off-site GHG emissions and to propose energy savings strategies that can be implemented to reduce both energy consumption and GHG emissions in Greece. In order to achieve the above objectives operating and electricity consumption data from ten WWTPs in Greece were collected. These WWTPs with a treatment capacity ranging from 10,000 – 4,000,000 pe, employed various treatment schemes that included conventional activated sludge systems with anaerobic sludge digestion, extended aeration nutrient removal activated sludge systems and nutrient removal activated sludge systems with anaerobic sludge digestion. In addition detailed energy analysis was conducted for Psyttalia Sewage Treatment Works (STW), the largest wastewater treatment plant in Greece that serves the Greater Athens Area with a population of approximately 4 million people, in order to apply and evaluate relatively simple operational changes that can potentially achieve energy savings and GHG emission reduction, at a justifiable cost.

METHODS

Survey of WWTPs in Greece to evaluate energy consumption and GHG emissions

Operational data were collected from 10 Biological Nutrient Removal (BNR) WWTPs in Greece with a treatment capacity ranging from 15,000 – 4,000,000 p.e. All WWTPs achieved the BOD_5, TSS and TN effluent criteria established by the 91/271 EC Directive. The objectives of the survey were to provide data that would allow to evaluate WWTP energy consumption in relation to treatment process and capacity, to identify the treatment stages that are the greater energy consumers and to assist in developing energy efficiency plans for WWTPs. At each WWTP the survey involved compiling data from each WWTP design study, drawings, utility bills and equipment inventory in order to develop an understanding of the wastewater and sludge treatment processes employed and the energy consumption at each treatment stage. In addition operational data were collected that involved influent flow, influent COD, BOD_5, TSS, TN and TP loadings, sludge disposal, biogas reuse (if applicable) and effluent wastewater criteria. Operational data for each WWTP were collected for the summer and winter period. According to the survey WWTPs were divided into the following two categories:

Category 1: Large WWTPs with a treatment capacity ranging from 100,000 – 4,000,000 p.e. with primary and secondary wastewater treatment. All five WWTPs that fell into this category employed anaerobic digestion for sludge treatment and biogas use for digestion heating. Additionally 3 WWTPs are using combine heat and power systems to produce heat and electricity from excess biogas.

Category 2: This category included small to medium size with a treatment capacity ranging from 15,000 – 100,000 p.e. All five WWTPs were extended aeration activated sludge systems with no primary treatment.

GHG gas emissions estimations included on site and off side production of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) emissions were calculated in units of CO_2 equivalent, by multiplying with 23 and 296, respectively (IPPC, 2001). The model applied to calculate GHG emissions was based on existing models developed by Bridle Consulting (2007) and Snip (2010). The major on site GHC emissions considered were generated from: 1) biological wastewater treatment, 2) sludge treatment, 3) biogas combustion for heating and electricity production and 4) sludge disposal. Off site gas emissions considered were from energy consumption. Off site gas emissions from chemical consumption were considered negligible because no chemicals were employed for pH control and denitrification.

Psyttalia WWTP

Psyttalia WWTP was chosen as a case study to evaluate the effect of operational parameters on energy consumption and GHG emissions. In August 2004 with the completion of Phase B, Psyttalia STW was upgraded to provide BNR to approximately 1,000,000 m^3/day average dry weather flow. According to the effluent requirements the biological treatment stage is designed to ensure that an effluent quality of 25 mg/l for BOD_5 and 10 mg/l for total nitrogen is achieved. The constructed activated sludge unit consists of 12 bioreactors with a total volume of 298,140 m^3, followed by 64 rectangular final sedimentation tanks with a total surface area of 52,150 m^2. Each bioreactor tank comprises of one anaerobic compartment, one anoxic compartment and five aerobic compartments all with a net depth of 9.4 m. Psyttalia WWTP is already practicing energetic optimization by recovering electrical energy from anaerobic digestion biogas and by employing an energy efficient aeration system that includes fine bubble diffusion, variable frequency drives blowers and an automated dissolved oxygen monitoring and control system. Additional energy efficiency improvements evaluated for Psyttalia WWTP included operational measures such as optimization of sludge age and oxygen concentration set points in each aerobic compartment.

RESULTS AND DISCUSSION

Evaluation of energy consumption and GHG emissions in Greek WWTPs

Energy consumption and GHG emissions for all WWTPs that took part in the survey is shown in Figures 1 and 2, respectively. The results show that average annual energy consumption ranged from 15 kWh/p.e. to 86 kWh/p.e.. Higher energy consumption was obtained in extended aeration WWTPs (WWTP 1 – WWTP 5) compared to conventional activated sludge WWTPs that employed anaerobic digestion for sludge treatment and used biogas for digestion heating (WWTP 6 – WWTP 10). Average annual energy consumption by extended WWTPs in Greece was approximately 44 kWh/pe versus 32 kWh/pe by conventional activated sludge WWTPs. Psyttalia WWTP, the only WWTP that employed combined heat and power production from biogas, exhibited the lowest annual energy consumption that was approximately 15 kWh/p.e.

GHG emissions ranged from 61 kgCO_{2e}/ p.e. – year to 161 kgCO_{2e}/ p.e. – year. As shown in Figure 2, extended aeration WWTPs (WWTP 1 – WWTP 5) exhibited higher GHG emissions compared to conventional activated sludge systems (WWTP 6 – WWTP 10). Average annual GHG emissions for extended aeration WWTPs and for conventional activated sludge systems were 80 kgCO_{2e}/ p.e. and 110 kgCO_{2e}/ p.e., respectively. The higher GHG emissions obtained in extended aeration systems were due both to the higher off site GHG production from higher energy consumption and the higher on site GHG emissions from the biological wastewater treatment process.

Evaluation of treatment processes impact on energy savings at Psyttalia WWTP

Psyttalia WWTP was chosen as a case study to evaluate the effect of operational parameters on energy consumption and GHG emissions. Based on the results biological wastewater treatment, primary treatment and sludge drying are the major energy consuming treatment stages that account for approximately 55%, 15% and 10% of the total power consumption. As a result aeration and sludge treatment offer the greatest opportunities for energy savings in Psyttalia WWTP. Therefore energy efficiency improvements evaluated for Psyttalia WWTP included operational measures such as optimization of sludge age and oxygen concentration set points in each aerobic compartment. Based on the results (Table 1) it is anticipated that the decrease of the dissolved oxygen set points at lower values of those of the existing situation results in an appreciable profit of energy consumption to the order of 6-10.1% of the total annual energy consumption for aeration purposes. Another possible practice is the operation of activated sludge unit with its minimum allowable sludge age which results in an appreciable energy decrease to the order of 6.2%. In order to achieve further decrease of the energy consumption a combined approach can be adopted which enables a decrease of both dissolved oxygen set points and sludge age. It should be mentioned that by adopting strategies of lower sludge age the cost for the treatment and handling of the additional excess sludge produced should be considered, as well.

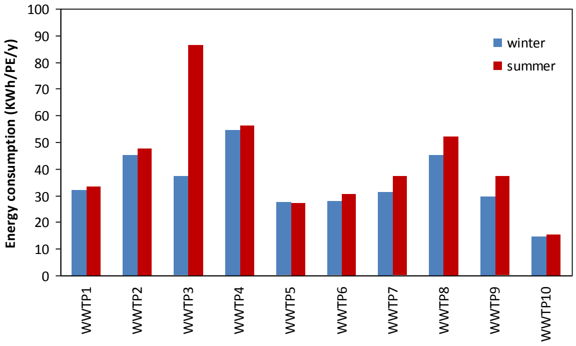

Figure 1: Energy consumption by Greek WWTPs

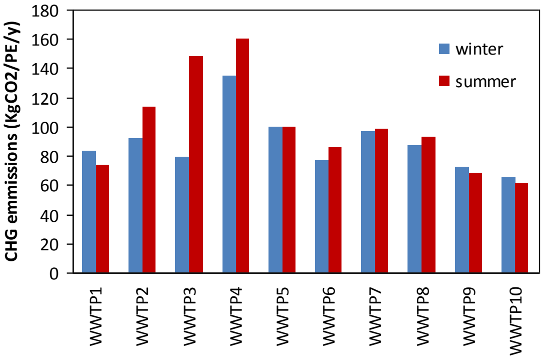

Figure 2: GHG emissions by Greek WWTPs

Table 1: Results of alternative scenarios for energy decrease

Scenarios*	Decrease in annual energy consumption of the aeration system (%)**
A1: Set points 3-2.5-1.5-1.5	6
A1: Set points 3-2.5-1.5-1.5	9
A1: Set points 3-2.5-1.5-1.5	7.1
A1: Set points 3-2.5-1.5-1.5	10.1
B: sludge age 6.1 d	6.2

*Scenarios A1-A4 enables four alternative dissolved oxygen set points at the four aerobic compartments, Scenario B1 assumes decrease of the average sludge age from 8.4 d to 6.1 d. **: Comparisons are made with the zero scenario where set points of the four aerobic compartments were equal to: 3.5-3-2.5-2 mg/L and sludge age was equal to 8.4 d.

CONCLUSIONS

Operational data collected from 10 Biological Nutrient Removal (BNR) WWTPs in Greece with a treatment capacity ranging from 15,000 – 4,000,000 p.e. showed that average annual energy consumption in WWTPs in Greece is approximately 38 kWh/population equivalent (pe), ranging from 15 kWh/p.e. to 86 kWh/p.e.. If one considers the great number of WWTPs operating in the European Union with a total treatment capacity that exceeds 400 million p.e., the energy savings and environmental benefits arising from efforts to decrease WWTPs energy consumption could be very significant. Therefore it is vital to recommend wastewater treatment processes for the mitigation of emissions and the reduction of energy consumption in WWTPs.

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(S33) Greenhouse gas emissions from wastewater treatment plants: A case study for meat processing industry

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Abstract

The aim of the presented study is to estimate the GHG emissions from the industrial wastewater treatment plants (WWTPs). The Greenhouse Gas Protocol (GHG Protocol) which is one of the most widely used international accounting tool for government and business leaders to quantify the greenhouse gas emissions, is used in the GHG estimations. In the paper, meat processing industry is selected as a case study, and the GHG emissions by WWTP of meat processing industry are estimated using GHG protocol. The plant's GHG is comprised mainly of "scope 2" and "scope 3" emissions related to the operation of the treatment process and associated equipment, and transportation as well. "Indirect GHG emissions (scope 2)" based on the electricity consumption from mechanic equipment at WWTP is calculated as 897.5 tons CO_2/year. The GHGs emissions due to electricity consumption in the operational building from air conditioner, computer and WWTP lighting is also considered in indirect emissions and estimated as 5.9 tons CO_2/year. Moreover, emissions from transport and distribution of chemicals, transportation of employees, transportation of wastes and transportation of coal (lignite) to company are also estimated in "Scope 3, as other indirect emissions". The other indirect emissions are calculated as 22 tons per year considering the vehicle type, distance, and other factors. Finally, total emissions of the WWTP are calculated as about 925 tons CO_2 per year.

Keywords
GHG (greenhouse gases), GHG protocol, carbon footprint, wastewater treatment plant (WWTP)

INTRODUCTION

Due to the increased concern on global warming, there is more awareness about emissions of greenhouse gases (GHG) in worldwide. Human activities such as agriculture, industry, waste disposal, deforestation, and especially fossil fuel have been producing increasing amounts of GHG and have led to a considerable increase in the concentrations of these gases. GHG generation in wastewater treatment plants (WWTPs) is noteworthy and thus considered as one of the main emission source of the greenhouse gases, i.e. carbon dioxide, methane, and nitrous oxide.

GHG emissions inventory studies quantify the amount of greenhouse gases emitted into the atmosphere by activities in a defined area over a specific time period. The Greenhouse Gas Protocol (GHG Protocol) is one of the most widely used international accounting tool for government and business leaders to understand, quantify, and manage greenhouse gas emissions. The GHG Protocol categorizes the emissions into three broad scopes. Scope 1 includes the direct greenhouse gas emissions occurring from sources that are owned or controlled by the company. Scope 2 comprises of indirect GHG emissions from consumption of purchased electricity, heat or steam. Scope 3 includes other indirect emissions, such as the extraction and production of purchased materials and fuels, transport-related activities in vehicles not owned or controlled by the reporting entity, electricity-related activities not covered in Scope 2, outsourced activities, waste disposal, etc. Both direct and indirect greenhouse gas emissions of the facility are considered to quantify the total gross GHG emissions.

All the above discussions lead to the fact that the first step in controlling GHG is to quantify them. The quantification reveals the targets and the priorities, thus guide on setting the GHG reduction goals. In this framework, an inventory study to quantify the greenhouse gas emissions produced by an industrial wastewater treatment plant is carried out. WWTP of a meat processing industry is selected as a case industry. GHG inventory of the WWTP is completed by using the GHG protocol to indicate the types of emissions produced from treatment facilities and from which parts of the treatment plant, and establish a baseline, from which the effect of operational changes on plant emissions can be measured over time.

MATERIAL AND METHODS

GHG inventory study is performed in WWTP of the meat processing factory located in the Kemalpasa region, Izmir, Turkey. Process and domestic wastewater has been treated in the plant with a capacity of 6,000 m^3/day. The WWTP consists of pre-treatment (screening and equalization), chemical treatment (neutralization, floatation, coagulation, flocculation), biological treatment (conventional aerobic activated sludge process), and sludge treatment units (thickening and dewatering). The flow scheme of the WWTP is presented in Figure 1.

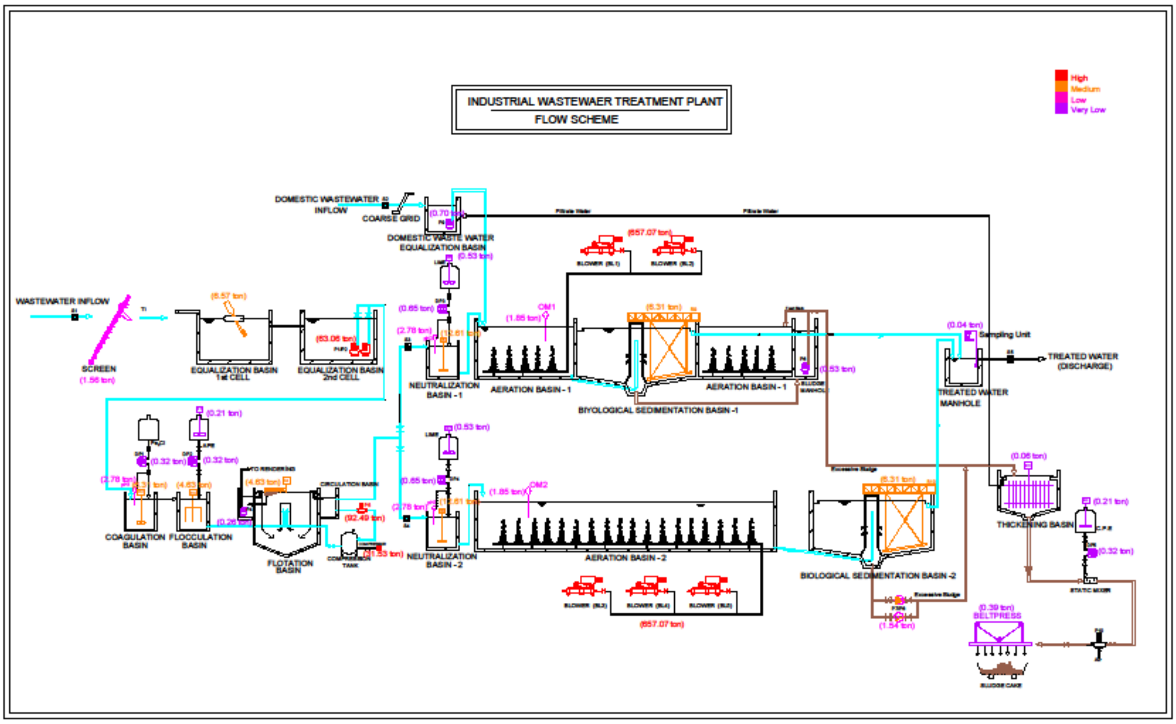

Figure 1. The flow scheme of the WWTP

In order to quantify the emissions, organizational and operational boundaries are established as first, and then emission sources are identified. The GHG emissions are calculated using GHG Protocol methodology. The plant's GHG is comprised mainly of scope 2 and scope 3 emissions related to the operation of the treatment process and associated equipment, and transportation as well. The electricity consumption of mechanic equipment is used to determine the indirect emissions of the WWTP. Emissions from transport and distribution of chemicals, transportation of employees, transportation of wastes and coal (lignite) to company are also estimated in Scope 3, as other indirect emissions.

RESULTS

In the examined plant, the GHG emissions are originated from two distinct sources. They are off-site GHG emissions resulting from the generation of electricity and from the use of fuels for transportation of chemicals, fuel, employers, and waste as well. Off-site generation of electric power consumed at WWTP is used in the calculations for indirect GHG emissions (Scope 2). The expected power use on site is calculated based on the electricity consumption of the mechanic equipment used in following processes; screening, equalization, coagulation and flocculation, flotation, sedimentation, activated sludge, thickening and dewatering. In addition to process uses, energy consumption in the operation building and site lighting are considered as indirect GHG emissions. In the study, the emissions from mechanic equipment are calculated as 897.5 tons CO_2/year. The GHGs emissions due to electricity consumption in operator building (air conditioner, computer and WWTP lighting) are found as 5.9 tons CO2/year (see Table 1).

Table 1. Indirect GHGs emissions from electricity consumption

Facility Information			**Consumption Data**		**Emission Factor (kg GHG/kWh)**		**GHG Emissions**	
Facility Description	**% of electricity used by the facility**	**Country**	**Fuel Mix**	**Amount (MWh)**	**CO_2**	**CO_2e**	**CO_2 (tons)**	**CO_2e (tons)**
Equipment in WWTP	100	Turkey	All	1,870	0,479929	N/A	897.5	897.5
Operating Building	100	Turkey	All	12,334	0,479929	N/A	5.9	5.9

Emissions from transport and distribution of chemicals ($FeCl_3$, lime, anionic and cationic polymers are bought from a company located 50 km away), transportation of employees, transportation of wastes and transportation of coal (lignite) to company are calculated in Scope 3, as other indirect emissions. In this context, transport for chemicals and also employees are taken into consideration. As can be seen from Table 2, CO_2 emissions are calculated as 22 tons per year considering the vehicle type, distance, and other factors. Total GHG emissions generated at meat processing WWTP are summarized in Table 3. As can be seen from the Table 3, electrical consumption is one of the significant emission sources of the examined WWTP. Among the mechanic equipment, blower and pumps are the highest energy consumed equipment because %88 of energy consumption has been used. Total GHGs emissions are calculated as about 925 tons of CO2e.

Table 2. The other indirect GHGs emissions form transportation tool

Activity Data						**GHG Emissions**	
Source	**Region**	**Trans.**	**Activity Data**	**Vehicle Type**	**Distance (km)**	**CO_2 (tons)**	**CO_2e (tons)**
Chemical transport	Other	Road	Vehicle Distance	Heavy Duty Vehicle - 1960-present	6,400	4.6	4.6
Employee service	Other	Road	Vehicle Distance	Light Goods Vehicle - Year 1983-1995	19,968	7.8	7.8
Coal transport	Other	Road	Vehicle Distance	Heavy Duty Vehicle - Year 1960-present	13,550	9.7	9.7

Table 3. GHG emissions from meat processing wastewater treatment plant

GHG Emissions		
GHG Source Type	**GHG Source**	**CO_2e (tons)**
Indirect	Blowers	657.1
	Pumps	160.2
	Scraper and Mixers	35.5
	Compressor	31.5
	Jet Aerator	6.6
	Measuring Devices	4.7
	Screening	1.6
	Belt press	0.4
	Operation Building	5.9
Other indirect	Transportation of chemicals, wastes, and employees	22.0

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(S34) Greenhouse Gases Emissions from a Continuous Nitritation Denitritation Process for Digester Supernatant Treatment.

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Abstract

The greenhouse gases (GHG), nitric oxide (NO) and nitrogen dioxide NO_2 emissions from a biological unit were continuously measured through an online analyser. The reactor performed a continuous nitritation-denitritation process to treat supernatants from mesophilic digestion of milk residues and pig slurry. Results on the liquid phase highlighted the reliability of the process, with average ammonia (NH_4-N) reduction of 95%. The continuous gaseous monitoring for one month revealed the emission of GHG from the reactor, with values of the nitrous oxide (N_2O) of about 0.11% on the influent NH_4-N load, and stripping of the dissolved methane and carbon dioxide. Formation pathways of the GHG, NO and NO_2 were further investigated through batch tests, to determine the correlations between the gaseous emissions and the dissolved oxygen (DO), NH_4-N and nitrites (NO_2-N) concentrations in the liquid phase.

Keywords
Anaerobic supernatant; continuous nitritation-denitritation process; greenhouse gases emission; nitrogen removal

INTRODUCTION

The presence of intensive livestock farmers conflicts with many environmental issues, as aquatic eutrophication due to nutrients release, acidification by gaseous ammonia (NH_3) and emission of greenhouse gases (GHG), as nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2). Although anaerobic digestion (AD) has been widely recognised as an essential treatment of zootechnical wastes for the organic matter stabilisation, with advantages in terms of energy production and GHG reduction (Appels et al., 2011), the nitrogen (N) content is only mineralized and not reduced. Hence, further post treatments of the digester supernatants are required, aiming for recovery or remove nitrogen. Biological short cut nitrification-denitrification (DN) for ammonium (NH_4) conversion in dinitrogen gas (N_2) has been widely investigated as an add-on process for N removal from complex matrices (Rajagopal et al., 2011), as the ammonia-rich digester supernatants. Several advantages can be achieved through the application of the short cut DN process to wastewaters, as reduction of oxygen requirement and external carbon sources, especially compared to the conventional nitrification-denitrification reactions. Notwithstanding these aspects, the environmental impacts on greenhouse gases emission from biological reactors are still under evaluation. Indeed, gaseous formation of N_2O, CH_4 and CO_2 from the wastewaters treatments has been validated. Several studies assessed that the formation of nitrogen oxides (nitrous oxide N_2O, nitric oxide NO, nitrogen dioxide NO_2) depends on the hydroxylamine oxidation, from intermediates due to the ammonia-oxidizing bacteria (AOB) activity or the chemical decomposition of NH_2OH, as well as on the nitrifier denitrification by AOB, under oxygen-limiting condition and high nitrite concentrations. Further, heterotrophic denitrification has been proved to contribute to nitrogen oxides formation (Kampschreur et al., 2009). The preliminary results on the continuous GHG emissions monitoring and the N removal performances of the DN process via nitrite, applied to pig digester supernatants, are presented in this paper. The overall quantification of gaseous emissions have been conducted together with batch experimental tests, to better evaluate the formation pathways.

MATERIALS AND METHODS

The continuous nitritation-denitritation process was applied in two consequential squared reactors, of 2400 L of total volume. The biological unit was constantly fed at 90 Ld^{-1} with the supernatant of pig slurry and milk residues, previously anaerobically digested in mesophilic conditions and dewatered. Each tank is equipped with a dissolved oxygen (DO), redox potential (ORP) and mixed liquor suspended solids (MLSS) probes, blowers and submerged mixers. The switching on and off of mixers and blowers, that ensures the alternation of the nitritation and denitritation phases, is based on the DO and ORP signals, to predict the ammonia variations inside the reactor. During the 46 days of monitoring, the MLSS was maintained at 9.4 gL^{-1} (MLVSS= 7.2 gL^{-1}), with an average nitrogen loading rate (NLR) of 0.1 $KgNm^{-3}d^{-1}$ and the hydraulic retention time HRT at 27 d. The denitritation process was enhanced by adding a 10% w/w methanol solution at C/N ration of 4.6. The influent and effluent flows, as well as the biomass, were weekly instantaneously collected and the physicochemical characterisation was performed according to Standard Methods (APHA, 2005). Tests to determine the ammonia (AUR), nitrite and nitrate (NUR) uptake rates were weekly conducted. The constant monitoring of the gaseous release from the first tank of the biological reactor was achieved with the MIR9000CLD analyser, which combines the measurements of the GHG and the aqueous vapour, through infrared spectroscopy (IRS), with the nitrogen oxides, analysed by chemiluminescence. The 25% of the reactor surface was enclosed with a cylindrical covering, submerged for 5 cm below the mixed liquor, to avoid a diluting contribution from the external air and to ensure a more precise offgas measurement during the anoxic phases. The air stagnation was prevented by providing the covering with an open tube (diameter of 10 cm, 1 m length) and placing the probe for gas suction at half height. An external aspiration pump ensures the gas sampling, which is divided and analysed through IRS and chemiluminescence, after being filtered for dust removal and cooled at 4°C. A software for data acquisition allows the elaboration of the emission values. Also, to clarify the GHG formation pathways, four batch tests were performed in different days on the first reactor, for a complete nitritation phase, which duration and air flow were set at 180 min and 6 Nm^3/h respectively. Samples were collected and filtered at 0.45 µm at defined timings throughout the nitritation phases, to determine the ammonia, nitrites and nitrates concentrations in the liquid phase. Table 1 summarizes the different operational conditions which were set to study the N_2O, NO, NO_2, CH_4 and CO_2 emissions.

Table 1. Parameters and setting conditions of the batch tests

Test n°	DO (mgL^{-1})	T Aerobic (min)	Qair (Nm^3h^{-1})	NH_4-N in (mgL^{-1})	NOx-N in (mgL^{-1})
A	0.3	180	6	463	1.15
B	0.3	180	6	80	1.03
C	2.1	180	6	313	0.47
D	2.0	180	6	113	0.90

RESULTS AND DISCUSSION

Kinetic tests determined AUR values on the average equal to 0.14 $Kg_{NH4\text{-}Nox}Kg_{MLVSS}^{-1}d^{-1}$ with NO_2-N incidence of 99%. The biomass speciation was also confirmed by the NUR rates, of about 0.11 $Kg_{NO2\text{-}Nred}Kg_{MLVSS}^{-1}d^{-1}$, with nitrite contribution of 100% during the whole monitoring period. Table 2 shows the average influent and effluent parameters to the biological reactor, to evaluate the removal performances of the short cut DN process. The digester supernatant was characterized by high alkalinity (7.9 gL^{-1}), solids (TSS=2.9 gL^{-1}) and COD (5.4 gL^{-1}, CODs/COD=50%) contents. The nitrogen contributions were determined by 1717 $mgNH_4\text{-}NL^{-1}$, 2020 $mgTKNL^{-1}$ (1793 $mgTKNsolL^{-1}$) and negligible amount of NOx-N. Although the complex matrix and the high ions amounts (1592 mgK^+L^{-1} and 1134 $mgCl^-L^{-1}$), no inhibition effect was noticed and the process assessed at removal performances of 95% and 89% for NH_4-N and total N respectively, with effluent concentration of 98 $mgNH_4\text{-}NL^{-1}$ and 238 $mgTNL^{-1}$. The effluent COD, which removal was about 79%, was mainly soluble (CODs =800mgL^{-1}), while the TSS amount in the outflow was equal to 312 mgL^{-1} (85% removal), mainly due to the colloidal feature of the matrix. The P content, mainly orthophosphate, reduce to 13 $mgPL^{-1}$ and 9 $mgPO_4$-PL^{-1}, with removal of 74% and 69% respectively.

Table 2. Biological short cut DN process - influent and effluent characterisation

	Alk (mgL^{-1})	TSS (mgL^{-1})	COD (mgL^{-1})	NH_4-N (mgL^{-1})	NOx-N (mgL^{-1})	Norg (mgL^{-1})	TN (mgL^{-1})	PO_4-P (mgL^{-1})	TP (mgL^{-1})
IN	7882	2920	5438	1717	7	281	2027	42	68
OUT	1963	312	923	98	2	137	238	9	13

The continuous monitoring of the N_2O, NO, NO_2, CH_4 and CO_2 emissions, both for the nitritation and denitritation phases, were measured for an entire month. The daily average values of N_2O, NO and CO_2 over time decreased with the nitritation time lengths, highlighting as a more stable oxidation process could reduce the gaseous emission. Average emissions as percentage on the influent ammonia mass load were determined as 0.11% of N_2O (maximum 1.11%), 0.05% of NO (maximum 0.12%) and 0.004% of NO_2 (maximum 0.1%), while the average CH_4 and CO_2 emissions assessed at 0.48 gd^{-1} and 4 gd^{-1} each. The batch tests, to evaluate the GHG formation pathways during the nitritation phase, highlighted the impact of the DO, ammonia and nitrites concentrations mainly on NO and N_2O emissions. All the tests revealed the almost absence of NO_2 in the gaseous stream, with average concentrations lower than 0.2 mgm^{-3} and no variations during time. An increasing concentration of NO and N_2O was measured during the nitritation phase in campaign A, at limiting DO condition (Figure 1.A). While NO profile raised with the ORP trend from 0.1 to 7 mgm^{-3}, suggesting that the oxide mainly formed during the ammonia oxidation process, a peak of N_2O (3 mgm^{-3}) was registered in the first minutes of the aeration phase, with a consequent unstable trend.

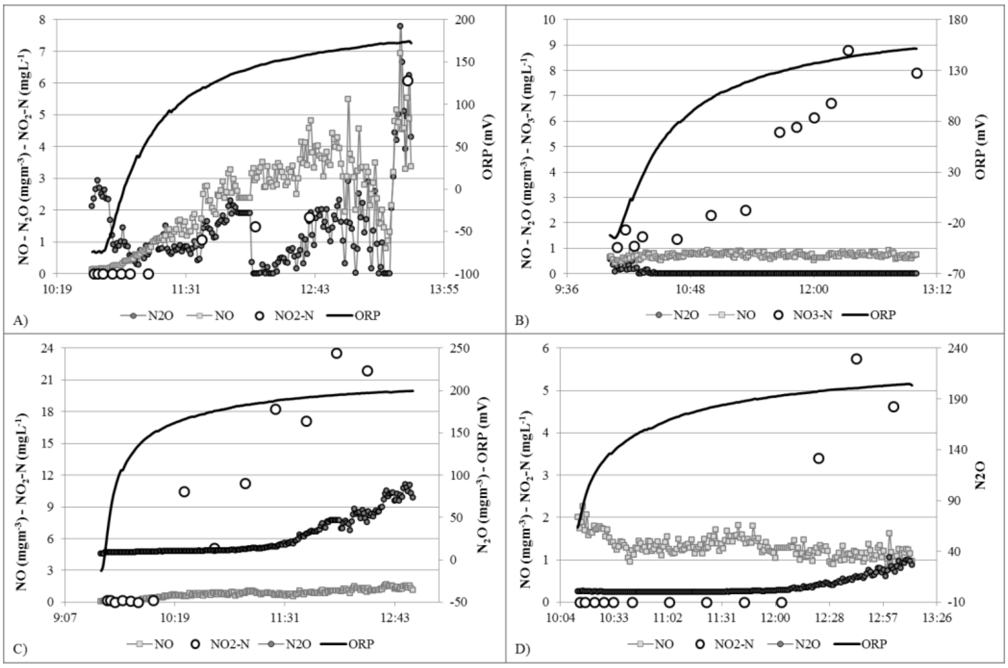

Figure 1. Gaseous and liquid trend of N_2O, NO and NO_x-N during the nitritation phases

The increasing concentration of NO_2-N in the liquid phase throughout the test appeared to be linked with the raising N_2O emission, probably related to the AOB oxidizing activity. Further, mainly in test A and lightly in test B, a peak of N_2O could be connected to stripping of the gas, formed in the previous heterotrophic denitritation phase. Test B, run with average DO amount of 0.3 mgL^{-1}, was characterized by almost constant NO emissions (1 mgm^{-3}) while the N_2O, that was only initially stripped as for 1.A with much lower amount of about 0.8 mgm^{-3}, was not measured until the end of the campaign. This aspect could be correlate to the absence of nitrites in the liquid phase, as shown in Figure 1.B, and to the lower ammonia concentration of 80 mgL^{-1} (Gustavsson et al., 2011). Tests at DO of 2 mgL^{-1} determined increasing N_2O emission during the nitritation phases, up to 90 mgm^{-3} (Figure 1.C) and 38 mgm^{-3} (Figure 1.D), related to maximum nitrites amounts in the reactor of about 24 $mgL^{-1}$and 5.7 mgL^{-1}. In any case, a direct correlation between the N_2O and NO emissions with the ORP values was detected, for redox values greater than 160 mV approximately. Also, the measurement of gaseous CH_4 has been conducted for all the campaigns and the preliminary results showed variable amounts (from 0.5 mgm^{-3} for test B to 30 mgm^{-3} for A), that peaked in the first minutes of aeration and decreased progressively during the test, suggesting the stripping of dissolved methane (Daelman et al., 2012) as major contribution rather than its biological oxidation. CO_2 emission was constantly registered to quantify its impact throughout each test, although the IPCC protocols do not include the carbon dioxide production from biogenic sources as a contribution to augmented atmospheric concentrations. CO_2 increased during the nitritation phases, from a minimum amount of 0.7 gm^{-3} (test B) to a maximum of 20 gm^{-3} (test A).

CONCLUSIONS

Continuous nitritation-denitritation phases to treat digested pig and milk residues supernatants allow to reach NH_4-N and TN removal percentages of 95% and 89% respectively, with effluent concentrations of 98 $mgNH_4\text{-}NL^{-1}$ and 238 $mgNL^{-1}$. Batch tests on the nitritation stages defined greater N_2O and NO emissions related to high DO, NH_4-N and NO_2-N concentrations in the reactor, linked mainly the oxidizing AOB activity. The continuous gaseous measurement highlighted average monthly N_2O, NO and NO_2 emissions of 0.11%, 0.05% and 0.004% on the ammonia load respectively. CH_4 and CO_2 emissions, mainly related to the stripping of dissolved compounds, were on the average equal to 0.48 gd^{-1} and 4 gd^{-1} each.

ACKNOWLEDGMENTS

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(S35) A microelectrode-based system for online monitoring of N_2O gas emissions during wastewater treatment

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Abstract:

Two Clark-type gas nitrous oxide (N_2O) microelectrodes were tested and validated for online gas N_2O measurements. The sensors were assessed with respect to temperature, flow and gas composition dependence. An exponential correlation between temperature and sensor signal was found, whereas flow and gas composition did not have any influence. The sensors had a linear response at the N_2O concentration ranges tested. The N_2O emission dynamics from two sequencing batch reactors were monitored using a microsensor and compared with a commercial online N_2O gas analyser and gas chromatography. Results show that N_2O emissions were accurately described with these microelectrodes.

Keywords:
Microsensors; Nitrous Oxide (N_2O); Online N_2O gas measurement

INTRODUCTION

There is a growing concern regarding the production of nitrous oxide (N_2O) from nitrogen removing wastewater treatment plants (WWTP) (Kampschreur et al., 2009). N_2O is an important greenhouse gas which can be produced during nitrification and denitrification(Wunderlin et al., 2012). N_2O can be analysed off-line via gas chromatography (GC). However, the use of grab samples for off-line analysis can lead to an underestimation of N_2O emissions due to their high variability over time. Currently, the majority of the studies use commercial online N_2O gas analysers. However, these analysers require a preconditioning of the gas sample (removing humidity and particles) and a minimum gas flow (0.5-1L/min depending on the analyser). This last step dilutes the concentration of N_2O, increasing uncertainty under the low N_2O concentration range. To overcome this limitation, a Clark-type N_2O microelectrode (UNISENSE A/S) was adapted to measure N_2O in the gas phase. In this study, the effect of temperature, gas flow, gas type and linearity at different N_2O concentrations were tested to check the reliability of the sensor. Its effectiveness was compared with a conventional infrared online gas analyser to assess gaseous N_2O emissions from lab-scale nitrifying reactors and in a full-scale WWTP. The goal of the work is to obtain an integrated measuring device that can simultaneously assess the liquid- and gas-phase N_2O production fluxes from WWTP. Such a device will facilitate on-line monitoring of N_2O, which can then be used during the modelling and optimisation of a WWTP to minimise its N_2O emissions.

MATERIALS AND METHODS

Two sensors were used for this study (Figure.1A,B), both N_2O microsensors (Unisense A/S, Denmark), were connected to a picometer and polarised overnight following manufacturer instructions. A commercial N_2O online gas analyser (VA-3000, Horiba, Japan)was used to validate the N_2O concentration in the tests described below.

Figure 1. Clark type gas N_2O microsensors used in this study: A-Sensor-2; B-Sensor-1.

Experimental Set-up

Flow tests:Air and nitrogen were tested and the gas flow was controlled by mass flow controllers (0.2 to 4 L/min). The temperature was maintained at 25°C.

Temperature test: The temperature dependencies of the zero current and N_2O defined concentrations were determined in the range 10 to 35ºC. Nitrogen and air were used as dilution gases to achieve the desired N_2O concentrations.

N_2O concentration test: Three different N_2O concentration ranges were tested (0-422.3 ppmv; 0-50 ppmv; 0-10 ppmv) using air and nitrogen as dilution gases. Temperature of the gas mixture was controlled at 25°C. The concentration of the gas flow was validated by a commercial gas analyser.

Repetitive concentration peak test:Consecutive tests were performed, changing the N_2O concentration from 0 to 10.4 ppmv. Nitrogen was used as dilution gas and temperature was controlled at 25°C.

Sequencing batch reactor (SBR) monitoring test: N_2O emission dynamics in two nitrifying lab-scale SBRs were monitored online, using a commercial N_2O gas analyser and Sensor-1, and off-line using grab samples for GCanalyses.

WWTP monitoring test: N_2O emission dynamic of a local domestic WWTP is currently being monitored using a commercial N_2O gas analyser and an N_2O gas microsensor. Results from this monitoring campaign will be presented at the conference.

RESULTS AND CONCLUSIONS

There is an exponential temperature dependency on the zero current and selected concentration for both sensors tested (Fig.2A). A similar dependency was also found for the commercially available N_2O microsensorsfor liquid phase measurements (Jenni et al., 2012). Measurements of N_2O in the gas phase undergo faster temperature variations compared to the ones in the liquid phase. Both microsensors had a linear response to N_2O concentration in all ranges tested (Fig.2B). Using air or nitrogen as dilution gas did not affect the linearity of the sensor. The two ranges with both gases had an $r^2 \geq 0.999$ and a very low difference between replicates, showing high stability (Table1). Changes in the gas flow in the defined range (0.2-4 L/min) (Fig.2C) did not affect the zero signal of the sensors. The average signal was 33.50±0.25 and 11.21±0.23 mV for Sensor-2 and Sensor-1, respectively. Both sensors demonstrate similar results when subjected to a repetitive N_2O concentration peak cycle (Fig.2D).

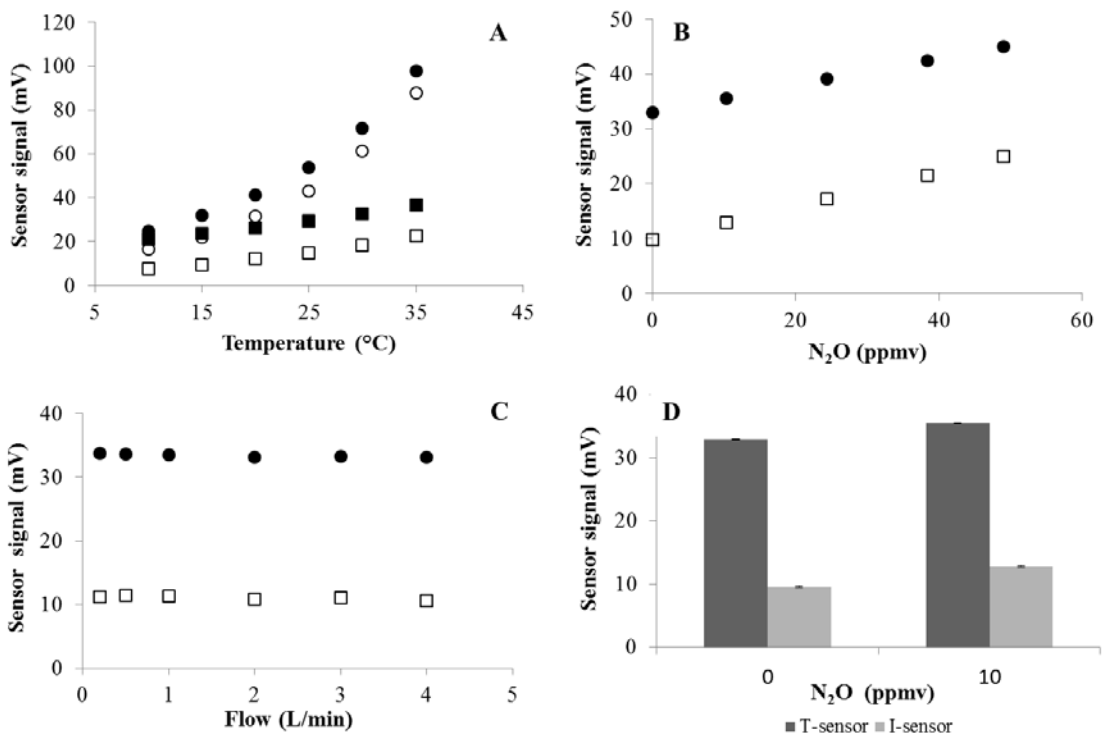

Figure 2. A-Zero and 48ppmv of N_2O current dependency on the temperature; **B-** Current dependency on N_2O concentrations at 25ºC; **C-**Zero current dependency on gas flow ;**D-** Current dependency on concentration at 25ºC for repetitive N_2O peak cycles (values presented are average of 3 tests and are presented with standard deviations).Dots (Black/White): Sensor-2; Squares (Black/White): Sensor-1.

Table 2. Sensor-2 and Sensor-1 dependence on temperature and N_2O concentration with air and N_2 as dilution gases.

Type of Sensor	**Equation**	**Standard deviation**	**Coefficient of determination**	**Gas**	**Range (ppmv N_2O)**
Sensor-2	Y=0.247x+32.94	a=±0.01; b=±0.01	R^2=0.999	N_2	0-50
Sensor-1	Y=0.310x+9.70	a=±0.01; b=±0.06	R^2=0.999		
Sensor-2	Y=0.265x+33.33	a=±0.01; b=±0.01	R^2=0.999	N_2	0-10
Sensor-1	Y=0.309x+8.60	a= ±0.01; b=±0.12	R^2=0.999		
Sensor-2	Y=0.270x+33.74	a=±0.01; b=±0.17	R^2=0.999	Air	0-50
Sensor-1	Y=0.303x+9.22	a= ±0.01; b=±0.05	R^2=0.999		
Sensor-2	Y=0.256x+34.07	a=±0.01; b=±0.06	R^2=0.999	Air	0-10
Sensor-1	Y=0.310x+11.18	a=±0.02; b=±0.22	R^2=0.999		

Also, Sensor-1 was used to monitor the N_2O emission dynamics in twolab-scale SBRs. Figure 3 shows the results obtained with the sensor, a commercial N_2O gas analyser and a GC. The sensor was able to accurately follow the N_2O dynamics with a small difference on the total emissions compared with the values given by the commercial online gas analyser (SBR-1: 16.45±0.92 mg N_2O-N and SBR-2: 0.74±0.08 mg N_2O-N).

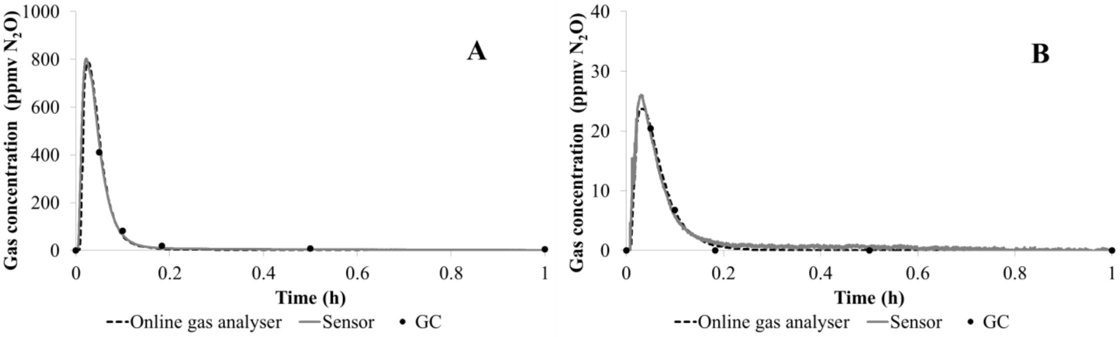

Figure 3. N_2O production dynamics in SBR-1(A) and SBR-2 (B) enriched with nitrifiers. Dashed line: commercial analyser; Grey line:sensor; Black dots: GC.

This study demonstrates that the adapted Clark-type gas N_2O microsensors can be used as a reliable alternative to standard methods for online detection of N_2O in the gas phase. The added advantage of this system is that only one experimental setup is required in order to analyse N_2O dynamics in the liquid and gaseous phases. The dependence of temperature on the sensor is now being modelled, while the sensors are currently being employed in afull scale WWTPs N_2O monitoring campaign.

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Environmental and Economic Assessment

(Wednesday, 25 June 2014, Aula T1, Polo Zanotto)

(K8) Willingness to consume products irrigated from recycled water: evidence from electrodermal activity experiments

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Abstract

In this paper we describe an experiment testing the effect of the descriptor “produced with recycled water” on the level of disgust elicited by food products. The subjects are divided into 2 groups. The first group is provided with a small box of raisins which bear professionally printed labels indicating that the vineyard these raisins were produced in was irrigated with recycled water. The box given to the second group indicates that the vineyard was irrigated with freshwater. Subjects are environmental engineering students and psychology students, affording assessment of the effect of background education. The test variables are the weight of the raisins consumed on-site and the electrodermal activity, recorded by a QR sensor.

Keywords

Electrodermal activity (EDA); psychophysiological methods; public acceptance; water recycling

This is an on-going experiment and takes place organized by the authors of the paper in two labs at thermal conform conditions.

Participants

40 environmental engineering students from Democritus University of Thrace and 40 Psychology students from Panteion University of Social and Political Sciences take place in this experiment.

Apparatus

In the literature there are evidences of existence of the so called “yuck factor” when people taste food whose origin is deemed to be from impure sources or food in whose production process where used impure sources for example vegetables and fruits irrigated with recycled water suitable for irrigation. In our experiment we will search for the existence of the “yuck factor” when subjects are called to taste raisins from two samples

The main apparatus for data collection was a fully structured questionnaire and an Affectiva Q sensor v 1.0. The sensor was used for measuring electrodermal activity (μS), electrode temperature (°C) and 3 Axis accelerometer (G’s). Furthermore, we will examine the student’s attitude towards disgust. For this we have professionally produced 2 different kinds of boxes for raisins. They are identical in pattern, content and design, apart from the fact that the first indicates that raisins come from “vineyards irrigated with recycled water”, while the second that they come from “vineyards irrigated with pure freshwater” (Figure 1). In this way we try to observe the changes, if any that will occur on the above elements when the subjects are eating raisins from the two different samples. Albeit both versions are being filled with the raisins coming from the same supplier, we will record differences in their reactions.

After they finish the tasting we weigh the two boxes in order to see the quantity that has been consumed from each box. Then the subjects are called to answer to a short questionnaire asking them, among other, to state their opinion about the taste, the appearance and the quality of the raisins they have consumed, to say if they have found any difference between the two samples and their willingness to buy raisins of the same quality as that in each box.

Stimuli

Conventionally produced raisins are used but they are placed in two types of boxes, one stated to be irrigated with recycled and another with freshwater.

The research approach is also depicted in Figure 2.

Figure 1. The two different versions we will examine for evaluating stimuli’s reactions

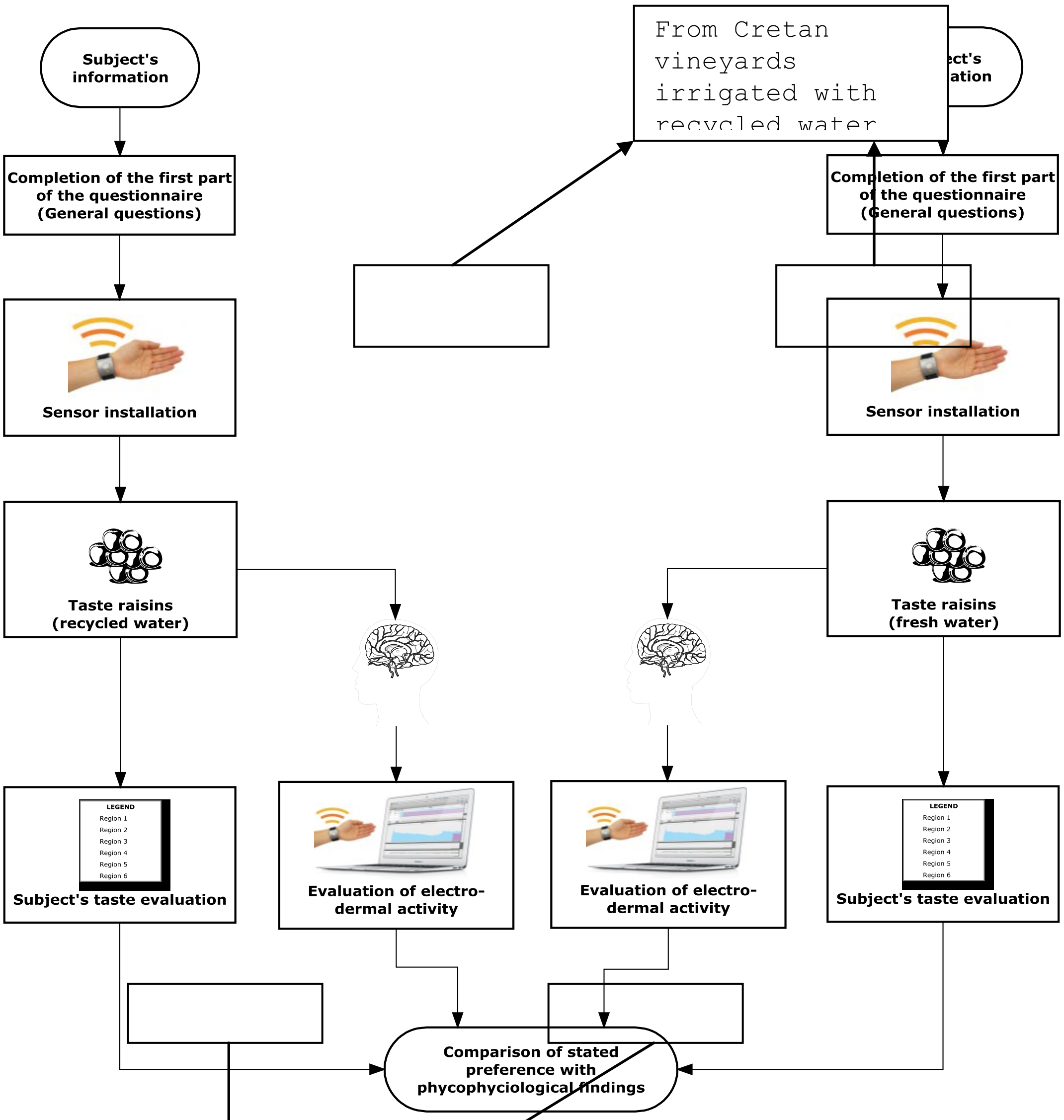

Figure 2. Research approach

From Cretan
vineyards
irrigated with
pure freshwater

This is an ongoing piece of research, preliminary findings show that subjects that are introduced with the recycled water version of raisins consume less raisins compared with subjects introduced with the freshwater version of raisins.

(P39) A tool to compare life-time costs of water supply and sanitation systems

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Abstract

Within the EU funded project CLARA a simplified planning tool that compares real costs of various alternatives of water supply and sanitation systems was developed. The tool aims to provide the missing link for the technical part of the overall planning process and allows comparing the life-time costs of different water supply and sanitation alternatives.In the presentation we will present the final version of the tool itself and show experiences from using the tool in the planning process in pilot communities in Ethiopia and South Africa, respectively.

Keywords
CLARA, life-time costs,sanitation, simplified planning tool, water supply

Introduction

Experiences from the EU FP6 research projects ROSA (http://rosa.boku.ac.at/) and NETSSAF (http://www.netssaf.net/) showed that knowledge on planning in general and practical knowledge on strategic planning in particular is lacking in African communities. Therefore one main objective of the FP7 project CLARA (Capacity-Linked water supply and sanitation improvement for Africa’s peri-urban and Rural Areas) was to develop a simplified planning tool for integrated water supply and sanitation systems for small communities and peri-urban areas that incorporates the key factors for successful implementation, i.e. operation and maintenance issues and reuse potential, form the beginning of the planning process, and that can be tailored to available local capacities. This simplified integrated CLARA planning tool was then tested and evaluated in different geographical African regions to incorporate different economic, cultural and social boundary conditions.

The CLARA project started in March 2011 with duration of 3 years. CLARA was coordinated by BOKU University, Austria, and has 15 partners. Besides BOKU there are 3 more European partners that have been all partners in ROSA and/or NETSSAF: ttz Bremerhaven, Germany (the coordinator of NETSSAF), EcoSan Club Austria, and BIOAZUL, Spain. The African partners cover 4 geographical regions: Eastern Africa (Ethiopia and Kenya), Southern Africa (South Africa), Western Africa (Burkina Faso) and Northern Africa (Morocco and Tunisia).

The CLARA simplified planning tool

In CLARA we did not aim to define a new overall planning approach, however, the CLARA simplified planning tool aims to provide the missing link for the technical part of the overall planning process by supporting local planners to find the best solution for water supply and sanitation in the planning objective. By using the tool it is possible to compare the real costs of various alternatives of water supply and sanitation systems. Environmental, social and health aspects will not be considered explicitly since it is assumed that these aspects are already considered in the framework conditions, i.e. it is assumed that all systems fulfilling the legal requirements benefit environment and health and are socially appropriate. That means that the tool cannot be used to compare a solution that fulfils legal requirements with e.g. the solution "no sanitation facilities" as these 2 alternatives do not have the same impact. However, the tool can be used to compare e.g. water-borne and dry sanitation systems.

With this assumption the comparison of alternatives can justifiably be reduced to comparing the costs of the alternatives, i.e. for investment, operation and maintenance, and re-investments over a specific project period (e.g. 50 years). Net present values of all costs are calculated and used for comparison.

The user of the CLARA simplified planning tool - the planner - is responsible for developing appropriate alternative solutions. Technologies are grouped in functional groups as defined in the Sustainable Sanitation and Water Management (SSWM; http://www.sswm.info) toolbox. These functional groups include: Water sources, Water purification, Water distribution, Water use, Waste collection and transport, Waste treatment, and Reuse. Technologies in the functional groups have to be compiled to systems, i.e. for using any wastewater treatment technology the treatment sludge has to be included as well.

The project partners assessed the design assumptions for the technologies implemented in the tool if they are in line with the local legal requirements in the CLARA countries.Country specific versions of the CLARA simplified planning tool have been prepared and tested during the planning process that is carried out in the 5 pilot communities in Burkina Faso, Ethiopia, Kenya, Morocco and South Africa, respectively.

Results

In the presentation we will present the final version of the CLARA simplified planning tool as well as the results from testing the tool in the CLARA pilot communities in Ethiopia and South Africa.

Below we show as an example the comparison of the costs of a water borne sanitation system (sewer, wastewater treatment plant) and a dry sanitation system (urine-diverting dry toilets, collection of urine and faeces, struvite production from urine and co-composing of faeces). Figure 8 shows the user interface of the tool, Figure 9 the selection of technologies within a functional group.
Figure 10 shows the results: The water-borne system has higher investment costs; however, the total costs over a period of 50 years for both systems are about the same (when not considering potential income from using liquid and solid fertilisers produced from human excreta).

Acknowledgements

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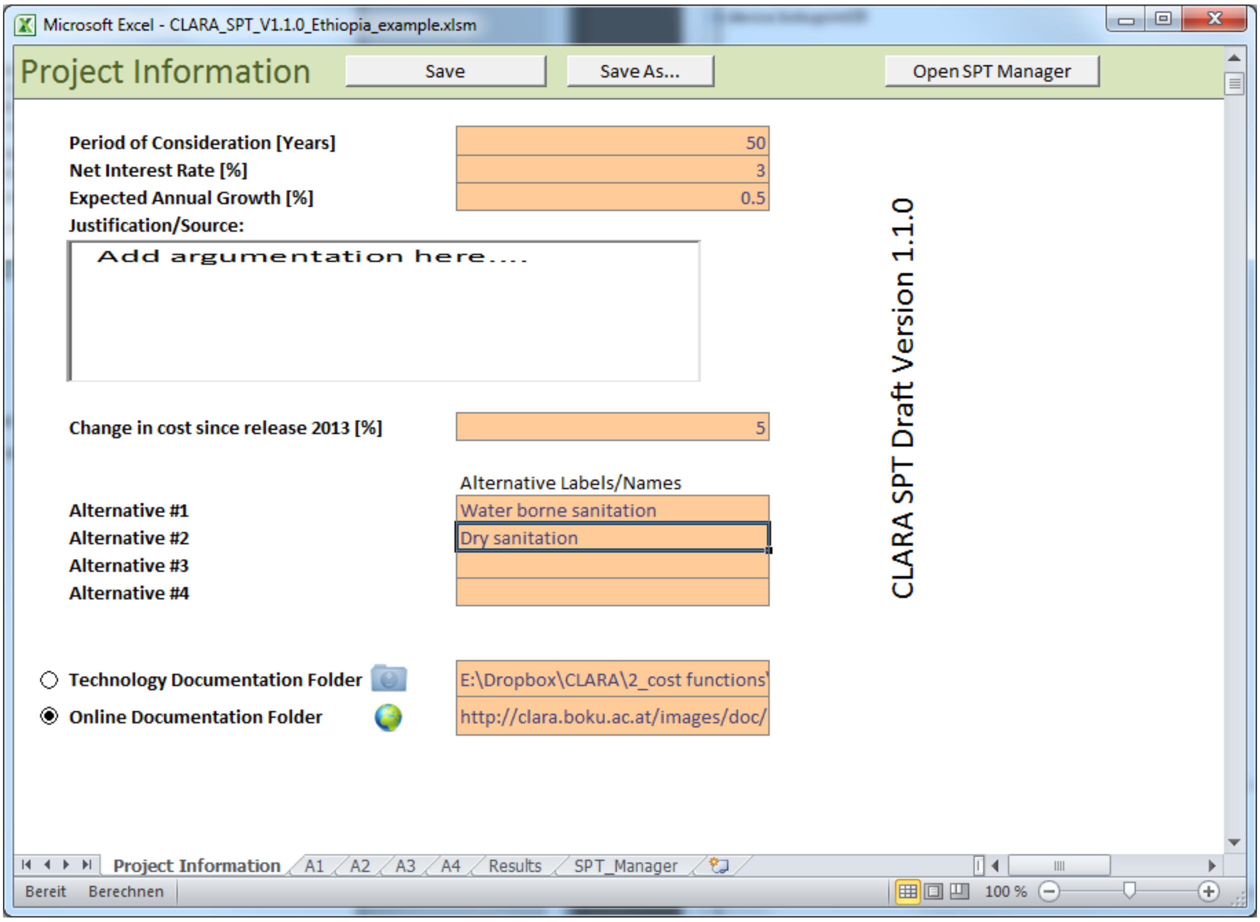


Period of Consideration [Years]	50
Net Interest Rate [%]	3
Expected Annual Growth [%]	0.5

Justification/Source:

Add argumentation here....

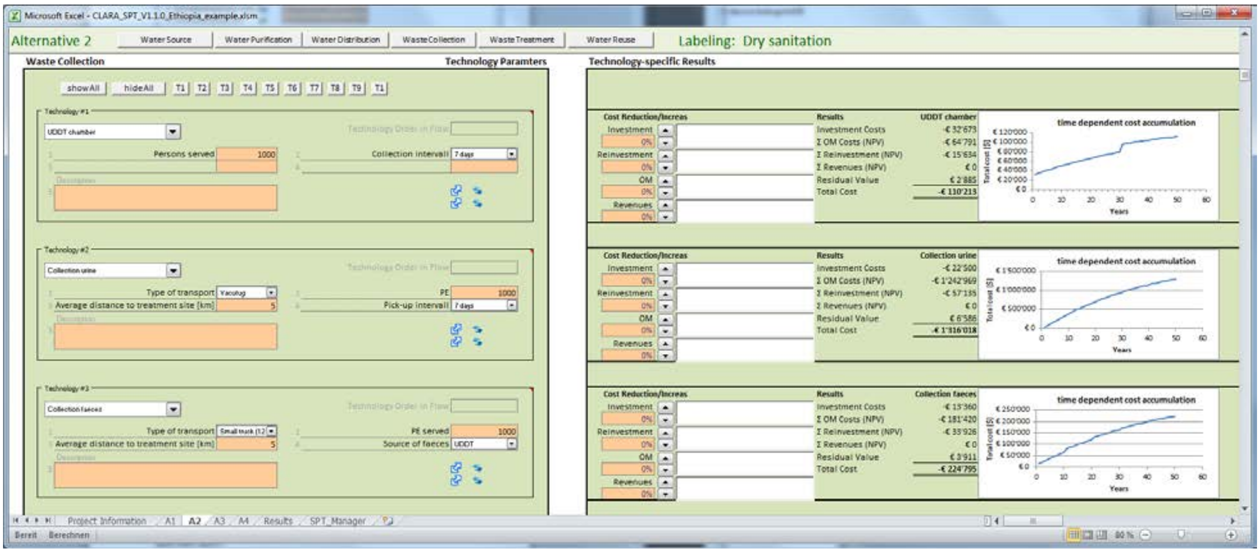
Change in cost since release 2013 [%]	5

	Alternative Labels/Names
Alternative #1	Water borne sanitation
Alternative #2	Dry sanitation
Alternative #3	
Alternative #4	

○ Technology Documentation Folder: E:\Dropbox\CLARA\2_cost functions\

● Online Documentation Folder: http://clara.boku.ac.at/images/doc/

Figure 8: User interface of the CLARA Simplified Planning Tool



Technology #1: UDDT chamber

Persons served	1000	Collection intervall	7 days

Technology #2: Collection urine

Type of transport	Vacutug	PE	1000
Average distance to treatment site [km]	5	Pick-up intervall	7 days

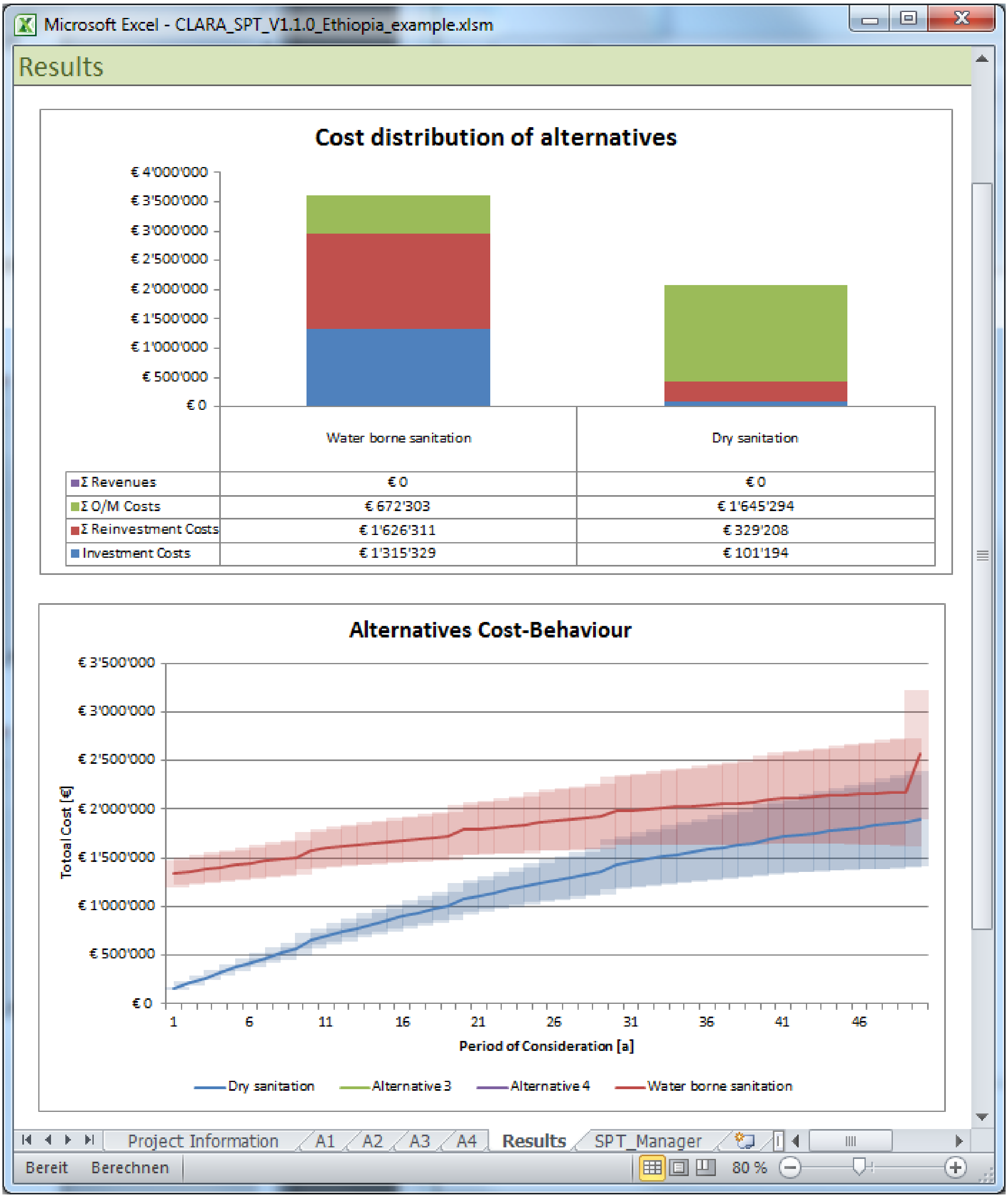
Technology #3: Collection faeces

Type of transport	Small truck (12	PE served	1000
Average distance to treatment site [km]	5	Source of faeces	UDDT

Results	UDDT chamber	Collection urine	Collection faeces
Investment Costs	-€ 32'673	-€ 22'500	-€ 15'360
Σ OM Costs (NPV)	-€ 64'791	-€ 1'242'969	-€ 181'420
Σ Reinvestment (NPV)	-€ 15'634	-€ 57'135	-€ 33'926
Σ Revenues (NPV)	€ 0	€ 0	€ 0
Residual Value	€ 2'885	€ 6'586	€ 3'911
Total Cost	-€ 110'213	-€ 1'316'018	-€ 224'795

Cost Reduction/Increas	UDDT chamber	Collection urine	Collection faeces
Investment	0%	0%	0%
Reinvestment	0%	0%	0%
OM	0%	0%	0%
Revenues	0%	0%	0%

Figure 9: Technologies in the "Waste Collection" functional group.



Cost distribution of alternatives

	Water borne sanitation	Dry sanitation
🟪 Σ Revenues	€ 0	€ 0
🟩 Σ O/M Costs	€ 672'303	€ 1'645'294
🟥 Σ Reinvestment Costs	€ 1'626'311	€ 329'208
🟦 Investment Costs	€ 1'315'329	€ 101'194

Alternatives Cost-Behaviour

Figure 10: Comparison of life-cycle costs of a water-borne and dry sanitation alternative for 1000 persons

(P40) Determinants of efficiency in Danish wastewater utilities

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Abstract

Efficient water management is a priority for the European Union, since the operational efficiency of many water utilities is very low compared to best practice. Several countries are restructuring the sector to improve cost savings. Bigger scale of operations and vertical integration strategies are promoted for achieving scale and scope economies. However, literature provides not convergent results on their existence. Then, quite scarce evidences are given on the effect produced by customer density on costs. This article offers some insights into this matter, analysing the Danish water market in 2010 using a two stage DEA approach with the aim to enquire the presence of scale, scope and density economies in the wastewater segment. The Danish wastewater is characterized by scope and density economies: firms which serve more than 100 inhabitants per km of sewers and contextually offer water and wastewater services achieve the best standard of efficiency. Scale don't exert a significant influence on global efficiency, even if technical pure efficiency statistically decreases when firm size grow up

Keywords

Denmark water industry; economies of density; economies of scale; economies of scope; wastewater

INTRODUCTION

The European Union (EU) considers efficient water management a priority. Many scholars have attempted to highlight the existence of economies of scale and scope in this industry to develop a comprehensive framework that can facilitate managerial and political decision making but the results are inconclusive (Berg and Marques 2011; Carvalho et al., 2012; Guerrini et al., 2013; Saal et al., 2013). By contrast, as highlighted by Abbott and Cohen (2010), in relation to wastewater activities, there is consensus that economies of scale do exist, although there is no clarity on the timeframe until when it is available. However, this consensus could be because the wastewater industry has received less research attention and most such studies have focused on entities undertaking water supply as well as wastewater activities (e.g., Ashton, 2000; Romano and Guerrini, 2011). While there is considerable evidence that scope economies exist for water production and distribution (Saal et al., 2013), results from studies on the joint provision of water and wastewater services differ. In particular, studies focused mainly on the United Kingdom and Portugal (for references, see Guerrini et al., 2013; Saal et al., 2013) revealed contrasting results. Moreover, the literature on the existence of economies of density in the water industry is quite scarce (Berg and Marques, 2011; Guerrini et al., 2013), and for this reason, further empirical studies are required. Therefore, this study aims to contribute to the literature by analysing the efficiency of water utilities operating in Denmark. We investigate the potential presence of economies of scale, scope, and customer density in the country's water utilities that have never been analysed with reference to these relevant issues.

DANISH WATER INDUSTRY

Denmark provides an appealing setting for comparing the performance of water utilities since it is characterized by the presence of a developed benchmarking system with publicly available, detailed data provided separately for water and wastewater facilities. Furthermore, in this country, companies of different sizes coexist and serve different areas and populations, as utilities involved only in water supply, only in wastewater services, or in both. Notably, the assessment of each activity's efficiency has significant value for decision makers and regulators. Furthermore, by focusing on a single country, we eliminate cross-cultural noise (owing to such factors as different legislation and geographical features) and thereby specify the optimal size, degree of investment diversification, and population density that will produce the maximum efficiency level in this particular setting (Carvalho et al., 2012; Guerrini et al., 2013).

The Danish water sector, organized into four river basin districts, is highly decentralized with 98 municipalities responsible for providing water and wastewater services to 5.58 million inhabitants in an area of 42,895 km². Municipalities monitor water operators and are responsible for the use, planning and protection of water, including water quality, and water supply and wastewater infrastructure. Similar to other European countries such as Austria and Sweden, Denmark allows private sector participation with a no-profit motive. Data from 2006 show that in the drinking water sector, about 60% of the Danish population is served by public operators owned by municipalities, while the remaining 40% is served by private operators in the form of consumer cooperatives and not-for-profit companies. Conversely, wastewater operators are almost all public companies, as in only a few cases have municipalities contracted out operations to private companies. Compared to other European countries, Denmark's water industry is characterized by low population density; a high level of decentralization (Carvalho et al., 2012); one of highest tariffs in Europe; and one of the lowest water loss rates (DANVA, 2010).

DATA AND METHOD

DANVA benchmarking report (DANVA, 2011) lists 101 Danish water utilities that provided water services in Denmark in 2010. In that year, they supplied approximately 54% of the Danish population with drinking water and treated wastewater from approximately 65% of the population. Of these, 39 firms supplied only drinking water, while 44 provided wastewater transport and treatment services. The remaining 18 firms provided both services to their customers. These water companies administered 1,966 bores, 239 waterworks, 26,615 km of distribution networks, and 49,139 km of sewer networks. In total, they provided 205 million m³ of clean water to approximately 3 million inhabitants and treated 581 million m³ of wastewater, covering 3.6 million inhabitants. We collected data for the 62 wastewater utilities (44+18) with respect to the populations served, length of water mains and sewers, financial statistics, and annual sales volume. The financial data referred specifically to information on wastewater management: transport costs, treatment costs, and customer handling costs in Danish krone (DKK).

The dataset analysed in this study consists of 372 data items on these 62 utilities. Table 1 contains the data statistics, which reveal notable differences in the sizes of the populations served.

To improve our knowledge of the sample observed, we divided this dataset into different groups. First, we categorized companies into clusters of mono- and multi-utilities. The former consisted of units that provided only wastewater services; the latter featured companies offering both services (water and wastewater). Second, considering the ratio of the population serviced to the kilometers of sewerage, we identified four groups of approximately equal size, based on their customer densities: very high density (VHD), high density (HD), low density (LD), and very low density (VLD). Adopting the same criteria, we distinguished three groups of equal size (large, medium, and small firms) on the basis of population served.

Our analytical method is based on that of Guerrini et al. (2013) and comprises two main stages. Stage 1 determines Data Envelopment Analysis (DEA) scores, using data on costs and volumes of water sold to obtain constant return to scale technical efficiency (CRSTE), variable return to scale technical efficiency (VRSTE), and scale efficiency (SE). Stage 2 includes preliminary outlier detection, to avoid extreme scores owing to incorrect data or selection of very unusual firms. Then, we regress the efficiency scores obtained through DEA on operational and environmental variables: firm size, the degree of investment diversification, and population density.

RESULTS AND DISCUSSION

Results are provided in table 2. Our data analyses highlighted significant differences across groups of firms involved in wastewater services in terms of operational scale, degree of investment diversification, and customer density. We found that firms that served more than 100 inhabitants per km of sewers (those in the VHD cluster) achieved the best standard of global efficiency and showed a good capability to purchase, combine, and consume inputs to treat a cubic meter of wastewater. Nevertheless, approximately 47% of the observed firms operated under the critical threshold of 40–50 inhabitants per km of sewer and achieved a low performance. Unfortunately, there are few solutions for these firms' problems, apart from servicing denser neighboring areas, should they exist. Considering that the sewerage coverage rate in Denmark is 100% (WHO/UNICEF, 2006), the choice to activate new connections to improve customer density is not feasible. As a result, the policy of the majority of Danish local authorities to keep water and wastewater services separate, that is, to ensure these services are provided by two different utilities in the same area, seems to penalize performance. Consequently, enlargement of the scope of Danish wastewater utilities should be incentivized. Finally, utility size exerts contrasting results on two efficiency scores (SE and VRSTE) whose effects neutralize each other when global efficiency is considered. Large firms achieve optimal structure, while pure technical efficiency decreases when scale of operations expand. This result implies that strategies that aim to extend the area served by wastewater utilities (such as covering new areas or merging with other companies) do not yield cost savings.

Table 1. Descriptive statistics of the sample observed.

	Max	**Min**	**Mean**	**SD**
Wastewater utilities				
Operation costs (DKK)	147,296,850	5,331,962	39,925,518	29,723,605
Volume of water inflow (m3)	11,812,097	626,287	3,113,549	2,026,060
Sewers length	2,496	55	819	494
Population served	533,875	8,486	61,470	84,074
Population density (pop/km of mains)	3849	16	146	498

Table 2. Regression analysis in wastewater segment.

Tobit regression	CRSTE	p>t	VRSTE	p>t	SE	p>t
Size	-0.047	0.145	-0.271	0.001***	0.237	0.002***
Water&Wastewater	0.091	0.079*	-0.007	0.874	0.061	0.226
Density	1.17	0.003***	3.29	0.000***	-0.165	0.267

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(P41) Productivity of Wastewater Treatment Plants including Greenhouse Gases: a Malmquist-Luenberger Approach

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Abstract

The number of wastewater treatment plants (WWTPs) worldwide has increasing significantly and the economics associated with their management have become more relevant. The assessment of the productivity of WWTPs is an important measure for identifying best practices and optimising resource-use. Although the productivity of WWTPs has already been evaluated in previous works they have just been taken into account the desirable outputs. However, the treatment of wastewater also involves undesirable outputs such are the emission of greenhouse gases and the generation of sewage sludge. This study analysis the productivity growth of a sample of Spanish WWTPs across the period 2003-2008 by using the Malmquist-Luenberger productivity index which models joint production of good and bad outputs. The results show a slight decrease in the productivity across the time period. Although changes in both efficiency and technology contribute to this decline, the main responsible is the negative shift of the efficient frontier.

Keywords

Wastewater treatment, productivity growth, Malmquist-Luenberger productivity index, undesirable outputs.

INTRODUCTION

The number of wastewater treatment plants (WWTPs) worldwide has increasing significantly and the economics associated with their management have become more relevant. Productivity growth indicators have been traditionally used in the field of economics to support the decision making process since they provide information about how output-input relationships change over time and /or differ across decision making units (DMUs). In general, water sector has not escaped to this trend and many works have been developed aimed to assess the efficiency of water utilities (Ferreira da Cruz et al., 2012). Recently, special attention has paid to assess the efficiency and productivity growth of WWTPs since their operation involves significant economic costs.

During the wastewater treatment process, desirable outputs are obtained alongside harmful by-products (undesirable outputs) which may lead to environmental damage. Evidence that wastewater treatment is not free of environmental impacts is the wide number of works focused on life cycle assessment (LCA) of WWTPs. Even though, it makes sense to take undesirable outputs into account when assessing productivity growth of WWTPs, none of the previous works in the field of WWTPs have considered this kind of outputs. In this sense, it should be emphasized that productivity changes appear to differ under two approaches (whether one incorporates undesirable outputs or not) (Färe et al., 2001).

Although there are several approaches to measure the productivity, economics have concentrated primarily on total factor productivity (TFP) indexes such are the Fisher and Törnqvist ones. In this context, the Malmquist Productivity Index (MPI) has become very popular because since it is based on Data Envelopment Analysis (DEA) approach and therefore, it does not require either price information or behavioural assumption in its construction but just information on input and output quantities.

The Malmquist Luenberger Productivity Index (MLPI) has been the most widely approach adopted to assess the productivity growth taken into account undesirable outputs (Zhang et al., 2011). The measurement of productivity growth in WWTPs based on DEA models has focused just on desirable outputs and inputs. Hernández-Sancho et al. (2011) assessed the productivity growth of a sample of Spanish WWTPs by estimating their MPI. This approach has ignored that the wastewater treatment involves the generation of undesirable outputs such are the emission of greenhouse gases (GHG) and the production of sewage sludge (SL). To overcome this limitation, the main objective of this paper is to assess the productivity growth of a sample of Spanish WWTPs taken into account the negative environmental externalities associated to wastewater treatment process. In doing so, the MLPI developed by Chung et al. (1997) has been estimated across the period 2003-2008.

METHODOLOGY

The assessment of the productivity change of the WWTPs including undesirable outputs is based on the estimation of the MLPI developed by Chung et al. (1997). This approach uses the directional distance function instead of the Sherphard output distance function used in the conventional MPI.

Letting $g = (g^y, -g^b)$ such that $g^y \in \mathfrak{R}_+^M$and $g^b \in \mathfrak{R}_+^M$. In our case, $g = (1, -1)$, i.e. desirable outputs are increased and bad outputs are decreased; $y \in \mathfrak{R}_+^M$is a set of desirable outputs; $b \in \mathfrak{R}_+^I$is a set of undesirable outputs and $x \in \mathfrak{R}_+^M$ is a set of inputs. Given $t = 1, \dots, T$ time periods and $k = 1, \dots, K$ decision making units (DMUs), Chung et al. [8] defined the MLPI as:

$$ML_t^{t+1}=\left[\frac{\left(1+\bar{D}_0^t(x^t,y^t,b^t;g^t)\right)}{\left(1+\bar{D}_0^t(x^{t+1},y^{t+1},b^{t+1};g^{t+1})\right)} * \frac{\left(1+\bar{D}_0^{t+1}(x^t,y^t,b^t;g^t)\right)}{\left(1+\bar{D}_0^{t+1}(x^{t+1},y^{t+1},b^{t+1};g^{t+1})\right)}\right]^{1/2} \qquad (1)$$

The MLPI as well as the MPI may be decomposed into two components namely efficiency change (MLECH) (Eq. 2) and technical change (MLTCH) (Eq. 3):

$$MLECH_t^{t+1}=\frac{\left(1+\bar{D}_0^t(x^t,y^t,b^t;g^t)\right)}{\left(1+\bar{D}_0^t(x^{t+1},y^{t+1},b^{t+1};g^{t+1})\right)} \qquad (2)$$

$$MLTCH_t^{t+1}=\left[\frac{\left(1+\bar{D}_0^{t+1}(x^t,y^t,b^t;g^t)\right)}{\left(1+\bar{D}_0^t(x^t,y^t,b^t;g^t)\right)} * \frac{\left(1+\bar{D}_0^{t+1}(x^{t+1},y^{t+1},b^{t+1};g^{t+1})\right)}{\left(1+\bar{D}_0^t(x^{t+1},y^{t+1},b^{t+1};g^{t+1})\right)}\right]^{1/2} \qquad (3)$$

To calculate the MLPI, four linear programming (LP) problems must be solved for each DMU. Two problems are solved in which all the observations are from the same period (t and t+1 respectively) and the other two problems are mixed period ones.

On the one hand, the productivity of the DMUs evaluated improves if MLPI > 1. On the other hand if MLPI < 1 then productivity declines. If MLPI = 1 then the productivity remains unchanged. A similar interpretation applies to the indexes MLECH and MLTCH.

DATA AND SAMPLE SPECIFICATION

The sample used for this analysis consists of 175 WWTPs located in the Region of Valencia on the Spanish Mediterranean coast, across the period 2003-2008. The 175 facilities embracing our sample use conventional activated sludge as secondary treatment. For assessing the productivity growth, two desirable outputs, two undesirable outputs and one input have been used. The desirable outputs are the two main pollutants removed from wastewater namely: (1) suspended solids and organic matter measured as chemical oxygen demand. Regarding environmental variables, two undesirable outputs have been considered. The first one is the emission of GHG expressed as Kg of CO_2 equivalent. The second undesirable output is the SL generated as by-product of wastewater treatment. As a result of the increasing growth in sludge production, problems of storage and disposal have become more important. The input is the economic cost of operating and maintaining each WWTP which includes energy, staff, reagents, maintenance and waste management costs.

RESULTS AND DISCUSSION

By solving the models described, a MLPI has been obtained for each of the 175 WWTPs evaluated (Figure 1 and Table 1). The average MLPI was 0.923 meaning productivity has decreased across the period of study around 7.7% (or 1.5% per year). The minimum MLPI value was 0.599 for the WWTP number 139 while the maximum one was 1.246 for the WWTP number 60. The fact that the MLPI is obtained at plant level is one of the most significant advantages of this methodology since allow WWTPs operators act in specific plants in order to improve their productivity.

Table 1. Summary results of productivity growth for 2003-2008.

	MLPI	MLECH	MLTCH
Mean	0.923	0.993	0.930
Std. Dev.	0.088	0.060	0.073
Minimum	0.599	0.500	0.653
Maximum	1.246	1.488	1.198

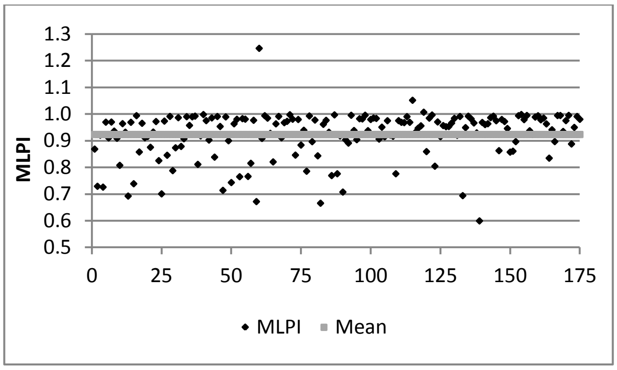

Figure 1. MLPI of WWTPs for 2003-2008.

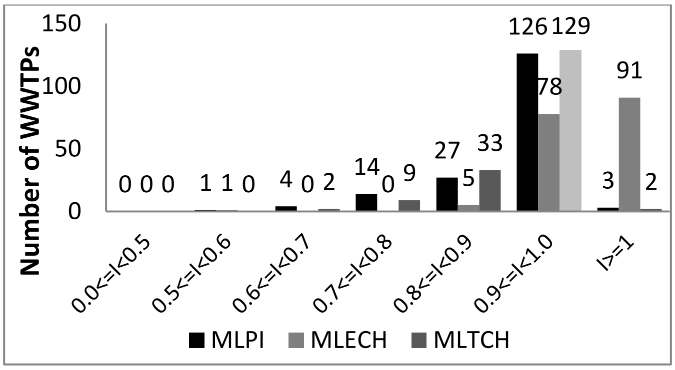

Figure 2. Groups of WWTPs according MLPI, MLECH and MLTCH.

The distribution of WWTPs with respect to MLPI (Figure 2) shows that only three plants (1.7%) have improved their productivity while the remaining ones (98.3%) had worsened. Within this second group, it should be noted that the majority of the plants (72.0% of the total) present a MLPI ranged between 0.9 to 1.0 meaning that productivity has remaining almost constant across the period of time analysed.

The second step of our assessment is to evaluate how the two components of the MLPI (MLECH and MLTCH) contribute to productivity growth at plant level. Following the same approach than previously, Figure 3 shows the MLECH and the MLTCH for the 175 WWTPs evaluated and Table 2 summaries the results. The average of the MLECH is 0.993 showing a slightly decline in the efficiency across the five years of observation. The MLECH values range between the minimum of 0.500 corresponding to the WWTP 139 and the maximum of 1.488 for the WWTP 60. The average value for the MLTCH, which by definition measures technical in-novation shows a negative offset of 7%. The range of MLTCH values is smaller than for MLTCH since the minimum value is 0.653 (WWTP 82) and the maximum one is 1.198 (WWTP 139).

Both components, MLECH and MLTCH, contribute to the decline of the productivity of the WWTPs analysed since both are lower than unity. However, Figure 2 verifies that the worsening on the productivity is mainly due to a decline in the MLTCH. In this sense, only two WWTPs (1.1%) present a technological improvement while the remaining 173 (98.9%) show a negative efficient frontier displacement. As well as for the MLPI, whiting this second group, most of facilities (73.7%) are ranged between 0.9 to 1.0. Regarding the MLECH, the results show that around half of the plants studied (52%) had improved their efficiency across the time study. In contrast, 44.5% of the WWTPs have reduced their efficiency by 10%.

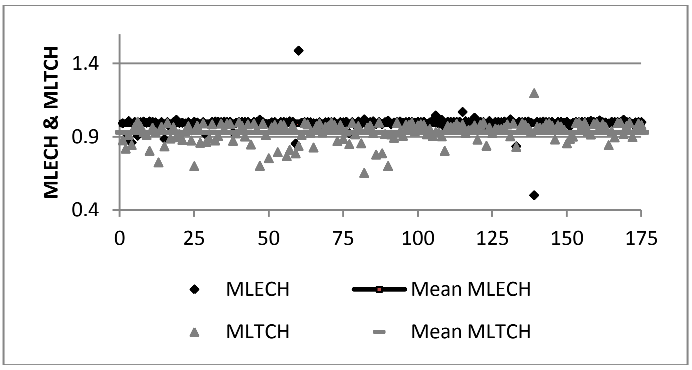

Figure 3. MLECH and MLTCH of WWTPs for 2003-2008.

CONCLUSIONS

The importance of adequate economic management of wastewater treatment plants (WWTPs) has been increasing as the number of these facilities has growth. In this context, the assessment of the productivity change is an useful tool enabling measures to be adopted for cost containment. Previous works assessing the productivity growth of WWTPs have considered that wastewater treatment is free of environmental impacts. In order to overcome this limitation and as a pioneering approach, it has been estimated the Malmquist-Luenberger Productivity Index (MLPI) for a sample of Spanish WWTPs. This indicator, based on the directional distance function, takes into account not just inputs and desirable outputs but also undesirable outputs, greenhouse gases (GHG) emissions and sewage sludge (SL) production for WWTPs.

The average of the 175 WWTPs studies shows a slight decrease in the productivity (7.7%) across 2003-2008. Although changes in both efficiency and technology contribute to this decline, technological change was primarily responsible since only two plants present a technological improvement. From a policy perspective, the fact that productivity worsening is due mainly to the negative shift of the production frontier involves that water authorities and WWTPs operators should invest in their facilities in order to update their processes. Moreover, the plants in which the efficiency has decreased also require improving their management by adopting the procedures used by the WWTPs located on the efficient frontier (best practice).

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(P42) Sustainability Assessment of the WWTP in the Baltic Sea Region: A Case Study in Lithuania

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Abstract

According to EU Strategy for the Baltic Sea region Lithuania with its neighbours obligates to overcome common challenges, ensure sustainable growth and till 2020 gain and maintain good conditions of the marine environment. To achieve this priority area for maintaining good quality of surface waters is given to wastewater treatment environment. During the last decade Lithuania made a huge progress in the field of wastewater treatment sector. However, wastewater treatment processes (WWTP) in the sustainability context has never been evaluated before. To determine the factors stimulating sustainable development of wastewater management infrastructure sustainable development indicators based on the methodology framework of life cycle assessment (LCA) in connection with functional unit was applied to case study. Results revealed that in the general context of sustainability the stability of plant varied greatly. Nine of the thirty sustainable indicators haven't reached the sustainability approach. Moreover, an opinion has been unanimously achieved that this assessment methodology may be a significant wastewater treatment plants development tool in analysis of the possibilities of managing wastewater treatment processes and its environment.

Key words

Wastewater; wastewater treatment plant; sustainability; life cycle assessment, Baltic Sea region

Introduction

In the last decade the majority of big Lithuania's wastewater treatment plants, with the people equivalent (PE) greater than 2000, were updated and/or reconstructed by effectively using, for example, EU structural support or national, regional, international institutions funds or private capital. However, because of unfavourable sponsorship conditions in smaller agglomerations, where PE is less than 2000, a lot of problems have sprung up for introduction or arrangement of wastewater collection systems and even for wastewater treatment.

In the period of 2014-2020 in the EU long range financial plans great attention will be paid to wastewater treatment and potable water quality improvement in small settlements. It will be the period which needs the arrangements made in advance so that the most optimal and steady technologies could be implemented by applying efficient management measures and tools, thus effectively exploiting the EU assistance and support.

In Lithuania waste water treatment processes (WWTP) in the sustainability context has never been evaluated before. Authors of the paper claim that sustainability assessment of the WWTP is necessary for clear each of the treatment process understanding, what should be done and improved for effective waste water treatment operating not just in technological way, but also in socio-cultural, economical and environmental. Literature review showed that LCA is the most steady and perfectly developed assessment tool which can be used for different sizes of WWTP, in conjunction with other analysis tools, like cost-benefit analysis or sustainability assessment, indicate which stages of the analysed object cycle have the strongest impact on the environment (Muga et. al, 2008; Gallego et. al, 2008; Molinos-Senante et. al, 2008). Moreover it is widely used by scientists for evaluating either an impact or benefit on the environment in connection with the chosen functional unit (Héctor, 2011; Foley et. al, 2010).

Goal and scope definition

Objectives

In 2013 the researches ranging over the part of the Nemunas flow in Lithuanian territory have determined that at Jurbarkas its pollution with organic compounds is the second by its extent, following the BOD_7 study data at Rusne, reaches 5 mg/l. It has been determined that the ecological river state reaches the highest average*,* value limit (PI Rupi, 2013). The main pollution source is concentrated pollution spreading from urban and rural settlements wastewater treatment processes as well as industrial activity.

Due to the mentioned aspect, Jurbarkas wastewater treatment plant has been selected as such which counts to be evaluated in sustainability context.

Functional unit

The main functional unit which was used in the research for evaluating the quantative impact on the environment is *the treatment of one cubic meter of wastewater treated*. This choice is directly connected to different technological processes constituting an easier base for comparing the results.

Description of the study area

The wastewater systems dependent on the plant collect wastewater from 10,200 consumers. Wastewater is treated by biological wastewater treatment processes in Jurbarkas. The designed capacity of the plant is 2540 m^3/d., its average wastewater treatment quantity is 1685 m^3 per day. Wastewater is treated by means of a traditional active sludge technology.

Life cycle assessment application

To carry on this research a number of proper balanced development indicators which involved functional, socio-cultural, environmental and economic steady state indicators were applied to WWTP during its whole life cycle.

Figure 1 presents the system of Jurbarkas analyzed WWTP. The system boundaries cover the primary stage processes (pollutants directly discharged into the atmosphere, effluent dilution) and some secondary stage processes (use of purchased energy and chemical materials). Seeking more consistent and explicit evaluation of the impact of the processes the WWTP processes have been separated according to the material flows, namely to effluent sludge and water lines.

The period of this research lasted for 4 years from 2009 to 2012, the data cover only the WWTP technological operation stage.

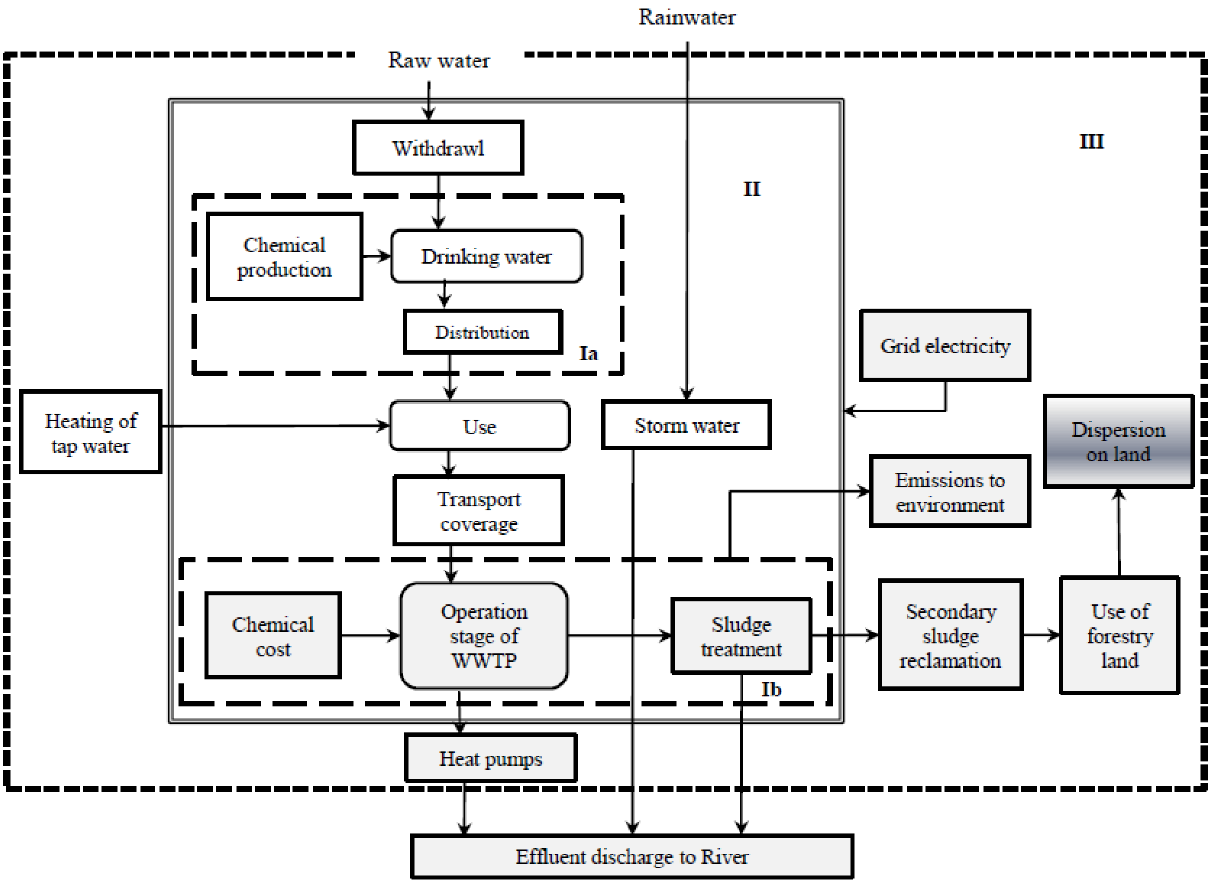

Figure 1. System boundaries for the urban water system

Where:
☐ - First order process;
▨ - Second order process.

The indicators show the flows of materials and energy in the system. Ia – *Drinking water treatment*; Ib - *Wastewater treatment;* II – Anthropogenic urban water extraction, use and management; III – Urban water system and peripheric systems connected to the analyzed one. Solid system blocks indicate the analyzed system processes (adapted according to Héctor G.L.).

Inventory analysis

Applied sustainability development indicators

With reference to four categories of sustainability development indicators, a limited but comprehensive set of indicators was selected to address the most important aspects of the wastewater treatment plant: functional (9), environmental (10), economic (4) and socio-cultural indicators (6) (Héctor, 2011):

- *Functional indicators*. Effectiveness indicators were used to evaluate the minimal technical requirements and influent-effluent quality; Efficiency indicators: pollutants removal efficiency in WWTP (%), Energy recovered from the WWTP (kWh inh.$^{-1}$d^{-1}), Actual ER as a percentage of design ER, Ratio of pollutants in wastewater; Number of system breakdowns for maintenance per day.
- *Environmental indicators*. Effluent quality: ratio of total pollutants in the receiving water compared to the WWTP effluent; Sludge quality: Ratio of solids sent to landfill compared to land application, Phosphorus (P) and nitrogen (N) recycling through the reuse of biosolids, Discharge of selected heavy metals to soil; Gas emission in kg CO_2 equivalent per day, Odour; Noise and Traffic; Pathogens removal.

- *Economic indicators*. Total costs per volume of wastewater treated (Lt/m^{-3}d^{-1}), Operational and Maintenance costs per volume of wastewater treated (Lt/m^{-3}d^{-1}), Energy costs per volume of wastewater treated (Lt/m^{-3}d^{-1}), Chemical costs (Lt/m^{-3}d^{-1}), User cost (Lt/m^{-3}).
- *Socio-cultural indicators*. Community Size Served; WWTP Footprint compared to Wastewater Treated; Labour required to operate the WWTP; Aesthetics - Measured Level of Nuisance from Odour; Community participation; Ratio of total staff to staff from WWTP community.

Overall sustainability evaluation

The categorisation system for sustainability evaluation based on the normalisation range from 0 to 100 "Very good" (0-25) - the indicator is sustainable (Muga et. al, 2008).

The impact scale from 0 to 100 indicates a tendency from the sustainable scenario to unsustainable one. The lower the impact value the closer to the centre they are, i.e. the smaller the area limited by a graph the more positive result is obtained. With reference to the normalised data (see Figure 1), the target plot has revealed that the plant is characterised by a varying degree of sustainability and adaptation capacity, thus the improvement needs to be made in all four selected indicator categories.

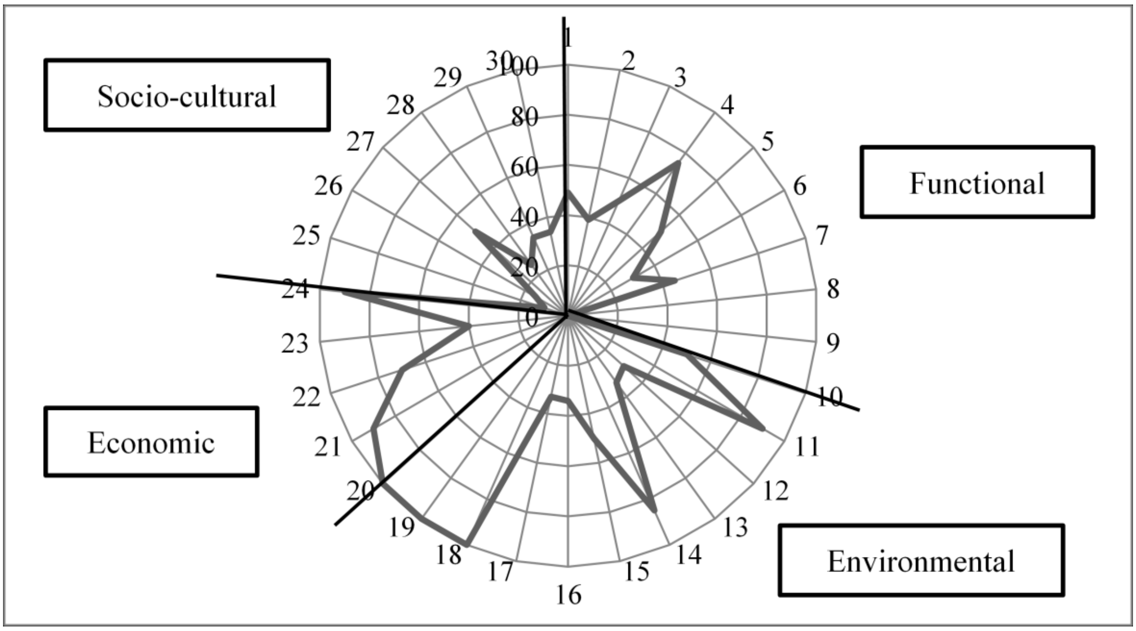

Figure 1. Data generalisation of Jurbarkas wastewater treatment plant

Results and Discussion

Research has shown that Jurbarkas wastewater treatment plants may be described to possess more sustainable than unsustainable features. According to the established categorisation of sustainability evaluation based on the best management principles, the improvement has been proposed to 9 unsustainable, 4 environmental, 1 functional, 1 socio-cultural and 3 economic indicators.

The need for chemicals for treatment processes in the plant is relatively high (1,200 t/yr.) which is the result of phosphorus (P) removal efficiency in the plant.

The concentrations of Copper (Cu), Zinc (Zn), Chromium (Cr), and Lead (Pb) are substantially high in the wastewater sludge – 1.8 mg/kg, 10.7 mg/kg, 4.1 mg/kg and 6.37 mg/kg respectively.

The public health risk of the generated wastewater was determined relatively high. Pathogenic organisms and dangerous chemicals are not examined in it.

All costs, including maintenance and operational costs, pumping energy costs and the cost of chemicals needed to clean the wastewater make about 2.66 Euro per day. The cost to consumers per one cubic meter of wastewater treated comprises 1.19 Euro. Depreciation, repairs, material costs and wastewater treatment costs account to 87%. Labour costs comprise 7.6%.

Improvement options include odour and optimisation of operating costs, removal of heavy metals by using the waste of chemically modified plants, bio electrochemical water and sludge decontamination, the use of probiotics for inactivating pathogenic organisms.

When starting to do this research it was quite unclear why in Lithuania no studies on WWTP in the context of sustainability have been carried out. To find it out it is worth analysing the aspects connected to sociology and communities, sewage treatment management and the work done by the Government as a chief agency in making decisions in the sphere of waste water management.

Sustainability development indicators (SDI) are frequently used in reports when evaluating either sustained efficiency of WWTP or its work conformity to certain requirements, but they are not used in planning or decision making when preventive measures are taken in the equipment designing stage which is of great importance and stimulation in seeking sustainable WWTP development.

Conclusion

Up to now in Lithuania no WWTP studies in the sustainability context have been done. Therefore, this research into "Jurbarko Vandenys" Ltd waste water treatment processes done at the national level and the results obtained might be a significant reason for using the SDI assessment methods for evaluating the operating WWTP in the sustainability context and for developing and adjusting newly built plants and in this way avoid unsustainable WWTP work in future when decisions are made at the planning stage.

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(S36) Water footprint assessment in Wastewater Treatment Plants

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Abstract
Wastewater Treatment Plants (WWTPs) play an important role inside the urban water cycle to protect receiving waters. However, the WWTPs processes produce also an environmental impact. Among the different methods to assess the environmental impact of WWTP operation, water footprint (WF) can be also used to evaluate the impact of a WWTP regarding the use of freshwater. This work presents an adaptation of the WF methodology to assess the WF of WWTPs. The application to a specific WWTP treating approximately 4000 m^3/d demonstrates a reduction of the grey water footprint of 86%, 46% and 96% for TN, TP and TOC respectively, while generating a blue water footprint of 375960 m^3/month. This means that when treating wastewater, there is a high reduction of the grey water footprint (compared to no treatment), although a small blue water footprint associated with the treatment appears.

Keywords
Wastewater treatment plants; water footprint assessment; grey water footprint

INTRODUCTION

Wastewater treatment plants (WWTP) play an important role in the urban water cycle to protect receiving waters. Since the construction and operation of WWTPs have also a significant environmental impact, it is necessary to have good methodologies to illustrate its importance inside the urban water cycle (UWS). One methodology to evaluate the role of these WWTPs in the UWS can be the water footprint. The water footprint is an indicator of the use of freshwater that takes into account not only the direct water use of a consumer or producer, but also the indirect water use. To the best of our knowledge, the application of the Water Footprint Assessment (WFA) methodology in WWTPs is limited to the work of (Liu et al. 2012), which evaluates the pollution discharged in rivers, and (Shao and Chen, 2013) which estimates partially the water footprint of the construction and operation of a WWTP. However, the first example estimates only the grey water footprint of anthropogenic emissions to major rivers, but not specifically from WWTPs, and the blue water footprint was not considered, and the latter example has two important limitations for a complete water footprint accounting; the first one is that the accounting was limited to the blue water footprint, while the second one is the no consideration of the sludge treatment. The objective of this work is to adapt the water footprint methodology and to demonstrate its applicability for a complete WWTPs WF assessment.

ADAPTED METHODOLOGY FOR WWTPs

To evaluate the water footprint of products and consumers, the Water Footprint Network (WFN) developed a methodology for WFA to evaluate the impacts on water consumption caused by an activity (Hoekstra et al. 2011). The WFA methodology addresses freshwater resources appropriation in a four-step approach: (i) setting the goals and scope, (ii) accounting for the water footprint of a process, product, producer or consumer as a spatiotemporally explicit indicator of freshwater appropriation, (iii) evaluating the sustainability of this water footprint, focusing on a multifaceted analysis of the environmental, economic and social aspects; and (iv) formulating strategies to improve the water footprint. This paper adapts the methodology from WFN and expands it with the definition of the grey water footprint calculation to be applied to WWTPs (Figure 1).

The general equation to calculate the water footprint (WF) of a process or product includes the blue (WF_{blue}), the green (WF_{green}) and the grey (WF_{grey}) water footprints and is defined as:

$$WF = WF_{blue} + WF_{green} + WF_{grey}$$

Equation 1: General equation for the water footprint calculation

Blue water footprint (WF_{blue}). In WWTPs, the blue water footprint accounts for water evaporated and water incorporated through the processes related with the WWTP unit operations (chemicals, electricity, residues management, transport and sludge treatment). On the other hand, the lost return flow is zero because the treated water is discharged into the same catchment.

Green water footprint (WF_{green}). In conventional WWTPs based on activated sludge systems, the green water footprint is not calculated because there is not any process evaporating water from the soil or thanks to vegetables or incorporating water from the soil.

*Grey water footprint (WF_{grey})***.** The grey water footprint is estimated by means of a mass balance at the WWTP discharging point (see Equations 2 and 3 and Figure 2). It should be calculated for each pollutant evaluated and then the maximum grey WF value among these considered pollutants will be considered as the Grey Water Footprint (Equation 1). In this case, we calculate the mass balance for TN, TP and TOC.

$$Q_e x c_e + WF_{grey} x c_{nat} = (Q_e + WF_{grey}) x c_{\max}$$

Equation 2. Mass balance at the WWTP discharging point.

$$WF_{grey} = \frac{Q_e x (c_e - c_{\max})}{(c_{\max} - c_{nat})} \quad [volume/time]$$

Equation 3. Grey WF equation based on the mass balance.

Where; Q_e is the effluent flow rate, c_e is the concentration of pollutant in the effluent, c_{max} is the maximum concentration of pollutant permitted in the receiving water body, and c_{nat} is the natural concentration of the pollutant in the receiving water body.

WWTP UNDER STUDY

The WF was calculated for La Garriga WWTP, which is treating 4000 m^3/d and discharging into the Congost river, in the Besòs river catchment (Spain). The system boundaries (Figure 2) include the input and output fluxes to the influent and effluent of the WWTP, the use of chemicals and electricity, the sludge treatment and the evaporation of water from the plant. The inventory data from the WWTP was obtained from the Consorci per la Defensa de la Conca del Riu Besòs (CDCRB) and the data from the river from the Catalan Water Agency (ACA) (Table 1). The water consumption related to the use of chemicals and electricity was obtained from the Ecoinvent 3 database. For sludge treatment the water consumption was obtained from Amlinger et al. (2008). The evaporation was calculated as the water evaporated considering the solar radiation on this zone from the Atlas of Solar Radiation in Catalonia (Generalitat de Catalunya, 2001) and the reactors surface of the WWTP.

RESULTS

The proposed methodology was applied to calculate the WF of the WWTP. In order to demonstrate the positive role of the WWTP we compared the WF for untreated wastewater discharging directly to the river and the WF including the treatment at the WWTP. Table 2 shows that wastewater treatment implies a reduction of 49% of the total WF. TP is the limiting factor for the grey WF calculation for the treated wastewater and TOC for the untreated. As illustrated in Table 2, a large water footprint for untreated water is due to the grey water footprint while, when implementing a certain treatment to the wastewater, there is a high reduction of the global water footprint, although a small blue water footprint associated with the treatment appears.

TAKE HOME MESSAGE

The applicability of the water footprint methodology in WWTP has been demonstrated. The WWTP under study provides a reduction of the water footprint of 86%, 46% and 96% for TN, TP and TOC, while generating a blue water footprint of 375960 m^3/month. Phosphorous removal should be a priority due to its higher impact after the treatment and lower reduction of the water footprint. The water footprint allows illustrating the beneficial role of WWTPs inside the urban water cycle.

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FIGURES AND TABLES

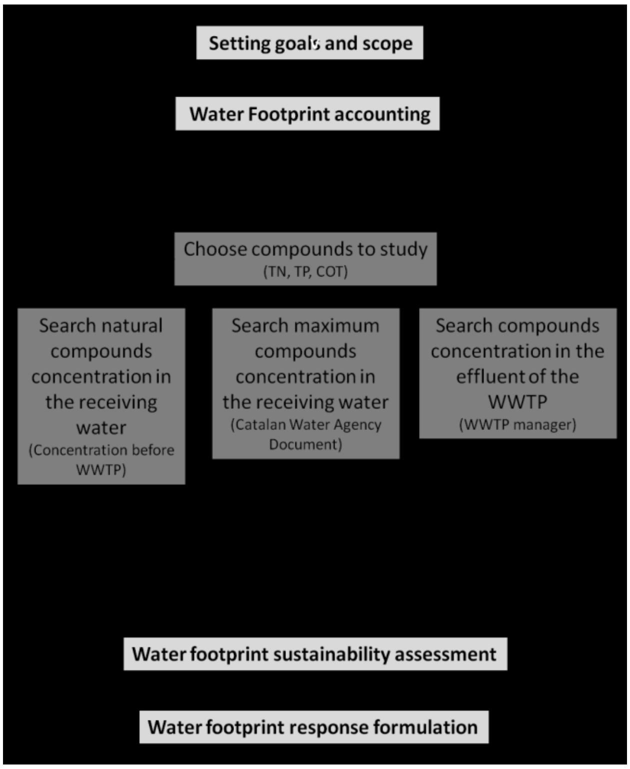

Figure 11. General framework to assess the water footprint in WWTPs, in dark grey the proposed

development to calculate the grey water footprint of WWTPs.

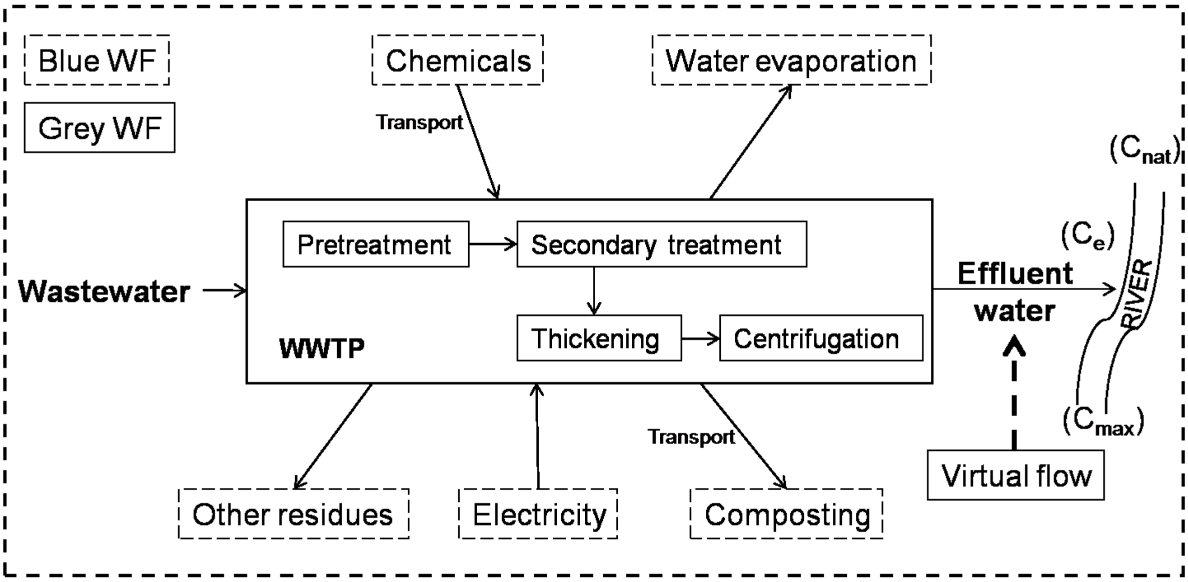

Figure 12. System boundaries for the WWTP under study.

Table 3. Input data for the WF assessment.

Blue water footprint		**Grey water footprint**			
Concept	**Amount**	**Pollutant**	**WWTP effluent concentration (Ce) (g/m^3)**	**Natural concentration (Cnat) (g/m^3)**	**Maximum concentration acceptable (Cmax) (g/m^3)**
ectricity (kwh/m^3)	0,4835	**TN**	9,66	1,03	2,65
Chemicals (kg/m^3)	0,0261	**TP**	3,55	0,04	0,17
Sludge to treatment (kg/m^3)	0,9166	**TOC**	11,18	2,07	5
Other residues (kg/m^3)	0,0286				
Evaporation (m^3/month)	237,2				
Transport (tkm/m^3)	0,0396				

Table 4. WF results (grey WF, blue WF, total WF and % of reduction)

UNTREATED WATER			TREATED WATER		
GREY WF (m^3/month)		BLUE WF (m^3/month)	GREY WF (m^3/month) (% reduction)		BLUE WF (m^3/month)
TN	3672231	0	TN	539317 (85,6%)	375960
TP	6415114		TP	3448115 (46,2%)	
TOC	7479507		TOC	261779 (96,5%)	
TOTAL WF (m^3/month)		7479507	TOTAL WF (m^3/month) (% reduction)		3824075 (48,9%)

(S37) Environmental assessment of bioenergy production through suitable wastewater and waste management

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Abstract

This study aims to analyse the potential environmental impacts of using waste activated sludge from a municipal wastewater treatment plant and the organic fraction of municipal solid waste for anaerobic digestion as a suitable disposal alternative as well as a bioenergy source. The electricity consumption in the system as well as the delivery and disposal of the wastes generated showed up to be the most important contributions to the environmental profile of this waste management system.

Keywords

Biogas yield; digestate management; environmental profile; waste activated sludge

INTRODUCTION

Waste activated sludge (WAS) and the organic fraction of municipal solid waste (OFMSW) represent a large amount of the biodegradable waste generated in Europe (Righi *et al.*, 2013). The biological treatment of organic wastes is being promoted as a potential alternative to landfilling (European Commission, 2010). The anaerobic digestion (AD) of wastes has the potential not only to provide a suitable scheme for organic waste management, but also to be a source of bioenergy.

GOAL AND SCOPE DEFINITION

This study aims to evaluate the potential environmental impacts of using WAS and OFMSW for AD as a suitable disposal alternative. Life Cycle Assessment (LCA) methodology was the tool selected for the environmental analysis. An Italian full-scale biogas plant associated with a wastewater treatment plant (WWTP) was inventoried in detail. The functional unit selected for this purpose was 1 tonne of feedstock fed into the anaerobic digester.

System boundaries

The system under study was divided in four main subsystems as indicated in **Figure 1**. In addition, avoided electricity production from the Italian grid was also taken into account. All inputs and outputs flows required in each subsystem were collected and taken into account within the life cycle inventory.

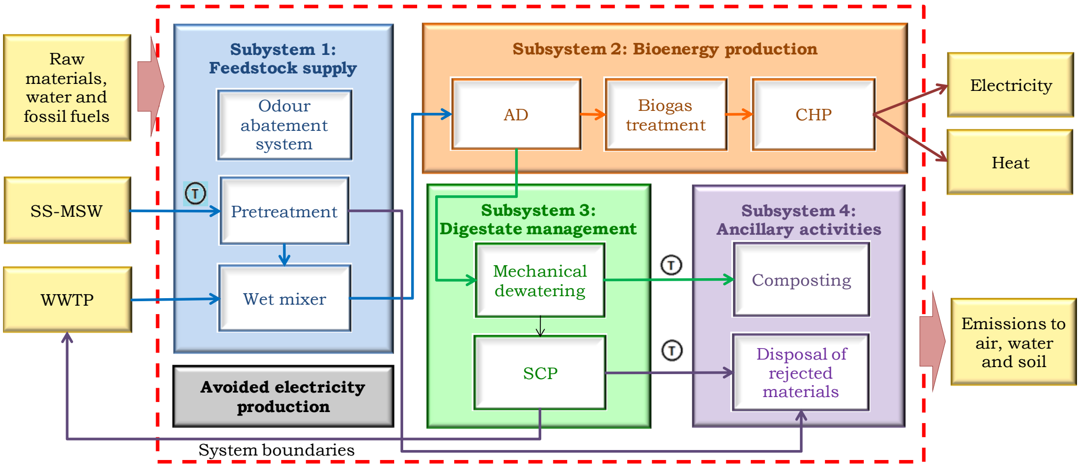

Figure 1.Flowchart and system boundaries of the system under study.

RESULTS

The environmental performance was assessed in terms of climate change (CC), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME) and fossil depletion (FD), using characterization factors reported by the ReCipe Midpoint (Goedkopp *et al*., 2009). **Figure 2** displays the relative contributions from each process within the system under assessment.

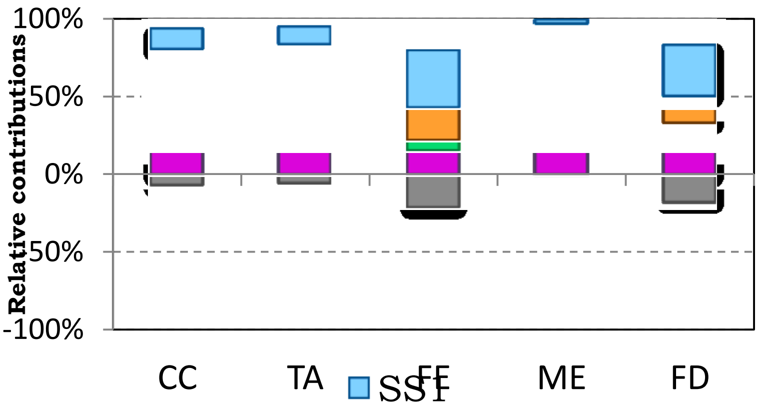

Figure 2. Relative contributions from subsystems involved to each impact category.

In light of the results, CC, TA and ME were mainly affected by the ancillary activities (SS4) (63%, 76% and 95%, respectively) which comprise waste transport and disposal. Concerning CC and TA, the impact was mainly produced by emissions from the composting of the digestate solid fraction, specifically methane and nitrous oxide regarding CC and ammonia in the case of TA. Concerning ME, the disposal in landfill of the rejected materials from SS1 and struvite from SS3 was the major contributor. However, it is important to note that struvite is not reused for local regulatory weaknesses that do not allow the reuse of the material (fertiliser) recovered from wastewater. Concerning FE and FD, the electricity consumption along the system caused most of impacts in these categories, due to the high ratio of non-renewable sources in the Italian electric profile. This electricity is consumed in the pretreatment of the feedstock (SS1) with 36% and 32% of the impacts, respectively and in the digester (SS2) with 21% and 17% of the impacts, respectively. The transport of the digestate to the composting plant (SS4) also had an important influence (16% in FE and 28% in FD). The avoidance of the electricity production from the Italian grid produced positive impacts (negative axis of the graph) in these impact categories. If struvite was used as a fertiliser, the environmental impact of the system would be 2.5-5.5% lower for all impact categories studied, as a result of the avoided management of struvite as a waste and the avoided production of an equivalent amount of phosphate-based fertiliser.

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(S38) LCA study of heterogeneous and homogenous Fenton processes for the treatment of an industrial pharmaceutical wastewater

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Abstract

The homogeneous and heterogeneous Fenton processes for the treatment of a pharmaceutical wastewater were evaluated using the life cycle assessment (LCA) methodology. Results indicate a strong influence of the hydrogen peroxide employed in these processes on the environmental impacts determined by the LCA. The heterogeneous Fenton-like process uses higher oxidant loadings than the homogeneous one. This was the major disadvantage of the heterogeneous process. On the other hand, the homogeneous process requires higher feedstocks of iron and acid/base agents along the process and several operation units to remove the iron salts from the treated effluent (energetically disadvantageous).

Keywords

Fenton process; industrial pharmaceutical wastewater; LCA; Eco-indicator 95.

INTRODUCTION

The effective removal of substances in pharmaceutical residual effluents is a challenging task due to the wide variety of chemicals produced in drug manufacturing plants, which lead to wastewaters of variable compositions and, in most of cases, resistant to the biological degradation. Advanced Oxidation Processes (AOPs) have been proposed as successful treatments for the degradation of pharmaceuticals present in wastewaters coming from different industries (Rivera-Utrilla et al., 2013). Among AOPs, homogeneous Fenton processes based on the generation of powerful HO• radicals from hydrogen peroxide in presence of Fe (II) dissolved in the aqueous medium, has been efficiently used as oxidation process for the treatment of a wide variety of pharmaceutical wastewaters (Rodriguez et al., 2011). However, the limited range of pH (2-3) in which the reaction proceeds and the need of iron removal from the treated effluent to comply with the European environmental regulations are the major drawbacks of this technology. The Chemical and Environmental Engineering Group (Rey Juan Carlos University, Spain) proposed an alternative heterogeneous Fenton process for the treatment of a wastewater coming from a pharmaceutical industry (Melero et al., 2009). The aim of this work is the comparison between the heterogeneous and homogeneous Fenton processes for the treatment of the pharmaceutical wastewater following the life cycle assessment (LCA) methodology. Thus, identification of their advantages and disadvantages in terms of their environmental impacts, feedstocks and energy requirements will be discussed. All the mentioned parameters as well as the catalytic performance in terms of the pollutants removals will be used to assess the overall environmental and efficacy of the processes.

METHODOLOGY

The study was carried out with SimaPro 7.1 software. The mandatory and optional elements of the LCA according to ISO 14040 were utilized by using Eco-indicator 95 method. The selected functional unit is the treated water in one hour (3 m^3) with inlet and outlet COD concentrations of 8000 mg/L and 1060 mg/L, respectively. The process boundaries of the homogeneous and heterogeneous Fenton processes are shown in Figure 1-a. The summary of the life cycle inventory (LCI) are depicted in Table 1.

RESULTS AND CONCLUSIONS

The different environmental impacts are shown in Figure 1-b for the homogeneous process. As preliminary study, the boundaries of the process were focused on the reactor system, being additional separation units for the removal of the homogeneous metallic species not taking into account. Results reveal a considerable contribution of the hydrogen peroxide in all the environmental effects. The heat to achieve the reaction temperature also shows a significant contribution to some environmental impacts. The strong dependence of environmental impacts with the hydrogen peroxide makes the heterogeneous Fenton process less environmental friendly than the homogeneous one. However, the heterogeneous process could be a friendlier alternative if lower hydrogen peroxide consumptions were achieved, because it allows decreasing some feedstocks related to the pH control and final iron elimination (H_2SO_4, NaOH and flocculant) and final sludge disposal, which have not been evaluated in this preliminary work.

Table 1. LCI for both Fenton processes

	Homogeneous Fenton	Heterogeneous Fenton
H_2O_2 (kg)	84	147
$FeSO_4$ (g)	525	-
$CuSO_4$ (g)	35	-
Heterogeneous Fe/SBA-15 (g)	-	24 (considering 50 days of use)
H_2SO_4 (g)	1449	-
NaOH (g)	7035	-
Flocculant (g)	20.8	-
Generated sludge, dry base (g)	1890	-
Temperature (ºC)	120	80

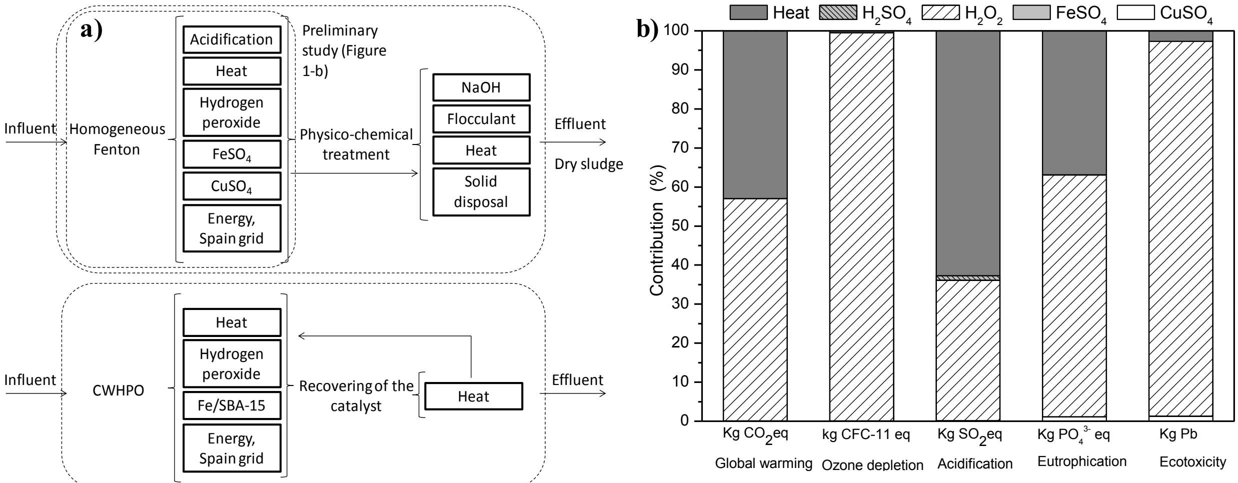

Figure 1. a) Process boundaries of homogeneous and heterogeneous Fenton processes and b) Contribution of the homogeneous Fenton reactor to environmental effects.

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Innovative case studies

(Wednesday, 25 June 2014, Aula T1, Polo Zanotto)

(I1) Current situation and future possibilities for the sewage sludge valorization

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Abstract

Thermal treatment is an efficient solution for the sewage sludge disposal, able to deal with the environmental problems related to some harmful elements inside sludge itself, as heavy metals, hormones, pharmaceutical derivates, etc. This presentation wants to show the several reliable technologies available today, able to fulfill the requirements for efficiency and cheapness. Other solutions with interesting potentialities are now in a research phase, and they show promising future possibilities of application also from the point of view of the environmental acceptability related to these technologies. In addition to the solutions for the sludge thermal treatment, it will be shown the issue of the phosphorus recovery from sewage sludge, a topical issue that will influence the choices for the sludge disposal in the next years.

Keywords

Sludge, incineration, phosphorus recovery, thermal recovery, valorization

THERMAL TREATMENTS OF SEWAGE SLUDGE

The use of the sewage sludge in agriculture is a controversial issue, due to the presence of inorganic and organic pollutants, included traces of drugs and hormones. For this reason, several European countries have introduced increasingly strict limits, aimed to decrease their use on large-scale.

In view of future strict limitations to the direct and indirect use of the sewage sludge in agriculture and in landfill, it is urgent to find alternative and reliable disposal systems.

Due to the difficulties mentioned above, several solutions can be taken into consideration. The most common and applied ways of disposal in Europe foresee the sludge mineralization with thermal treatments, especially mono-incineration and co-combustion in WtE plants and industrial plants. In this case, sludge is valorized for its energetic content and the disposal cycle is closed, with the final discharge of the combustion ashes. These processes are realized for several years on industrial-scale plants and they provide a reliable concrete solution. Due to the availability of the disposal sites, of the localization of the waste water treatment plants, the infrastructures, etc., it could be found solutions combined and/or integrated in the existing plants, by optimizing environmental and economical aspects.

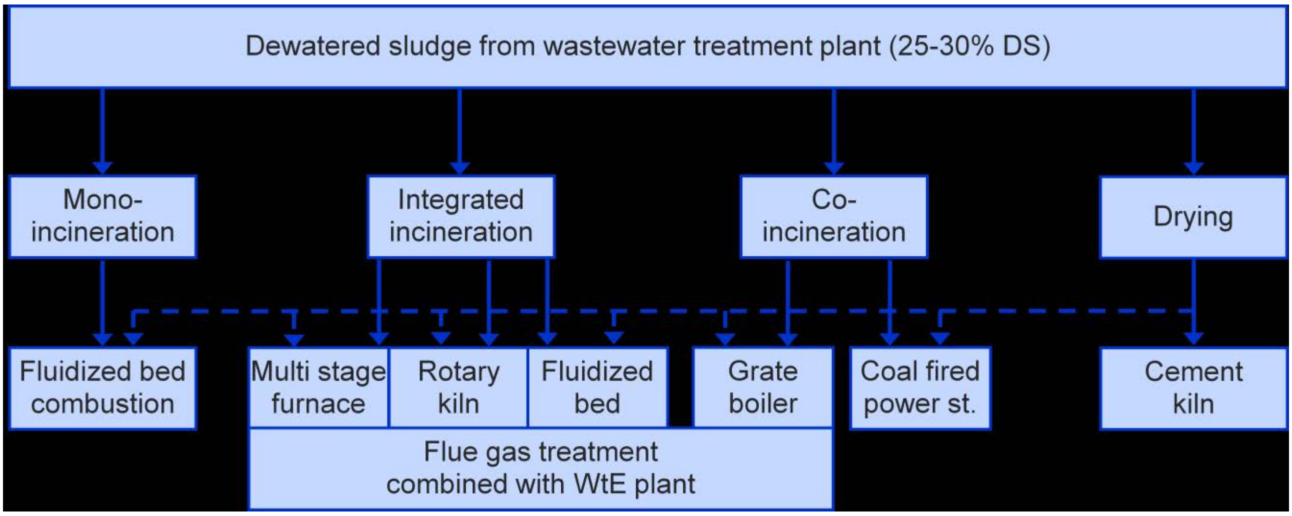

Figure 1. Ways of thermal disposal of sewage sludge

Recently innovative processes are proposed, like pyro-gasification and hydrothermal carbonization (HTC), that have had particular interest for the potential advantages with environmental impacts. However, these processes are still in a research phase and realized only on pilot-scale plants.

PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE

Phosphorus is an essential element for the life and the vegetal growth. The extraction of the mineral phosphorus is located in few countries, and the 70% of the known deposits of the world are placed in Morocco. Therefore, almost all the countries import phosphorus from abroad.

Currently, approx. the 80% of the mineral phosphorus is used for the production of fertilizers, while the remaining 20% is used for the production of cleaning agents and food additives.

Phosphorus, therefore, is collected with waste water to treatment plants, where it is concentrated in the sludge. Therefore, wastewater treatment represents a very important potential resource for the phosphorus recovery.

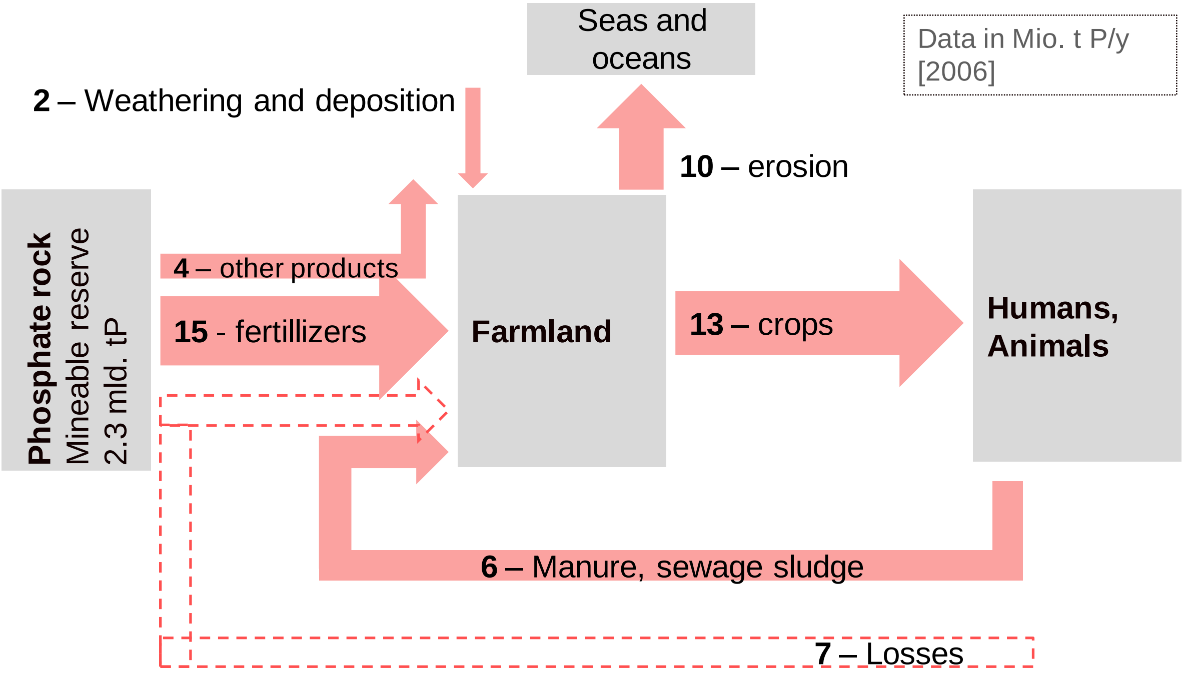

Figure 2. Phosphorus cycle

In the current state of art, phosphorus recovery is possible in several phases of the wastewater treatment process:

1. Outlet waters from treatment plants
2. Drain water recycle in the water line
3. Dewatered sewage sludge
4. Ashes from sewage sludge combustion

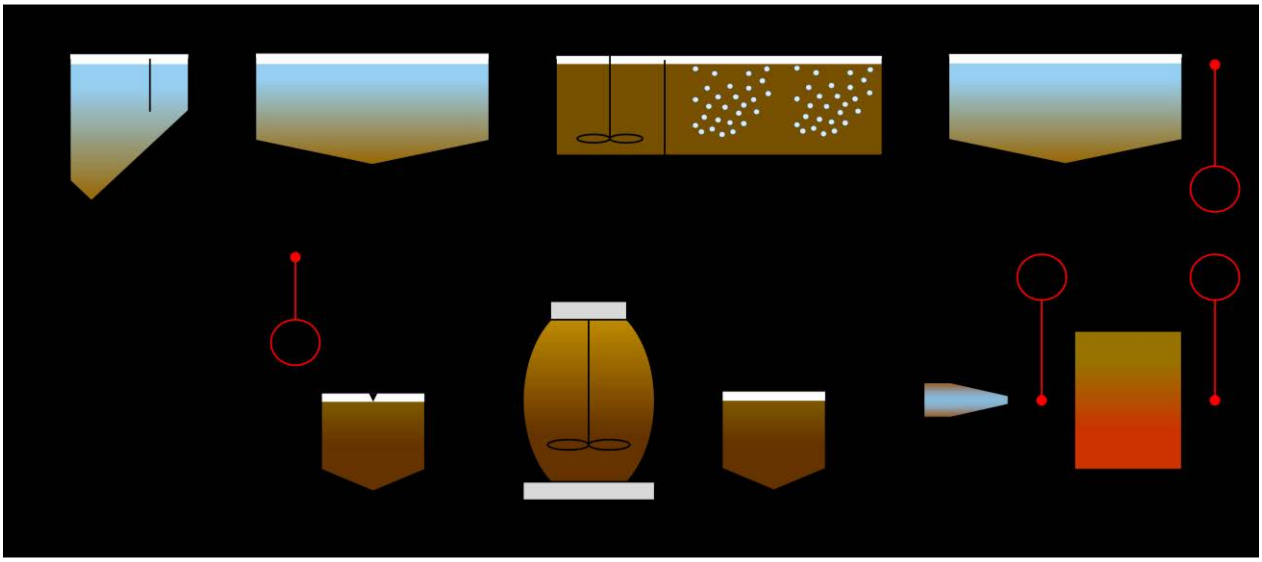

Figura 3. Possible locations for the phosphorus recovery in a waste water treatment plant

At the locations 1 and 2 of the Figure 3, concentrations of phosphorus in wastewater are very low, while at the locations 3 and 4 phosphorus is chemically bound and needs to be dissolved before the recovery procedures, but its concentrations are very higher.

In the last years many solutions for the recovery of phosphorus have been developed by means of wet-chemical processes and thermal metallurgical processes applied on sewage sludge.
The most promising solutions for the future foresee phosphorus recovery processes at the locations 3 and 4. In particular, phosphorus recovery from ashes from sludge incineration is today possible by means of processes technologically evolved, but economically still not profitable. In this sense, sludge mono-incineration represents an interesting solution.

The presentation will show a multi-criteria analysis of the several technologies for the sludge treatment: this analysis will concern both the technical and the economical aspects.
Furthermore, it will be evaluated the effect, technically and economically, of the phosphorus recovery integration in the technologies mentioned above.

(I2) Short-cut enhanced nutrient abatement (SCENA) from anaerobic supernatant at pilot and full scale

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Abstract

Ammonium and phosphorus rich reject water from the dewatering of anaerobic digested sludge must be properly managed to recover resources and optimize the sustainability of biological nutrient removal in wastewater treatment plants. This work investigated the integrated scheme of nitritation/denitritation and via nitrite enhanced phosphorus removal coupled to alkaline fermentation liquid of sewage sludge as an in situ best available carbon source. Despite the problematic characteristics of the influent, the via nitrite bioprocesses were stable in the pilot scale plant. Using the alkaline silicate mineral of wollastonite to buffer pH in the fermenter, the conversion rates for external carbon source were 0.30±0.4 gSCVFA/gTVS, while the propionate and butyrate contents were optimized. The via nitrite nutrient removal rates were 15±2 $mgN\text{-}NH_{4oxidized}/gMLVSS\cdot h$; 40±10 $mgN\text{-}NO_{2reduced}/\ gMLVSS\cdot h$; 10±3 $mgP\text{-}PO_{4bioaccumulated}/gMLVSS\cdot h$. The cost comparison between conventional scheme and SCENA estimated a potential annual net income of approximately 35000 euros for a actual treatment potential of 50000 PE.

Keywords

Nitritation-denitritation; via nitrite enhanced phosphorus uptake, anaerobic supernatant

INTRODUCTION

Enhanced nutrient removal at municipal wastewater treatment plants (WWTPs) can be partly and efficiently carried out by treating the ammonium and phosphorus rich reject water produced from the dewatering of anaerobic digested sewage sludge. In conventional plants this flow constitutes 10-30% of the total nitrogen load (Gustavsson, 2010). Phosphorus concentration in reject water produced by the dewatering of anaerobically digested activated sludge, can be up to 130 mg/L (Oleszkiewicz and Barnard, 2006, Ivanov et al., 2009), while higher P concentrations may be reached when anaerobic co-digestion of sewage sludge and organic waste are applied (Malamis et al., 2014). Thus, reject water is returned to the activated sludge tank and contributes from 10 to 50% of the nutrients in the main stream of WWTPs. Furthermore, innovative schemes aiming at energy neutral or positive municipal WWTPs are considering anaerobic digestion as a core unit for energy recovery from enhanced removal of solids through primary sedimentation. Thus, the separate enhanced nutrients bioremoval from the anaerobic supernatant of sewage sludge is becoming a core process unit within the new conceived WWTPs. Among the different treatment technologies for sludge reject water, the innovative biological processes proved to be the most economically and environmentally sustainable in terms of nitrogen removal (STOWA, 2012). In fact, complete autotrophic nitrogen removal is widely considered the best sustainable and reliable solution for sludge reject water, which should be followed by phosphorus recovery processes to optimize the nutrients management. In fact, via nitrite autotrophic/heterotrophic processes (nitritation/denitritation) needs external carbon sources, which could negatively affect the economical and environmental sustainability. On the other hand, the autotrophic nitrogen removal process is much more sensitive to environmental and operational parameters. In contrast to nitrogen, phosphorus is a limited resource, which must be recovered from wastewaters and reused (Gilbert, 2009). Struvite is generally considered as the optimal phosphate mineral for recovery and could potentially be used as a slow-release fertilizer. However, if the economic and life cycle costs are taken into account, phosphate recovery as struvite was not considered the best approach, and efforts were addressed also to the use of (composted) P-rich sludge for effective fertilization (Hao et al., 2013). Therefore, the via nitrite enhanced phosphorus removal associated with nitritation-denitritation (SCENA - Short-cut enhanced nutrients abatement) can realize the optimal side stream nutrients management in WWTPs. The SCENA system demonstrated its feasibility for the treatment of digester supernatant produced from the co-digestion of waste activated sludge (WAS) and the organic fraction of municipal solid waste (OFMSW), when the best available carbon source was recovered from OFMSW alkaline fermentation (Frison et al., 2013).

This paper deals with the pilot-scale operation of the SCENA system and the forthcoming full scale development in the municipal WWTP of Carbonera (Veneto Region, Northern Italy). It presents and discusses the integration of a conventional municipal WWTP, where the in situ best available carbon source for denitritation and via-nitrite enhanced P uptake is recovered from alkaline fermentation of sewage sludge.

MATERIAL AND METHODS

The SCENA pilot scheme consists of a sludge alkaline fermentation (SAF) unit coupled to a short-cut sequencing batch reactor (scSBR). The integrated SAF-scSBR has been set up within the conventional, municipal WWTP of Carbonera (Veneto, Italy). The system is applied to treat the real anaerobic supernatant for the short-cut N removal and via nitrite enhanced P bioaccumulation. It is composed of three main units: the sewage sludge alkaline fermentation unit (reaction volume 500 L, preceded by a coarse screen to prevent retain gross material present in the primary sludge), a tubular membrane (UF) filtration skid for the solid/liquid separation of the fermentation effluent, an SBR (3 m^3) for the treatment of the anaerobic supernatant to remove nutrients via nitrite pathway. The system is treating up to 6 m^3/d of anaerobic supernatant that is generated from the full-scale anaerobic digester of sewage sludge in Carbonera. The main processes involved are:

- ✓ Nitritation/denitritation coupled with the best available mix of short chain fatty acids (SCFAs) to enhance the denitrifying via nitrite biological phosphorus removal (DNBPR).
- ✓ Sludge alkaline fermentation to recover the best available mix of SCFAs for P removal and/or PHA production (which is not presented and discussed in this paper)
- ✓ Membrane filtration for the solid/liquid separation of the fermentation.

In addition, cheap and reliable system-wide process control may be realized by indirect parameters, namely: pH, conductivity, oxidation-reduction potential (ORP).

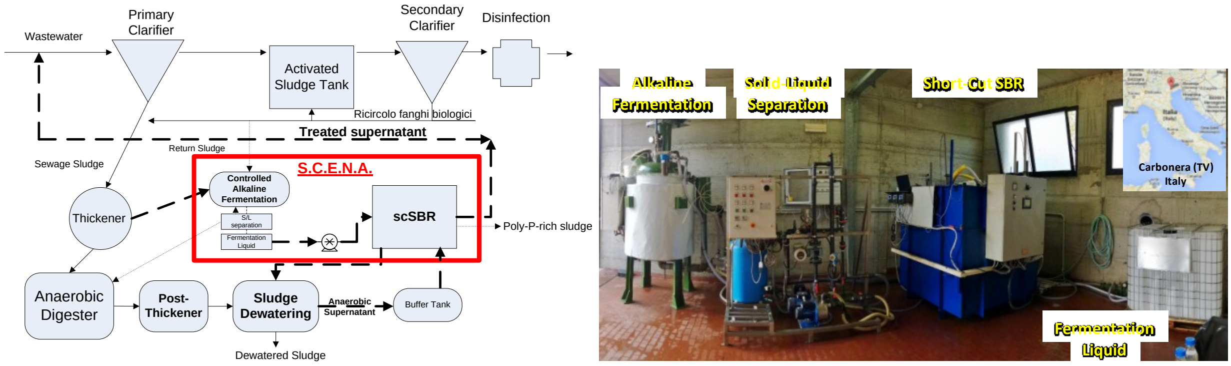

Figure 1. a) Integration of SCENA system in the conventional WWTP; b) SCENA pilot scale plant

According to the overview recently published by Desloover et al. (2012), the N_2O mitigation strategies were implemented according to Table 1. In addition, promotion of the mineral CO_2 sequestration is achieved by the use of alkaline silicates for pH buffering in the acidogenic fermentation (Salek et al., 2013).

Table 1 N_2O mitigation strategies implemented within the SCENA system

Objective	**Required approach**	**SCENA approach**
Minimize aerobic N_2O production	- Ensure high DO and adapted aeration regime; - Ensure constant DO (no repeated changes from anoxic to oxic)	DO during nitritation was always in the range 1.5-2 mg/L Only one aerobic/anoxic change is done
Maximize anoxic N_2O consumption	- Careful choice of the external carbon source	The alkaline fermentation liquid is rich of SCFA (i.e. propionate and butyrate) which minimize N_2O emissions (Zhu and Chen, 2011)

RESULTS AND DISCUSSION

Characteristics of the supernatant and start-up

The SCENA system was inoculated with conventional activated sludge coming from the full scale municipal WWTP of Carbonera. The start-up was carried out in two stages according to Frison et al. (2013). Due to extraordinary operation of the full scale wastewater treatment plant (i.e. low temperature), low performance and transient anaerobic digestion conditions were observed during the 150 operation days (Table 2). In spite of these problematic conditions (i.e. sCOD:N ~ 2) for autotrophic growth and nitrite oxidizing bacteria (NOB) suppression in the scSBR, the complete via nitrite pathway was achieved in around 30 days.

Table 2 Characteristics of digester liquor from the Carbonera WWTP

	Days 1-60	**Days 61-150**
pH	7,5±0,1	7,3±0,2
sCOD	520±30	155±38
$N\text{-}NH_4$	270±24	439±19
$P\text{-}PO_4$	25±3	43±3
Alkalinity ($mgCaCO_3/L$)	1065±170	1735±100

Alkaline fermentation and impact on denitritation and DNBPR

In WWTP required to meeting increasingly stringent nutrient requirement, the pre-fermentation of primary sludge to recover SCFA for BNR systems is a almost spread alternative to purchased carbon. Acid fermentation and its dosing to the main treatment line for the conventional BNR is a known practice (WERF, 2011). The innovation of SCENA system consists of: (1) the alkaline fermentation of sewage sludge; (2) the use of wollastonite for pH buffering; (3) the addition of sewage fermentation liquid in the anoxic phase of the nitritation-denitritation for the separate via nitrite enhanced nitrogen and phosphorus removal.

During the pilot scale trials the fermentation rate was as high as 0.30±0.4 gSCVFA/gTVS, while the average composition of the fermentation liquid optimized the contents of propionate and butyrate (Table 3), so as to enhance the via nitrite phosphorus removal (Ji and Chen, 2010). Optimal fermentation

HRT was in the range 5-7 days according to the content of primary and waste activated sludge, while semi-batch conditions were considered to obtain a stable production of SCFAs.

Table 3 Characteristics of alkaline fermentation liquid

Acetate	Propionate	Butyrate	Valerate
32 %	30 %	21 %	17 %
sAUR	sNUR	sPUR	
mgN-$NH_{4oxidized}$/gMLVSS·h	mgN-$NO_{2reduced}$/ gMLVSS·h	mgP-$PO_{4bioaccumulated}$/ gMLVSS·h	
15±2	40±10	10±3	

Full scale development and economic impact

The CAPEX and OPEX conventional activated sludge (modified Ludzack-Ettinger (MLE) + chemical P removal by alum) and SCENA systems were preliminary compared for the treatment of the nutrient loadings associated with digester supernatant (Table 4).

Table 4 Preliminary cost comparison for management of nutrients associated with digester supernatant (interest rate 4% was used for CAPEX)

Costs		MLE	SCENA
CAPEX: for MLE [a]	€/year	1277	0
CAPEX: for SBR [a]	€/year	0	389
CAPEX: for sludge fermenter [a]	€/year	0	449
OPEX: EE for aeration [b]	€/year	72060	54084
OPEX: Sludge disposal [c]	€/year	13607	7884
OPEX: Aluminium Polychloride (PAC)[d]	€/year	10439	0

[a] Payback time = 25 years; [b] 4 kWh/kgO_2, 0.2 €/kWh; [c] 400 €/kg$TS_{disposed}$; [d] €/tonAl 5500

In the specific case of Carbonera, even major net incomes are expected because the SCENA system will be realized by revamping the existing structures. The full scale plant is under construction and will be fully operating by the end of 2014. Future evaluations will incorporate sustainability considerations (i.e. LCA, usability of the removed phosphorus).

CONCLUSIONS

Nitritation/denitritation and via nitrite enhanced phosphorus removal from anaerobic digested supernatant were obtained in pilot scale by the in situ recovering of best available carbon source. Removal rates of 15±2 mgN-$NH_{4oxidized}$/gMLVSS·h; 40±10 mgN-$NO_{2reduced}$/ gMLVSS·h; 10±3 mgP-$PO_{4bioaccumulated}$/ gMLVSS·h were observed and annual net income of 30-40 k€/year were estimated for a municipal WWTP with actual treatment capacity of 50 000 PE.

ACKOWLEDMENTS
The authors thank Alto Trevigiano Servizi Srl for funding and technical assistance.

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(I3) Water and wastewater treatment in hot and cold climate: open issues and possible solutions

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During its work Simem experienced different climate and work conditions.

Typical problems of hot climate, like India, Bangladesh and Brazil, are the hot temperature and in some case the high quantity of humidity in the air. The most sensitive parts are blowers and electrical panels, and during the design and implementation special attention should be given to the cooling system of the machines and of the rooms, and ventilation of the control panels, in order to avoid overheating and corrosion.

In some case the problem is solar radiation and the dust; particular attention should be given to the choice of material, especially the rubbers, and to the choice of protection against dust and rain.

In cold climate, like Russia, typically plants are realized indoor, but in some case we had to realized a plant outdoor. Our experience shows that an outdoor biological plant works without problems also during the winter, with – 30 °C. For the pipelines we used thermal insulation material and heating cables. In order to avoid problems of cooling of the water in the clarifier, we realized an equalization tank, which feed the system during 24h, and a lamella clarifier instead of a circular clarifier. The water velocity and the continuous flow allows the system to work smoothly and to prevent freezing.

Keywords
Wastewater treatment, cold and hot climate, technical problems and solutions

(I4) High-Rate Sieve Microfiltration as Primary Treatment Process for Municipal Wastewater Treatment

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Abstract

In this paper, we examine how high-rate sieve microfiltration can be successfully applied instead of primary sedimentation and easily integrated in a wastewater treatment plant in order to enhance TSS removal while protecting downstream treatment processes from fluctuations in TSS concentration and overloading. Batch and continuous flow filtration experiments were carried out at the City of London Wastewater Treatment Plant (Pottersburg, London Ontario, Canada) using wastewater collected from different locations across the WTP (i.e., untreated sewage and primary influent). Different sieve sizes ranging from 54 um to 350 um were tested on each wastewater stream in triplicate, and, for each testing point, TSS microfiltration performance and hydraulic throughput of the filter were quantified via column experiments. In both cases, very promising results were obtained indicating that good hydraulic throughput and TSS removal (≈40-50%) could be simultaneously achieved using sieve sizes < 300 microns, without pre-treating the wastewater. Moreover, it was found that, unlike primary sedimentation, sieve microfiltration behaves as an extremely robust process against variation in TSS concentration and flowrate, making this process ideal for WTP with downstream biological treatment processes sensitive to TSS concentration such as trickling filters and membrane bioreactors.

Keywords

TSS removal, sieve microfiltration, primary treatment, wastewater

Introduction

High-rate sieve microfiltration promoted by plastic or metal microscreens is not uncommon in wastewater treatment, and applications include primary and tertiary treatment, as well as treatment of combined sewer overflows (Ljunggren, 2006). Although operating in a similar filtration regime (e.g., microfiltration), microscreens should not be confused with the membranes which are much smaller pore sizes and, consequently, can accommodate a reduced hydraulic loading. In Europe and, specifically, in Norway, the use of moving belt microfiltration (commercially available as Salsnes filters, http://www.salsnes-filter.no/) is well established (Rusten and Lundar, 2006), and numerous applications are reported to operate successfully and uninterruptedly both as a primary separation process before biological treatment or as the only treatment before ocean discharge.

Given the small footprint and the robust performance displayed by this technology, the use of high-rate sieve microfiltration has expanded in other Countries including North America, China and Latin America. With these regional applications operating on drastically different wastewater qualities, new challenges and opportunity for process optimization and scale up are emerging, which must be address through rigorous testing and experimentation.

Material and Methods

In this paper, we test high-rate sieve microfiltration performance using different wastewater qualities (untreated sewage, de-gritted wastewater or influent to the primary clarifier and primary effluent or influent to the activated sludge process) and sieve sizes, in order to understand the interplay between TSS size fractions and filter media. Two types of experiments were carried out. First, a static filtration experiment was conducted, in which the wastewater was fractionated in subclasses of TSS to gain insight into TSS size distribution. Secondly, the same wastewater was subjected to a dynamic filtration experiment in a column filtration apparatus (Fig. 1) in order to evaluate whether the role of thin-cake formation or shear forces on filtration removal efficiency. At time=0, the valve underneath the filter holder is suddenly opened and the filtration process starts. An electronic scale positioned below the filter is used to measure the hydraulic throughput of the filter as a function of time. Using the set of equations available in the literature (Tien, 2012) to describe thin-cake filtration process, it is possible to convolve the time-dependent hydraulic and the TSS removal curves to ultimately obtain the expected removal performance under full scale operation.

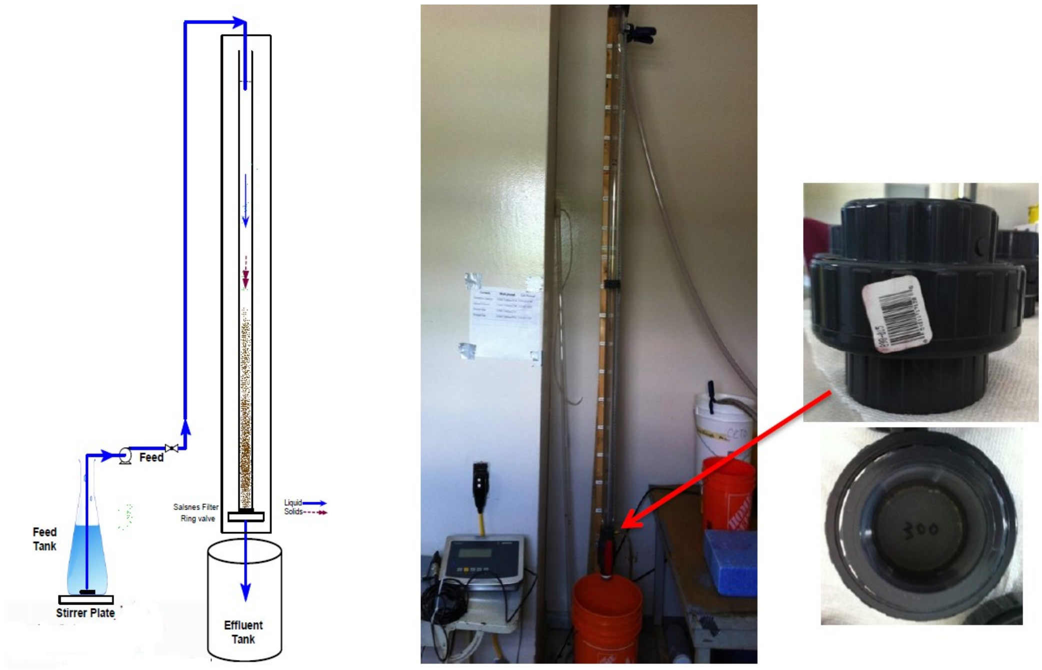

Figure 13 – Column filtration apparatus used during high-rate sieve microfiltration

Results and Conclusions

A subset of column test results is shown in Figure 2. The Y-axis represents the filtrate volume (L) while the X-axis is the time (sec). The blue, horizontal line shows the amount of volume initially loaded in the column (2L), while the red line underneath indicates the 1L mark. By modeling the observed data using the appropriate filtration governing equation of a variable-flow, variable-pressure filtration experiment, it is possible to estimate a number of key variables for accurate sizing such as the relative contribution to hydraulic and TSS removal performance of the two distinct filtration regimes (i.e., drainage and thin-cake filtration regimes), the instantaneous flow distribution, and the impact of important operating variables such as sieve speed and submerged filter area.

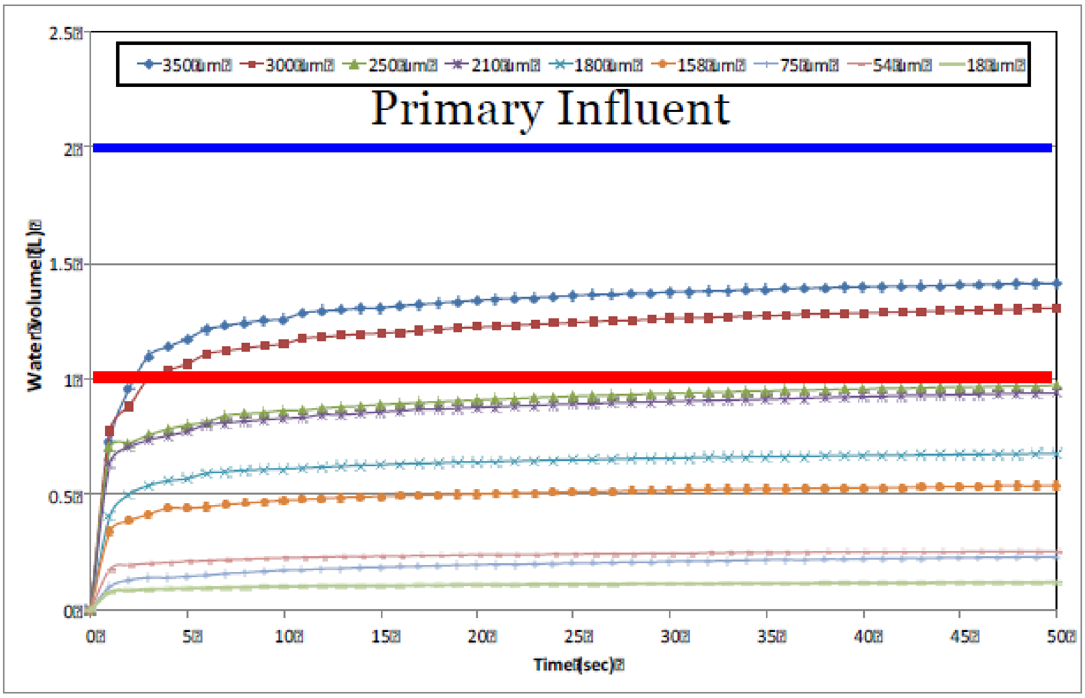

Figure 14 Dynamic response obtained during column experiments conducted with different sieve sizes.

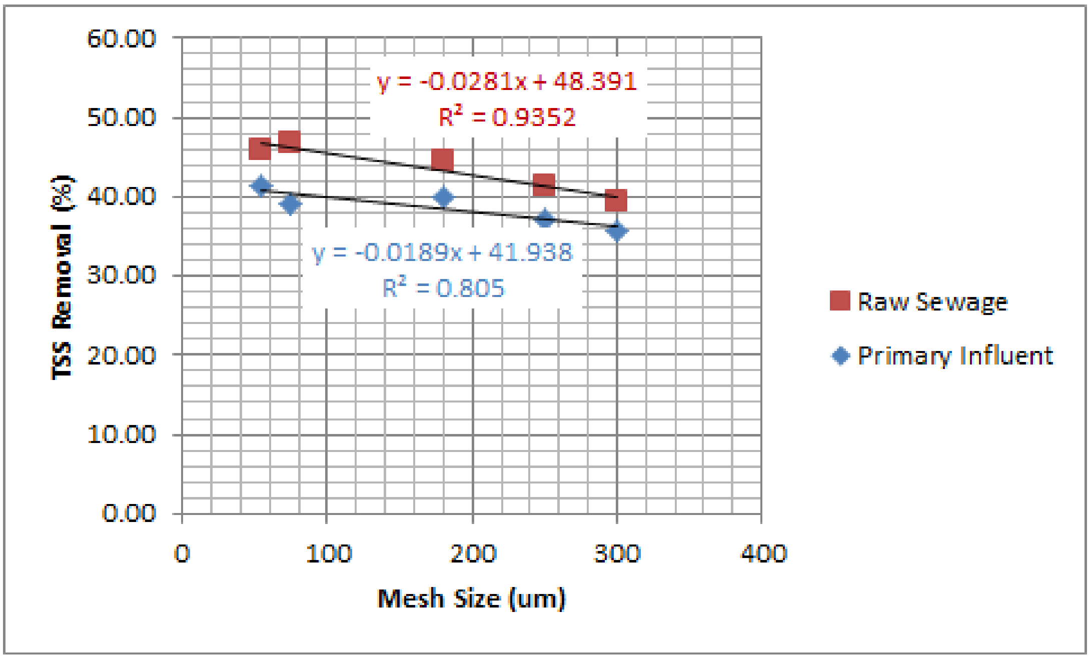

Figure 15 Observed TSS removal for raw sewage (red) and primary influent (blue)

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Modelling and Process Integration

(Wedneday, 25 June 2014, Aula T2, Polo Zanotto)

(K9) Wastewater modelling and population living style

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Abstract

The paper aims to improve an available influent model for creating input files to dynamic WWTP simulators, taking into account a larger set of pollution descriptors (major ions such as calcium, etc, micropollutants such as heavy metals), and information on the population living style (presence in the catchment depending upon the activity and age).

Keywords

Living style; metals; micropollutants; modelling; population structure

INTRODUCTION

The ambitious goals set up by Jeppsson et al. (2013) for future developments of the Benchmark Simulation Model 2 platform require to refine the influent model presently available. Two keys issues can be distinguished:

- Ability to calculate pH all over the WWTP, which requires information on phosphorus but also on major cations and anions which participate to the ionic balance. Furthermore calcium and magnesium are involved in phosphorus fate in the anaerobic digester
- Ability to take into account catchment population living style changes: reduction of potable water consumption, greywater and rainwater reuse, implementation of grinder sink, etc.

To these issues should be added the ability to describe the fate of micropollutants (heavy metals, household chemicals, personal care products, pharmaceuticals, etc) and to be adaptable to catchments of different size and location (temperature, rainfall).

Municipal wastewater treatment plants (WWTP) are usually designed based on an average load calculated from the number of inhabitants in the catchment and the assumed per capita pollution load. However, these loads are not generated homogenously during the day, the week or the year. In general, a diurnal pattern is assumed (De Keyser et al. 2010; Gernaey et al., 2011), with morning and evening peaks and minimal loads at night and midday, which can be modelled by combining periodic functions (Bechmann et al., 1999). The main assumption is that the peaks correspond to the activities of inhabitants going to or returning from work. Different patterns have been observed in Japan (Kim et al., 2009). A sharp morning peak is noted for all variables (flow, suspended solids, chemical oxygen demand (COD) and nitrogen). However, additional clear maxima are observed at mid-day and in the evening for the flow, in the evening for the suspended solids, and at midday for the nitrogen species. Indicator bacteria (coliforms and *E. coli*) exhibit a discharge pattern similar to that of nitrogen species. Across Europe, the timing, the importance and the composition of meals (breakfast, lunch and dinner) differ between countries (de Castro, 2004). Furthermore, modern household appliances, such as dish or laundry washing machines, can be timed without human activation. A diurnal model has been also suggested by Ort and Gujer (2008) in their modeling of the adsorption of some micropollutants (carbamazepine, diclofenac and tonalide) in sewers. A set of 50 patterns at different time-scales was designed by de Keyser et al. (2010) to describe the release of pollutants in urban areas. I

Information on the population structure and lifestyle would certainly help to improve these models. Such an approach has been considered in investigating residential heating consumption (de Meester et al., 2013) but not, to the best of our knowledge, for wastewater production. Based on a database of pollution dynamic profiles collected for different catchments, proposals to adapt the Gernaey et al.'s model (2011) can be made.

MATERIALS AND METHODS

Several catchments have been monitored, for one day to a week, at the rate of one sample per hour, as much as possible by dry weather:

- Villages close to large urban centres (with pollution discharged to different WWTPs)
- Villages included in a large urban area (mixed or separated sewage network, industrial and commercial areas)
- Residential areas with or without an hospital
- Large and medium size urban areas

Classical parameters (pH, conductivity, COD, SS, nitrogen species) have been measured as well as major anions and cations. Heavy metals, some household substances and pharmaceuticals have been also monitored for some samplings.

Details on the population structure and way of life have been extracted from national statistical database (age distribution, home-work and home-school travels, etc).

SOME RESULTS

Figure 1 illustrates some of the experimental results comparing the discharge of classical pollution (nitrogen, COD) and the discharge of heavy metals in a catchment. A diurnal pattern is observed for most metals. In general such a pattern is also observed for potassium (highly linked to human metabolism) but not for calcium and magnesium: for them (and whatever the catchment under study) the maximal concentrations are often observed during the night, probably because of infiltrations.

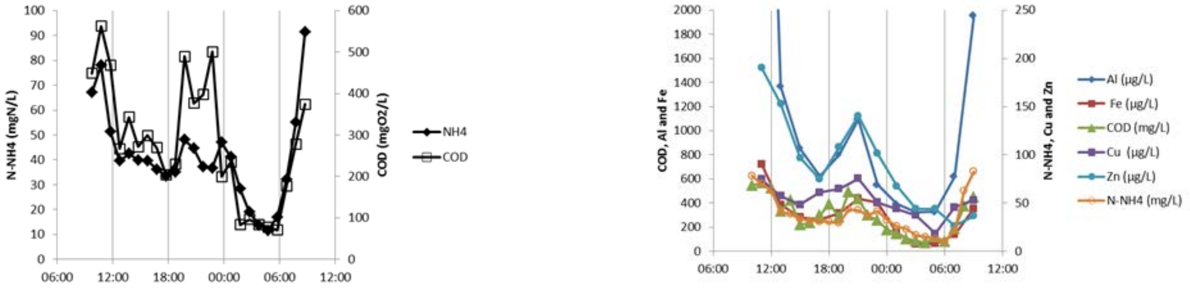

Figure 1: Example of diurnal pattern for some classical pollution parameters and heavy metals

Figure 2 illustrates the change in the number of inhabitants for two catchments during the day. Ludres has a large industrial and commercial zone and a large increase of the population is seen during the day. In Fléville, which has a small industrial zone, the number of inhabitants is constant. But in purely residential urban areas or villages, the number of inhabitants decreases during the week day and is constant during weekends, inducing large pollution loads during the week ends than during the week days.

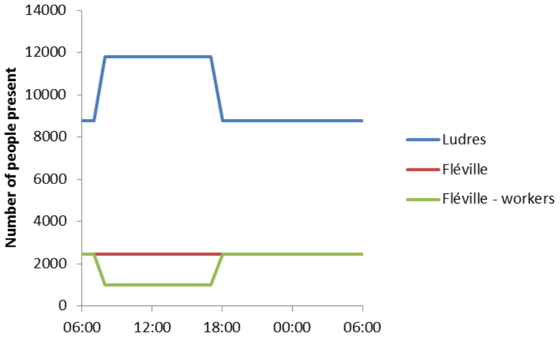

Figure 2: Number of people present as a function of the time of the day for two catchments

The comparison of the diurnal flowrate pattern for household in Gernaey's et al (2011) model and an experimental flowrate pattern in a catchment where the number of people increases during the day, show the effect of the lunchtime. Therefore instead of using a diurnal pattern with two strong peaks (morning and evening) we prefer to use a smoother flowrate (and pollution) diurnal pattern and combine it with new patterns describing the number of people (adults/children, working/non-working adults, etc) present in the catchment

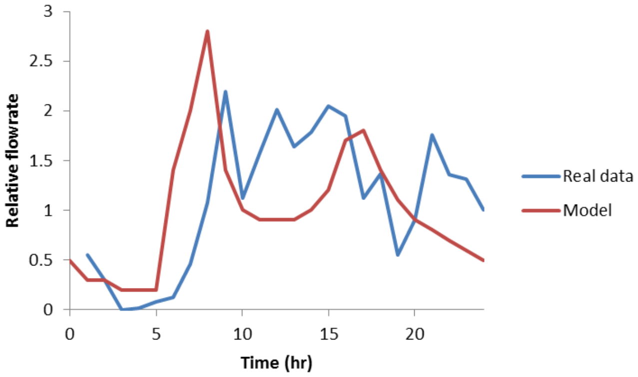

Figure 3: Comparison of wastewater flowrate profile

ACKNOWLEDGEMENT

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(P43) Model-based observers for monitoring of biological nitrification of urine in decentralized treatment

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Abstract

Biological nitrification is considered a vital step to enabledecentralized treatment of source-separated urine. However, rapid changes in the load to this process are known to result in rapid build-up of nitrite,which can destabilize the process. A further complication is that no direct, online measurements of nitrite are available. It is for this reason that model-based observers are tested as soft-sensors for online nitrite estimation.

Keywords
Decentralized wastewater treatment; Extended Kalman Filter; nitrification; nitrite; soft sensor; Unscented Kalman Filter.

INTRODUCTION

Nitrification is an aerobic process by which ammonium is biologically oxidized to nitrate in two steps: from ammonium to nitrite by the ammonia oxidizing bacteria (AOB) and from nitrite to nitrate by the nitrite oxidizing bacteria (NOB). Biological nitrification is often part of conventionalwastewater treatment plants.More recently, biological nitrification has been proposed to stabilize decentralized treatment of source-separated urine (Udert and Lienert 2013). The resulting nitrified urine can further be distilled to produce a nitrogen fertilizer and the complete process is geared to urbanenvironments in emerging and developing countries (Udert and Wächter 2012). Under normal circumstances, the AOB are substrate limited as soon as about 50% of the ammonia has been nitrified and the alkalinity in the wastewater is consumed. While this is achievable under stable influent conditions, increases in the ammonia load to the urine nitrification process can result in a rapid accumulation of nitrite. Such accumulation leads to inhibition of NOB, further slowing down the second nitrification step until stopped entirely, with possible complete loss of NOB biomass. Therefore, knowing the nitrite concentration is key to long-term operation under load-changing conditions. However, among today's many online sensors, there is yet none that can measure nitrite continuously and reliably in municipal wastewaters. Moreover, current expectations are that nitrite-nitrogen concentrations can rise up to 200 mgNO_3-N/l in the reactor, which is higher than the range for typical ISE sensors for ammonia and nitrate. The offline method that is currently employed by practitioners, i.e. nitrite strips or sampling, necessitates manpower.A reaction time in the order of hours, possibly days, is required to implement an appropriate action and prevent the reactor from failing, thereby excluding such offline analysis for this purpose.

On the other hand, some key variables such as nitrate nitrogen concentration and pH can be measured reliably today, and others are likely to exist within the near future (ammonium nitrogen concentration). These signals are considered to contain indirect information about the nitrite concentration. For this reason, soft sensing is a promising approach to obtain a reliable, online estimation of the nitrite concentration. Soft sensors denote a subset of observers, which are used to estimate unmeasured quantities by utilizing information from additional process parametersand existing measurements. Typical applications for soft sensors include process monitoring and control(Vargas *et al.* 2000)as well as fault detection and identification(Prakash*et al.*2005, Villez *et al.*2013). In this contribution, we demonstrate the potential of observers for nitrite estimation in the absence of a direct measurement. Our ultimate goal is to test the developed soft-sensorsin a real case scenario with an operational reactor and with a set of online sensors (Udert and Wächter 2012, Hug *et al.* 2013).

MATERIALS AND METHODS

In this paper, we use a very simplified version of a model describing a nitrification reactor (Hug *et al.* 2013) in order to test and demonstrate the selected observers.Here, we assume that the system is defined by the three state variables: S_{NH3}ammonia concentration, S_{HNO2}nitrite concentration, and S_{NO3}nitrate concentration, and the two processes: growth of AOB, and growth of NOB. Furthermore, it is assumed that the oxygen concentration, the volume of the reactor and the biomass activity are kept perfectly constant. The nitrifying reactor is modeled as a system of three ordinary differential equations expressing the rate of change in the concentrations of ammonia, nitrite and nitrate:

$$\frac{dS_{NH3}}{dt} = -\frac{S_{NH3}}{K_{NH3} + S_{NH3}} \times \frac{I_{HNO2,AOB}}{S_{HNO2} + I_{HNO2,AOB}} \times A_{AOB} \tag{1}$$

$$\frac{dS_{HNO2}}{dt} = \frac{S_{NH3}}{K_{NH3} + S_{NH3}} \times \frac{I_{HNO2,AOB}}{S_{HNO2} + I_{HNO2AOB}} \times A_{AOB} - \frac{S_{HNO2}}{K_{HNO2} + S_{HNO2} + \frac{S_{HNO2}^2}{I_{HNO2,NOB}}} \times A_{NOB} \tag{2}$$

$$\frac{dS_{NO3}}{dt} = \frac{S_{HNO2}}{K_{HNO2} + S_{HNO2} + \frac{S_{HNO2}^2}{I_{HNO2,NOB}}} \times A_{NOB} \tag{3}$$

where K_{NH3} and K_{HNO2} denote the affinity constants for NH_3 and HNO_2, respectively, $I_{HNO2,AOB}$and $I_{HNO2,NOB}$denote the non-competitive inhibition constants for HNO_2 for AOB and NOB and A_{AOB} and A_{NOB} denote the biomass activities. The constants are given in Table 1. Note that A_{AOB} and A_{NOB} have been taken as averages of the values used in Hug *et al.* (2013).

Table 1. Kinetic constants for the microbial processes (Hug *et al.* 2013).

Constant	Value	Unit	Constant	Value	Unit
K_{NH3}	0.50	mg NH_3-N/l	$I_{HNO2,NOB}$	0.06	mg HNO_2-N/l
K_{HNO2}	0.0004	mg HNO_2-N/l	A_{AOB}	57	mg COD/(l·day)
$I_{HNO2,AOB}$	1.61	mg HNO_2-N/l	A_{NOB}	6.5	mg COD/(l·day)

The Kalman filter algorithm is used to find statistically optimal estimates of both measured and unmeasured variables that are described as internal states in a linear dynamic system (Welch and Bishop 2006). The Extended Kalman Filter (EKF) is the equivalent algorithm for nonlinear dynamic systems. The main disadvantages of using the EKF are the requirement of an explicit Jacobian for the linearizationand the possibility of algorithm divergence when the system is highly nonlinear (Julier *et al.* 2000). The Unscented Kalman Filter (UKF) was introduced as a different approach to nonlinear estimation, tackling the issues of the EKF and avoiding the need for linearization, resulting in a more accurate and easier implemented algorithm (Julier and Uhlmann2004). Among the several existing versions of the UKF, we chose the algorithm presented by Wan and van der Merwe (2001), howeverusing a continuous formulation of the state equation and a discrete measurement equation.

All equationswere implemented in Matlab. First, the system (1)-(3) was simulated from time 0 to 50 days, using the initial values

$$S_{NH3}(0) = 100, S_{HNO2}(0) = 0, S_{NO3}(0) = 0. \tag{4}$$

The simulated concentrations of ammonia and nitrate were considered to be measurements and given as input to the EKF and UKF, respectively, therein assuming that nitrite was not measured. For both EKF and UKF, the following values were used:

$$Q = \begin{pmatrix} 0.01 & 0 & 0 \\ 0 & 0.01 & 0 \\ 0 & 0 & 0.01 \end{pmatrix}, R = \begin{pmatrix} 10 & 0 \\ 0 & 0.2 \end{pmatrix}, P_0 = \begin{pmatrix} 150 & 0 & 0 \\ 0 & 150 & 0 \\ 0 & 0 & 150 \end{pmatrix} \tag{5}$$

$$\hat{S}_{NH3,0} = 150, \hat{S}_{HNO2,0} = 40, \hat{S}_{NO3,0} = 5 \tag{6}$$

where *Q* is the system noise covariance matrix, *R* the measurement noise covariance matrix,P_0 the initial error covariance and $\hat{S}_{NH3,0}$, $\hat{S}_{HNO2,0}$ and $\hat{S}_{NO3,0}$ are the initial guesses for the state variables. For this specific test case, we opted for a medium-large covariance in P_0 and a relatively small covariance in Q. The different values in R indicate that nitrate measurements can be trusted more than ammonia measurements, and is based on currently available real-life experience with such sensors. For the UKF, the following scaling parameters were used:

$$\alpha = 10^{-3}, \beta = 2, \kappa = -5, \quad (7)$$

where α is set to a small positive value, $\beta=2$ is optimal for Gaussian distributions, and $\kappa=3-L$,Ldenoting the length of the augmented state vector (Wan and van der Merwe 2001).The above simple tests are currently extended to test for (1) more complex models, including pH and oxygen dynamics and (2) conditions in which the simulated system model and the model observer are not necessarily the same.

PRELIMINARY RESULTS

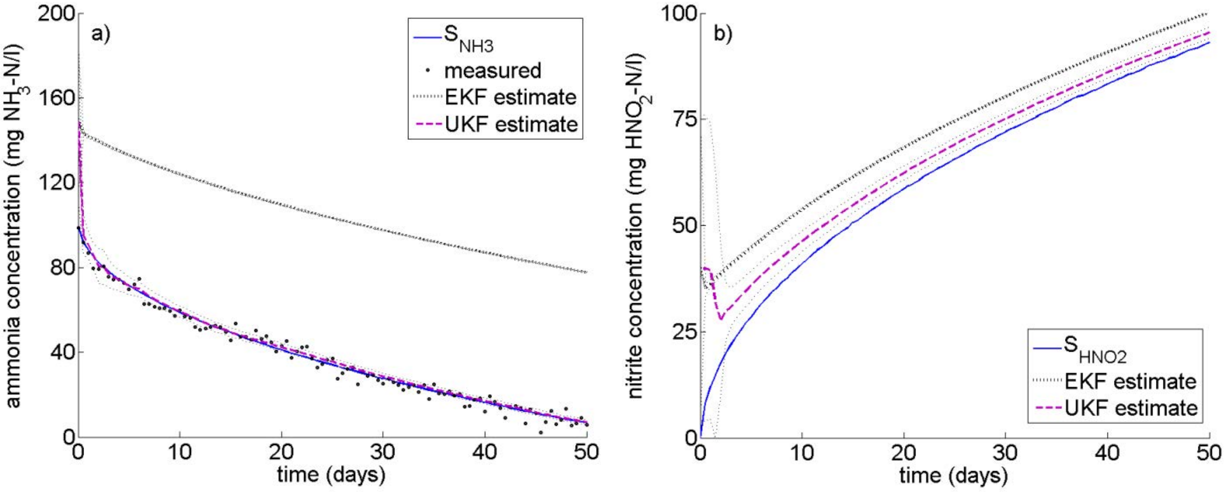

Figure 1. **a)** Ammonia concentration (solid, blue), measured ammonia (solid w. marker, dark red), EKF estimate of ammonia (dash-dot, dark gray), and UKF estimate of ammonia (dashed, magenta) as functions of time; **b)** nitrite concentration (solid, blue), EKF estimate of nitrite (dash-dot, dark gray), and UKF estimate of nitrite (dashed, magenta) as functions of time.

Both the EKF and UKF were tested on the same, simulated data. These data were obtained as discussed above. Most importantly, there is no direct measurement of nitrite concentration and the observers are set up to estimate its value. Figure 1a shows the internal state ammonia, the simulated measurement of ammonia and the estimates obtained with EKF and UKF, respectively. The estimates are also plotted with three standard deviations. In Figure 1b we see the internal state nitrite with the two estimates from EKF and UKF. The divergence of the EKF is most visible for ammonia, where the EKF-estimate never really estimates the state to a satisfying degree. The UKF on the other hand is able to track the states reliably, therefore showing a robustness against ill-defined prior means at time zero. Nitrite, as an unmeasured state, is estimated better with the UKF than with the EKF, i.e. the estimate obtained with the UKF converges faster and is closer to the true values.

CONCLUSIONS AND PERSPECTIVES

The EKF and UKF algorithms were both successfully implemented and applied to a simulated test case, which describes a simplified nitrification reactor. Under the assumption that nitrite, one of the three state variables, was unmeasured, and using the same initial data for both algorithms, the UKF performed better than the EKF. The UKF results in a reasonable estimate of the nitrite concentration, despite ill-defined initial guesses. Furthermore, the EKF lacks robustness to ill-guessing of initial states. The UKF, on the other hand, requires tuning of the scaling parameters, which is not yet completed.

As future work, we will test the same simplified observer model, as described in this paper, with a more complex simulated system as well as with full-scale data obtained from an operating reactor. Additionally, we will include pH and oxygen in the observer model if that is necessary to obtain reliable estimates. Moreover, we envision e.g. an evaluation of the effect of the model simplification, comparison of different sensor sets and evaluation of the importance of an online ammonia sensor.

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(P44) Plant-Wide Model simulations for studying phosphorous recovery and energy costs in WWTPs

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Abstract

This abstract presents the usefulness of mathematical models and simulation tools to describe the dynamic behaviour of advanced wastewater treatment plants taking into account technical, environmental, energetic and economical aspects. The main objective of this work is to build and validate a mathematical model based on the Plant Wide Modelling (PWM) methodology able to assess phosphorous recovery and energetic aspects. A real WWTP is selected for the validation of the model. Additionally, a comparison based on simulations of different operational strategies will be carried out in order optimise the operational strategies to maximise phosphorous recovery and minimise energetic costs.

Keywords

Energetic analysis; Mathematical modelling; Nutrient recovery; Plant wide modelling

INTRODUCTION

In the last decades, mathematical models and simulations tools have been proven to be very valuable tools for several goals such as design, diagnosis and elaboration of optimised management strategies. Since the publication of the ASM1 model in the 1980s (Henze *et al.,*1987) mathematical models have become very prominent and in this sense different works have been published: ASMs, ADM1, RWQM1, BNRM. The focus in these models has been the description of biological processes, always very specific for the system under study. However, nowadays there are more restrictive limitations in effluent quality, there is a general concern about the scarcity of some natural resources or there exist attempts to operate processes in a sustainable and environmental-friendly way reducing energy consumption and minimizing greenhouse gas emissions. The concern of scarcity of natural resources has pushed, for example, the development of different techniques for phosphorous recovery, since some studies suggest that half of the current economically viable phosphorus reserves will be consumed for the years 2060-2070 (Steen, 1998; Driver *et al.,* 1999). The work of Shu *et al*. (2006) shows that phosphorous recovery as struvite by means of precipitation processes is technically feasible and economically beneficial (Pastor *et al* 2007). Therefore, the development of models able to describe precipitation-redissolution of minerals is of high importance. Additionally, the current economic situation has led to an increasing awareness of the importance of energy recovery. A survey of the US Environmental Protection Agency indicates that an estimated 3% of USA energy consumption is used for drinking water and wastewater services, in Sweden and in the UK, the corresponding numbers are, respectively, 1% and 3%, while in Israel it is around 10% (Olsson, 2011). Under this frame, it is essential that the models developed in this context consider aspects that have been neglected or not solved by models up to date.

In order to achieve these premises, new and innovative combinations of emerging and conventional technologies and configurations in WWTPs can offer sustainable solutions for obtaining the required effluent quality and, simultaneously, optimising the recovery of valuable by-products and energy. The complexity of these configurations and processes with recirculations and interrelations among the different units makes it necessary to consider a plant-wide perspective in order to establish an optimum solution for the design or operation of the entire plant (Copp *et al.,* 2003; Grau *et al.* 2007; Jeppsson *et al.,* 2007). Thus, one of the challenges the scientific community should face in coming years is to develop methodologies and guidelines to construct models in a systematic and rigorous way, which are able to describe new and complex technologies, include energy balances, cost functions and recovery systems and describe global WWTPs in which the different treatments should be considered as a whole and not as individual units.

In this context, the work proposed by Fernández-Arévalo *et al.* (2012) upgrades the Plant-Wide Modelling methodology to accomplish the requirements mentioned above and proposes the CEIT models library which gathers all information needed for model construction. The main objective of this paper is to build a mathematical model based on the CEIT models library which will be validated using a real wastewater treatment plant. Additionally, an exploration by simulation will be undertaken, which will consist in checking the possibility of upgrading the plant under study, in order to include phosphorous recovery techniques maintaining minimum energetic consumption.

CEIT MODELS LIBRARY OF DYNAMIC MATHEMATICAL MODELS

The mathematical model presented in this abstract has been constructed using the CEIT models library (Figure 1) proposed by Fernández-Arévalo *et al.* (2012).

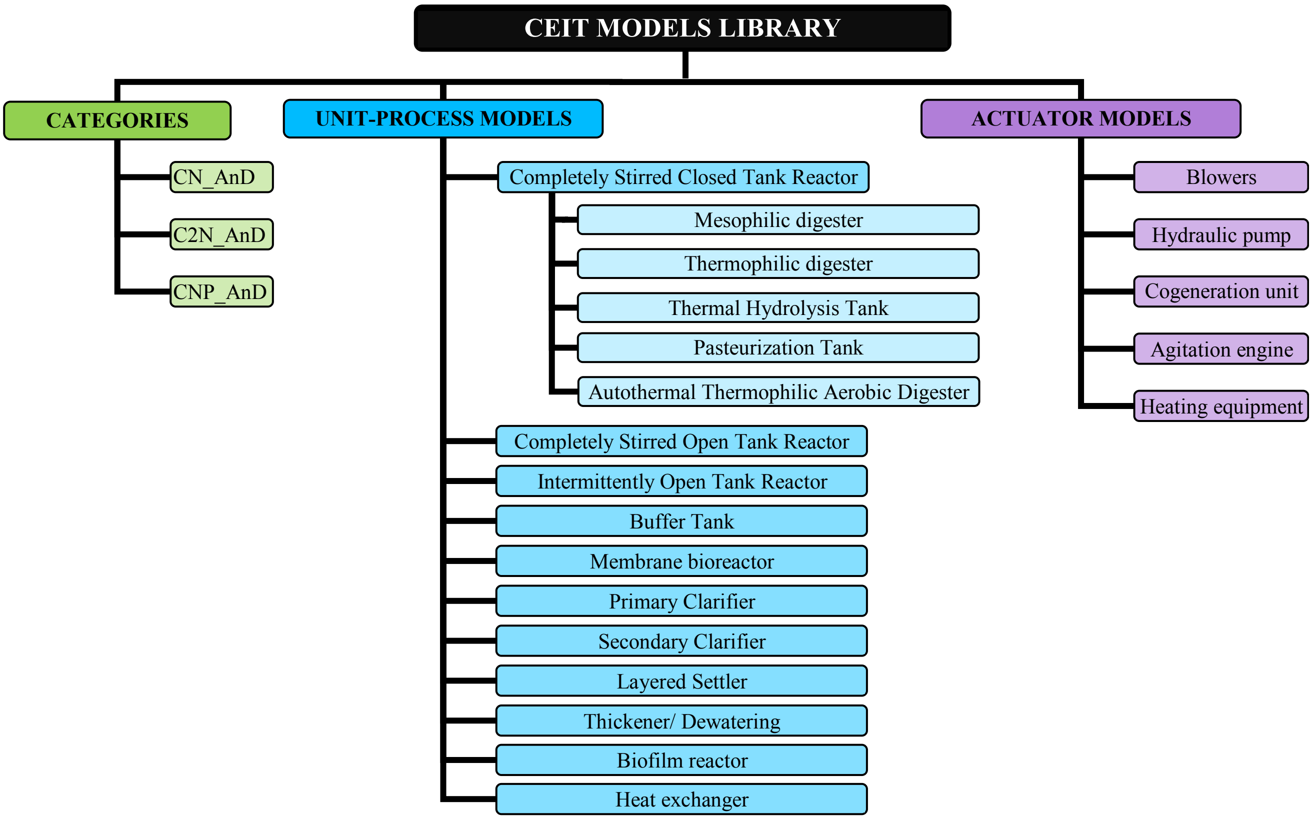

Figure 1. Schematic representation of the CEIT models library of dynamic mathematical models.

The library´s models are based on the Extended Plant-Wide Model (E-PWM) methodology (Grau *et al.*, 2007; Fernández-Arévalo *et al.*, 2013) that allows the construction of dynamic mathematical models in a systematic and rigorous way, ensuring the total elemental mass, charge and energy continuity and facilitating further connections among different unit process models. The fundamentals of this methodology make it a suitable tool to construct compatible and directly connectable mathematical models so as to analyse the WWTPs as a whole. The library compiles information arranged by different aspect to be considered in the construction of the model, so that the modeller can select the ones that are interesting for the case under study following these three steps: (i) selection of the category, the library contains different categories which compile the model required for the representation of biochemical, chemical and physic-chemical reactions; (ii) selection of the Unit Process models, where the mass and heat transports are defined depending on the phases considered in the unit processes under study and (iii) selection of the actuators models required in the costs estimation. In the following paragraphs the details for the model constructed for this paper are presented.

Category selection

The selection of the category has to ensure the right description of the biochemical, chemical and physic-chemical reactions that may take place throughout the plant. The biochemical reactions considered in the model constructed in this paper are those necessary to describe biological organic matter and phosphorous removal under different environmental conditions. The chemical transformations considered in this model are the weak acid-base and complex ion-pairing equilibrium reactions between VFAs, inorganic carbon, nitrogen, phosphorous, calcium, magnesium and potassium. Finally, two types of physic-chemical transformations are considered: (1) liquid-gas transfer, regulated by gaseous partial pressure according to Henry's law of dissolution; and (2) the precipitation-redissolution equilibrium. The sparingly soluble salts considered in this model are: $Ca_3(PO_4)_2$, $CaCO_3$, $MgCO_3$, $MgNH_4PO_4$, KNH_4PO_4, $MgHPO_4$ and $FePO_4$ for which the reaction rate is regulated by the development of supersaturation.

Mass and heat transports definition for a multi-phase reactor

Traditionally, in the ASM models, since only water media is considered, the state-vector (M) involves all state-variables in water phase and analogously, the Petersen matrix (E) and the kinetic vector (ρ) involve all the transformations considered in the model. Taking into account that in current technologies more than one phase can be considered in a single unit-process, the equations required to models definition are multiplying. With the purpose to develop flexible and easily understood models, the E-PWM methodology proposes a phase-based modelling approach (Fernández-Arévalo *et al.,* 2013), selecting first phases present in the system and afterwards the transformations happening in each phase. Each phase (aqueous, gaseous or solid) as an independent system with its corresponding mass vector (M) will be considered. Accordingly, each phase will have an independent matrix ($\tilde{\bar{E}}\cdot\bar{\rho}$) to define the transformations that take place in the phase (such as, for example, bacterial growth, or chemical equilibria reactions in the aqueous phase) and another set of matrices ($\tilde{\bar{E}}\cdot\bar{\rho}$) to define the transformations between different phases (such as evaporation/condensation, stripping/absorption, precipitation/dissolution or deposition/sublimation). This way of distinguishing the different phases allows the modeller to construct mathematical models as complex as required in a systematic and modular way.

For the model constructed in this paper, three phases are considered. (i) the water phase, which correspond to the volume of the mixed liquor; (ii) the gas-off phase, which represent the gaseous phase in contact with the free surface of the mixed liquor; and (iii) the solid phase, which is the phase representing the precipitates formed during the process. The representation of the restructuration of the model can be seen in the Figure 2. Each phase included in the model is considered as a completely stirred reactor and mass and heat balances are applied to each of the phases present in the model.

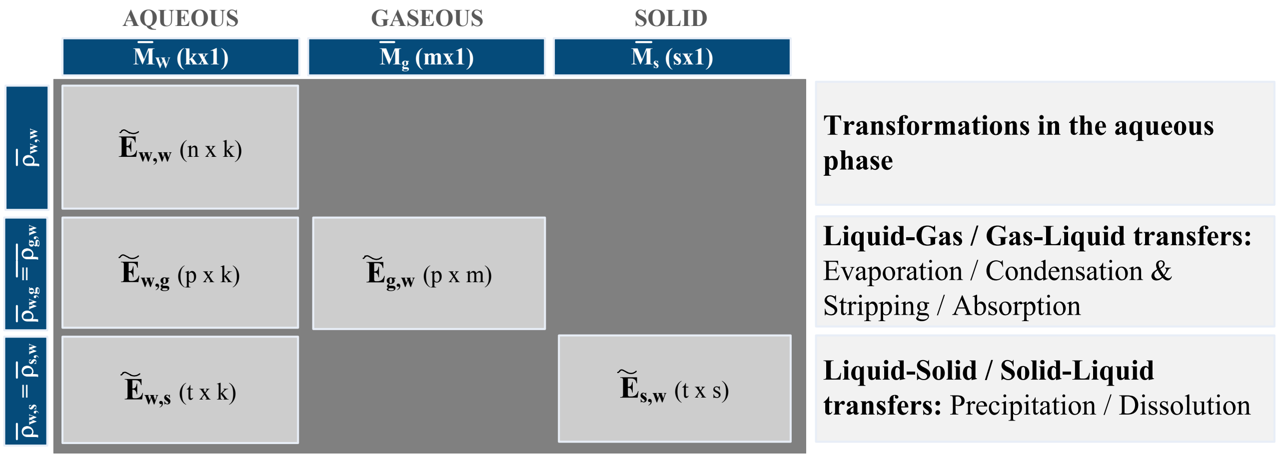

Figure 2. Schematic representation of the matrix restructuration

Actuators models

The actuator models may have a dual function; it can be used to estimate the energy costs of the system (such as pumps, blowers and agitation engines), and it can provide the calorific energy needed by the system expressed as an input of heat (cogeneration units, heating equipment, etc.).

CASE STUDY

The main objective of this case study is to check the capability of the model to optimize the configuration and the operation strategies of a WWTP in order to maximize the recovery of phosphorous. With this purpose a real WWTP has been selected as a case study, implementing its configuration in WEST (www.mikebydhi.com) simulation platform. Based on a full-scale case study, two alternative scenarios will be compared in terms of energetic and economic costs: (i) in the first scenario phosphorous is precipitated chemically in the water line and a phosphorous rich sludge is produced and (ii) in the second scenario, phosphorous is accumulated in the water line biologically by means of phosphorous accumulating organisms. In both cases, the phosphorous accumulated in the water line is released in the anaerobic digestion, obtaining a phosphorous and ammonia rich supernatant. This effluent is treated by a precipitation unit in which struvite is obtained as a final product.

CONCLUSIONS

A mathematical model based on the CEIT model library has been built and is presented in the abstract. The capability of the model will be demonstrated by reproducing a real wastewater treatment plant. Finally, a simulation study will be carried out to analyse the possibility of upgrading the plant under study for phosphorous recovery for minimum energetic costs.

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(P45) Modelling simultaneous anaerobic methane and ammonium removal in a granular sludge reactor

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Abstract

A mathematical model was applied to evaluate the influence of microbial kinetics of the process operation on the coexistence of nitrite dependent anaerobic methane oxidizing bacteria (N-DAMO) and anaerobic ammonium oxidizing bacteria (Anammox) in a single granule. Only if the influent contained the exact stoichiometric ratios at which both bacteria got enough nitrite, complete ammonium and methane removal could be realized. At high nitrogen biomass loadings N-DAMO lost the competition against Anammox bacteria. In addition, was the influence of granular size evaluated showing that a granules size of up to 0.75mm enabled a simultaneous ammonium and methane removal efficiency above 85%.

Keywords

Anammox, anaerobic methane oxidation, granular sludge, modelling, simulation

INTRODUCTION

During anaerobic digestion methane is formed which can be used for energy generation through cogeneration. However, some of the methane remains in a dissolved state in the effluent of the anaerobic digestion (reject water) and may escape into the atmosphere during downstream processing. Given the large global warming potential of methane, being about 25 CO_2 equivalents over a 100 year time horizon, even small quantities of methane emissions can largely affect the carbon footprint of a wastewater treatment plant (WWTP). Since reject water typically contains high ammonium concentrations and little or no organic carbon, Anammox-based system are often applied to remove nitrogen in an autotrophic way. To prevent greenhouse gas emissions, it would clearly be beneficial if dissolved methane could be biologically removed from the reject water at the same time as nitrogen. Recently a new bacterium (Candidatus *Methylomirabilis oxyfera*) was discovered capable of oxidizing methane with nitrite as electron and converting it to nitrogen gas and carbon dioxide (Ettwig *et al,* 2010). A combination of biological anaerobic methane oxidation (N-DAMO) and anaerobic ammonium oxidation (Anammox) could hence solve the methane emissions caused from reject water. Some early experiments have already been done, demonstrating the possible coexistence of both bacteria performing simultaneous removal of methane and ammonium (Leusken et al., 2011). Since both bacteria have a doubling time of more than ten days proper biomass retention is needed to handle large volumetric flows and loading capacities such as encountered in a WWTP (Ettwig *et al.*, 2010; Strous *et al.*, 1998). Granular sludge reactors are a type of biofilm reactors in which biomass is grown in the form of dense, fast-settling granules, resulting in compact systems which allows a high loading rate due to a large biofilm surface area in the reactor. Therefore, granules offer a good option for simultaneous growth of both N-DAMO and Anammox bacteria combine both slow growing bacteria in one granule. Due to the slow growth rates of the involved bacteria, experimental work aiming at process optimization can be very time consuming. Mathematical models have been shown earlier to be useful to optimize the performance of granular sludge reactors (Batstone *et al.*, 2004; De Kreuk *et al.,* 2007). In this study, a mathematical model is applied to evaluate the influence of process operation on the coexistence of anaerobic methane and ammonium oxidizing bacteria in a single granule.

GRANULAR SLUDGE REACTOR MODEL

A one-dimensional biofilm model was set up to describe growth and decay of anaerobic methane oxidizers (N-DAMO) and anaerobic ammonium oxidizers (Anammox) in a granular sludge reactor. The model was implemented in the Aquasim software. The reactor volume was considered to be fixed at 400 m^3. Spherical biomass particles (granules) are grown from an initial radius of 0.01 mm to a predefined steady state granule radius such that the reactor eventually contains 100 m^3 of particulate material, comprising both active biomass as well as inerts generated during endogenous respiration. The reactor behaviour has been simulated at a flow rate of 2500 $m^3 \cdot d^{-1}$ at a total nitrogen concentration of 1000 g $N.m^{-3}$ and 200 g $COD.m^{-3}$of methane, respectively. These values are based on typical values as measured in reject water (Bandara et al., 2011). Furthermore, it was assumed that the total nitrogen concentration fed into the system consisted of 430 g $N.m^{-3}$ of ammonium and 570 g $N.m^{-3}$ of nitrite, corresponding to stoichiometric-optimal nitrite:methane and nitrite:ammonium ratios for conversion with methane and ammonium, by N-DAMO and Anammox, respectively.

RESULTS AND DISCUSSION- Competition for nitrite and ammonium

N-DAMO bacteria mainly grew in inner part of the granules, which can be explained by their slower growth rate, whereas Anammox mainly grew in the outer part of the granule. The inner part of the granules was consisting of inerts (Figure 1). In the model different NO_2^-/totalN ratios (total N 1000mgN/m^3) were tested at a fixed COD concentration (200 gCOD/m^3) to study at which influent composition both bacteria could coexist. At lower ratios (ammonium in access) N-DAMO bacteria were out competed by Anammox bacteria. However, at ratios close to the stoichiometric equilibrium (NO_2, NH_4, CH_4) needed to completely remove methane and ammonium, N-DAMO bacteria could retain in the system. At high ratios Anammox bacteria got restricted by ammonium leading to an accumulation of nitrite in the bulk (Figure 2).

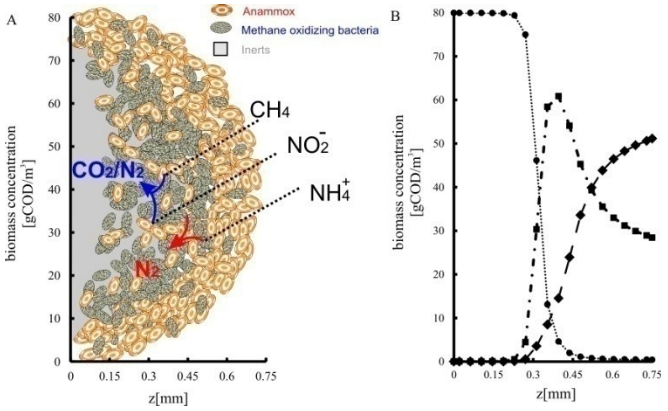

Figure 1. A) schematic view as well as B) modelling image of a distribution of (♦) Anammox and (■) N-DAMO bacteria as well as (●) inerts as a function of granular diameter.

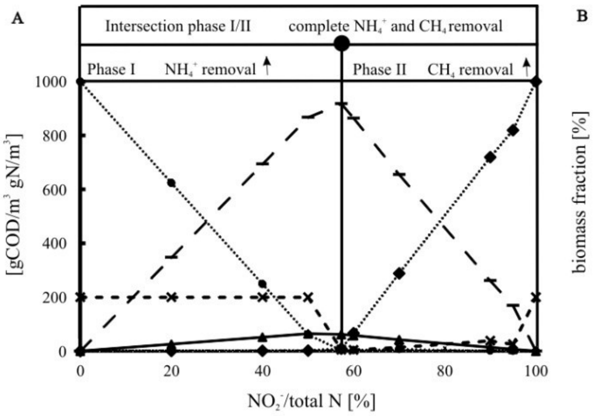

Figure 2. Reactor performance in terms of (●) ammonium, (x) methane, (▲) nitrate, (♦) nitrite, and (–) N_2 at different nitrite over nitrogen ratios.

Influence of volumetric biomass loading rate and granular size

For granule radius in a range of 0.1-0.75 mm both types of bacteria coexisted in approximately equal amounts leading to a simultaneous methane and ammonium removal above 85%. At higher granule sizes inerts increase due to substrate depletion in the inner core of the granule hence restricting microbial growth. In addition, N-DAMO bacteria decrease at higher granules radius due the lower diffusion coefficient of methane compared to ammonium. Bigger granules favoured Anammox bacteria whereas smaller granules enabled the coexistence of both bacteria in one granule (Figure 3). The effect of changing the total biomass volume on the bulk liquid concentrations as well as on the biomass fractions of both bacteria was evaluated based on media containing the stoichiometric ratios needed for a complete ammonium and methane removal (Figure 3). When only little biomass was in the reactor (biomass volume lower than 50m^3) Anammox dominated the system (Figure 3 phase I). At a biomass volume from 50m^3 until 100 m^3 both bacteria started to compete for substrate and space (no inerts). During this transition period

(50m^3 until 100 m^3) the removal efficiencies, which could be explained by ammonium and nitrite affinity constants (data not shown). From 100 m^3 on N-DAMO bacteria dominated the granule and the oscillation in bulk liquid concentrations stopped. When N-DAMO dominated the system (>100m^3) simultaneous ammonium and methane removal could be realized (Figure 3 phase II). The results showed that the volumetric biomass loading rate needs to be sufficiently low to allow simultaneous methane and ammonium removal.

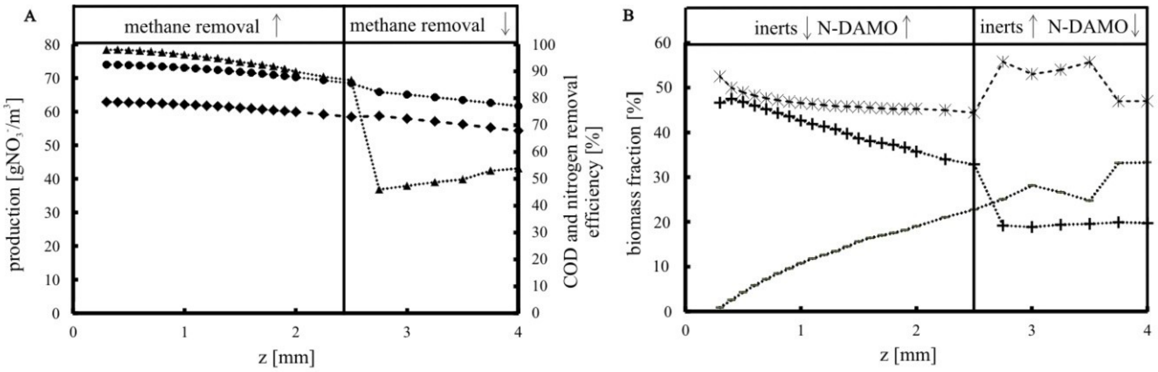

Figure 3. Influence of granule diameter on (A) reactor performance in terms of methane (▲) ammonium (●) removal efficiency and nitrate production (♦) as well as (B) biomass concentrations of Anammox (Ж), N-DAMO (+), and interts

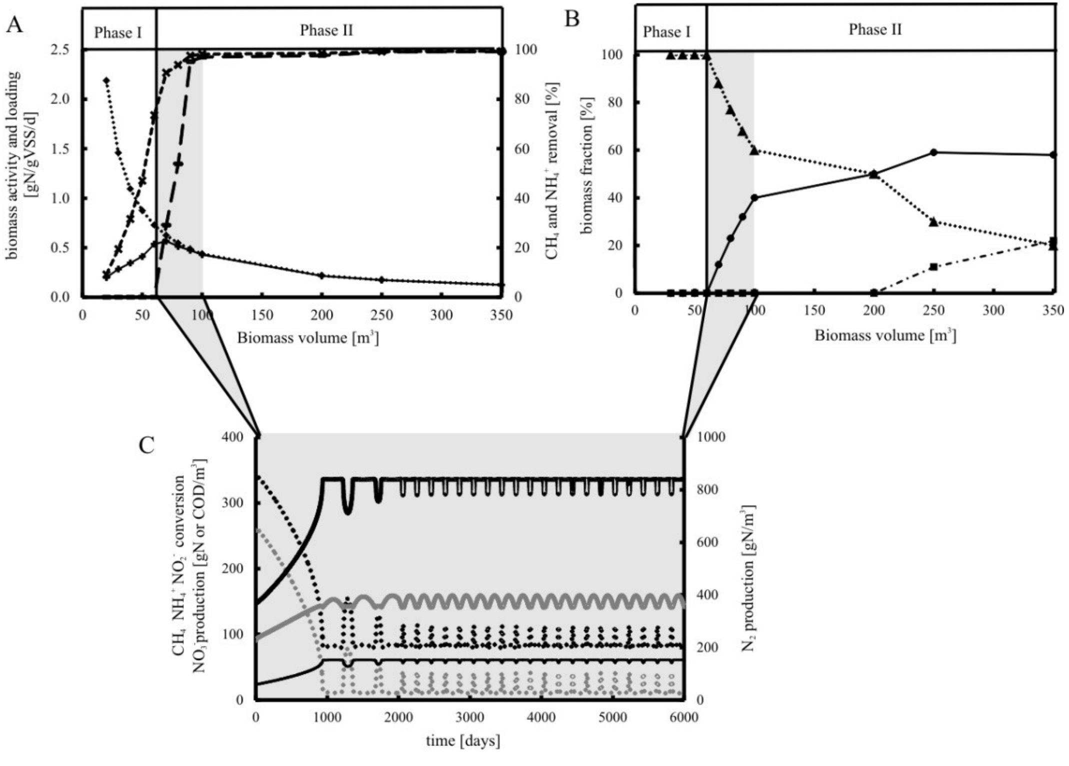

Figure 4. (A) Reactor performance of (♦) biomass loading, (+) biomass activity, (x) nitrogen removal efficiency, and (-) methane removal efficiency as well as (B) biomass profiles of (▲) Anammox bacteria, (●) N-DAMO bacteria, and (■) inerts at different biomass volume fractions in the reactor. The total volume of the reactor was considered to be 400 m^3. In phase I (A) no methane was removed and (B) no N-DAMO were present. In phase II (A) methane was removed (B) and N-DAMO grew in the system. (C) only in this period oscillations occurred.

CONCLUSIONS

- Simultaneous anaerobic methane and ammonium removal, through N-DAMO and Anammox bacteria respectively, was described for the first time through a mathematical model, which was subsequently applied to simulate these reactions in a granule sludge reactor.

- Bigger granules favoured Anammox bacteria whereas smaller granules enabled the coexistence of both bacteria in one granule
- The volumetric biomass loading rate needs to be sufficiently low to allow simultaneous methane and ammonium removal. At high loading rates, N-DAMO are outcompeted by Anammox bacteria.
- The stability of simultaneous anaerobic methane and ammonium removal is severely affected by the ammonium and nitrite affinity constants of N-DAMO and Anammox bacteria.

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Efficient Technologies - Design and Optimization

(Wedneday, 25 June 2014, Aula T2, Polo Zanotto)

(P46) Design of a Free Water Surface Constructed Wetland Based on a Novel Dynamic Model

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Abstract

The study of a well-controlled pilot-scale experiment with two parallel systems shallow basins of wetland free water surface, one planted with species Typha Latifolia and the other not planted, enabled the development of a dynamic mathematical model, following the ASM (Activated Sludge Model) framework. The pilot system was operated so as to achieve both organic matter removal and nitrogen removal. The key processes accounted for were ammonification, heterotrophic growth, nitrification, algal growth and plant transpiration. The predictive ability of the model is satisfactory, as tested with a free water surface constructed wetland of 400 population equivalent, with the sole modification being the inclusion of oxygen limitation in the nitrification process rate. The model was used for the full-scale design of a wetland system. The required inputs include the inflow rate Q_{in}, and the climatic data (temperature and rainfall rate Q_{rain}) for the design region. In addition the requirements of the effluent quality need to be specified. Then the required area and the level of vegetation are determined through the proposed step-by-step procedure. In the example case study presented, the imposed effluent quality was in average annual values (BOD_5=25mg/L and TN=15mg/L). A total wetland surface of 11ha is needed and if two sequential basins are used, the first with and the second without plants, then the total wetland surface would be reduced by approximately 27%, controlling only the maximum initial vegetation on the first wetland basin.

Keywords
Design; full-scale; free water surface; total nitrogen removal; constructed wetland surface area

INTRODUCTION

Assuming the limitation of total nitrogen removal is due to the plants, a reliable way in understanding the plant role is the performance of an experiment in a small pilot unit. The pilot unit was designed **[1]** to operate in two identical basins, one with plants (Typha Latifolia) and the other without plants. The vegetation coverage was sparse in the basin with plants, and aerobic conditions dominated within. The key processes which described completely the contaminant removal were: (i) Aerobic heterotrophic growth, consuming organics and ammonia; (ii) autotrophic growth (nitrification); (iii) ammonification of organic nitrogen (iv) algal growth consuming nitrate nitrogen (suspended algae "phytoplankton" in the basin with plants and "periphyta" at the bottom of the basin without plants) **[2]**.

The mathematical model assumed the above processes, following the approach of activated sludge models **[3]**. Given the model structure, the model parameters were determined in order to describe the behavior of both basins during one year operation of the pilot unit. The model validation was done using the data from the operation in a second year. The basin with plants had average annual removal efficiency 82% of the BOD_5 and 65% of the total nitrogen, respectively.

The model effectiveness was examined in a full scale unit of 400 population equivalent for the year 2008. The nitrification process appeared limited in virtue of the low concentrations of the dissolved oxygen (D.O.). This fact was attributed to the full vegetation coverage of that system **[4]**. The limitation was described by multiplying nitrification process rate by a factor ($S_O/K_{OA}+S_O$), where S_O is the dissolved oxygen concentration (average annual value was 1mg/L as measured) and K_{OA} the saturation constant for oxygen was taken as 0.7mg/L from the literature. This was the only required model modification.

WETLAND DESIGN

4000 population equivalent was assumed, giving an influent flow rate of Q_{in}=480000 [L/d]. An organic loading of 60 [g/(atom·d)] and a total nitrogen loading of 12 [g/(atom·d)] were assumed **[5]**. Then the influent organic concentration was 0.5 [gBOD$_5$/L], whereas the total nitrogen concentration was 0.1 [gN/L], of which 0.06 [gN/L] is ammonium nitrogen and 0.04 [gN/L] organic nitrogen, while the nitrate nitrogen was assumed to be zero.

The rainfall data were found in average monthly values in mm/d from the closest meteorological station (Rio Patras) for the years 2010, 2011 and 2012 and were fitted by a 3rd degree polynomial for Q_{rain} [L/(d·m^2)] with t in days, giving:

$$Q_{rain} = 1.512e-07 \cdot t^3 + 4.611e-05 \cdot t^2 - 0.033362 \cdot t + 4.2115 \qquad \{1\}$$

In accordance with the pilot-scale data, the model was modified in order to predict i) the mass increase of the plants m_p [g_plants] and ii) the water absorption by the plants Q_{plants} [L/d]. The mass increase rate of the plants (dm_p/dt) is correlated with nitrogen take up with water by the plants. An average annual experimental percentage of nitrogen 1.33% [gN/g_dry_plants] is assumed compared with 1.37% **[6]**. The plant growth is described by equation {2}, where t [days] is the time, C_N [mgN/L] is the total nitrogen concentration and b [g_plants/mgN] is the yield of plant mass per total nitrogen taken up:

$$\frac{dm_P}{dt} = b \cdot Q_{plants} \cdot C_N \qquad \{2\}$$

The water absorption rate Q_{plants} is given as the evapotranspiration plant rate and depends on the air temperature T_a [ºC] of the design region, but also on the plant mass, according to equation {3}, where θ_p is a dimensionless temperature coefficient and a [L/(g_plants·d)] is a constant (reference of the absorbed water amount per plant mass at 10 ºC):

$$Q_{plants} = a \cdot \theta_P^{(T_a-10)} \cdot m_P \qquad \{3\}$$

For the region ambient temperature data were received for the average monthly values for the years 2010, 2011 and 2012 from the same meteorological station. Their average monthly terms were determined in order to give a 3rd degree polynomial T_a at [ºC] for time t [days], according to equation {4}, which was used in equation {3}:

$$T_a = -2.1618e-06 \cdot t^3 + 0.00067924 \cdot t^2 + 0.032439 \cdot t + 8.8246 \qquad \{4\}$$

Furthermore, the model application requires an estimate of the water temperature T_{water} [ºC] of the wetland. This was done through the equation {5}, resulting from a steady state energy balance, where f is the transport coefficient with a typical value of 0.5 [m/d], A_P [m^2] is the basin surface of the wetland and Q_{in} is given [m^3/d] **[7]**:

$$(T_i - T_{water}) = \frac{(T_a - T_{water}) \cdot f \cdot A_P}{Q_{in}} \qquad \{5\}$$

For T_a equation {4} was used, whereas for the inlet wastewater temperature T_i [ºC] a literature value of 15.6 ºC was assumed **[5]**. The year-round average effluent quality x_{av} of any parameter x was determined using equation {6}:

$$x_{av} = \frac{1}{365} \int_0^{365} x \cdot dt \qquad \{6\}$$

DESIGN RESULTS

Defining the wetland height as h=0.35m, the basin surface A_P gives its volume. The dynamic model came from the modification of the pilot-scale model allowing for oxygen limitation of the nitrification process, including the six above equations. It was first run in the AQUASIM environment without initial vegetation m_{po}=0 [g_plants]. Its application (**Figure 1**.) showed that the total minimum required surface was A=110000m^2 fulfilling the imposed effluent quality.

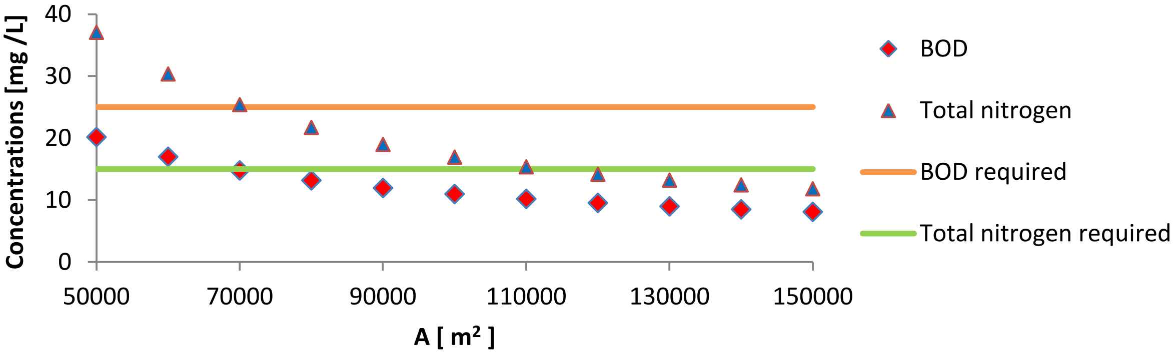

Figure 1. Predicted average annual effluent values for BOD_5 and total nitrogen TN as a function of surface area.

The only difference in the presence of vegetation in the wetland basin, is that the plants absorb water resulting in changes of the effluent flow rate E. The term Q_{plants} is crucial for the water balance and it is dependent on the vegetation mass, according to equations {2} and {3}. Consequently, given the surface requirement to achieve effluent quality, there is a maximum initial vegetation mass m_{po} max for which the minimum effluent flow rate during the year is always positive (E_min>0), so that the basin liquid volume is maintained constant. Specifically, for A=110000m^2 or 11ha, it was found that $m_{po_}$max=219.4t_plants (**Figure 2**.). The dynamic model then predicts a total annual vegetation mass m_p=592.5t_plants or 53.86t_plants/ha. If the average annual humidity is 75.13%, then the total annual dry mass of 13.39t_dry_plants is comparable with the typical literature dry mass value 15.30t_dry_plants in constructed wetlands systems for the species Typha Latifolia, as given in **[8]**.

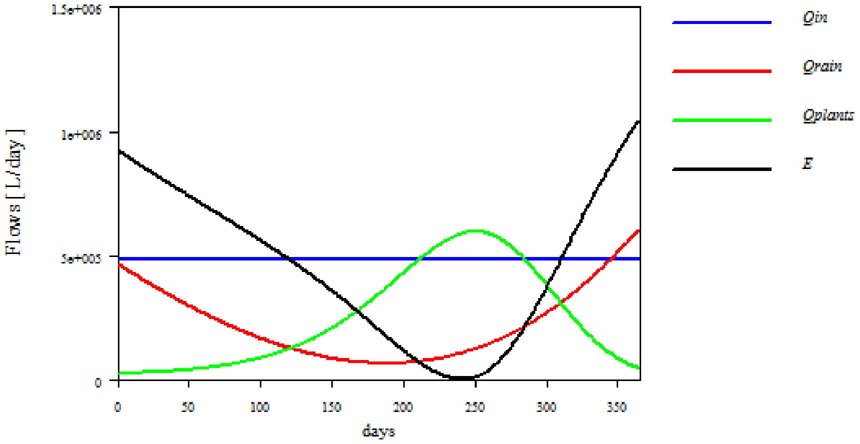

Figure 2. Year-round in and out flows of a full-scale wetland for a surface area A of 11ha.

When the total required surface A was divided in two sequential basins, assuming that the first basin has a surface A_1=55000m^2, the maximum initial vegetation mass was $m_{po1_}$max=85.4t_plants. Assuming that the second basin contains no plants, its surface A_2 that can achieve the required effluent quality is A_2=25000m^2. (**Table 1.**). Therefore, a total area A of 8ha (less by 27.2% than the corresponding surface in the one basin system) is required.

Table 1. Total nitrogen effluent quality for a full-scale wetland system with two sequential basins for various second basin surfaces A_2 with and without plants, following a 5.5 ha basin with plants.

A_2	TN with plants	TN without plants	TN required
ha	mg/L	mg/L	mg/L
5.0	13.0	10.2	15
4.0	14.8	11.2	15
3.0	17.1	13.0	15
2.0	-	16.5	15
2.5	-	14.5	15

CONCLUSIONS

The design of a wetland for a basin based on the developed dynamic model includes: 1.Finding the total minimum required surface without plants in order to achieve the imposed effluent quality in BOD_5 and total nitrogen. 2. Determination of the maximum initial vegetation for the above surface which will ensure positive effluent flow rate throughout the year. 3. The prediction of the annual vegetation mass demanded for harvesting once a year. The total required surface may be reduced when two sequential basins are used. It was seen that it is best to have the first basin with plants and the second without. This methodology is suggested for wetland design, when removal not only of the organic matter, but also of nitrogen is required. The developed dynamic model is useful for the design, simulation and optimization of free water surface constructed wetland treatment systems.

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(P47) An Optimization Based Framework for Design and Retrofit of Municipal Wastewater Treatment Plants: Case study on side-stream nitrogen removal technologies

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Abstract

Existing WWTPs need retrofitting due to several different reasons such as: change in the wastewater flow and composition, change in the effluent limitations, as well as changes in the wastewater treatment trends. Specifically, increased nitrogen limitations in the regulations for the WWTP effluents gave rise to development of innovative nitrogen removal technologies mostly used for water streams resulting from sludge treatment. In this study we propose a superstructure optimization concept based on mathematical programming to manage the multi-criteria WWTP design/retrofit problem and generate novel and optimal network designs for domestic WWTPs. Alternative treatment technologies are represented in a superstructure; each of which is described by a generic model in terms of input-output mass balance. The superstructure is coupled with a database containing data for both performance and economics of the alternative technologies. The superstructure optimization problem is formulated as a Mixed Integer (Non)Linear Programming problem and solved in GAMS for different scenarios represented by different objective functions and constraint definitions. Finally, a case study is formulated to perform a retrofit study addressing the nitrogen removal problem in order to highlight the use of the framework.

Keywords

Design; modelling; superstructure optimization; uncertainty analysis; wastewater treatment

INTRODUCTION

Wastewater treatment process synthesis can be defined as the step in the design of a WWTP where the design engineer selects unit processes from a number of alternatives and interconnects them to create the process flow diagram. Process synthesis is also performed during retrofitting studies in the sense that a new task can be added to the existing treatment line or one or several processes can be changed as a result of the emerging needs. This task has become a complex integrated decision making problem with a number of aspects are being contemplated in the early stage decision making stage (Hamouda, 2009). A wide range of parameters, i.e. organics, nutrients, pathogens, heavy metals etc., were included in the emission and immission based regulations with the limit values getting more and more stringent. In Europe, the change in the legislation regarding total nitrogen content of the effluent wastewater directed the research into developing innovative treatment technologies for nitrogen removal from nitrogen rich water streams in a WWTP without expanding the existing tank volumes of the plant (Hellinga et al., 1998, Henze et al., 2008). These technologies have relatively small tank volumes and can work on short sludge retention times (SRT) due to high growth rate of microorganisms at readily high temperatures of the influent streams (sludge stabilization and dewatering reject water streams). Moreover, since they use different paths of nitrogen cycle, they save oxygen and carbon sources. The fact that, there are many different technologies are present for reject water stream makes the process selection complicated. There are several different factors to be considered namely; the current nature of the nitrogen removal in the main line, utility consumption, area requirements etc. (Henze et al., 2008).

Currently, wastewater treatment process synthesis is mainly based on expert decisions and previous applications. This approach takes values like environmental issues, water reuse, by-product recovery (if possible) and public impacts into account and identifies the alternatives based on experience, similar existing solutions and brainstorming to come up with the most viable WWTP network (Daigger, 2005). This study proposes an alternative approach to cast the decision making problem using mathematical programming techniques for process synthesis and design of domestic WWTPs under uncertainty.

THE FRAMEWORK

A schematic representation of the framework for superstructure based optimization methodology is shown in Figure 1. The framework is adapted from the mathematical programming based optimization theory developed for chemical process synthesis and design by Quaglia et al. (2013), in the context of the WWTP design problem.

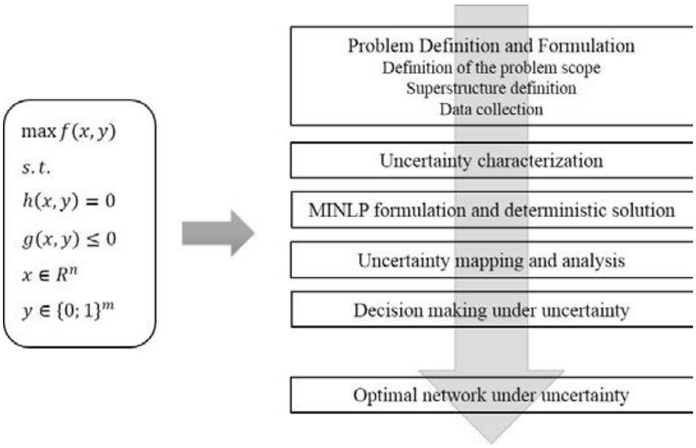

Figure 1. The superstructure based optimization framework (Bozkurt et al., 2013)

The first step of the framework is where the problem is defined; the objective function is selected together with the characteristics of the wastewater and emission limits. In the same step, the superstructure containing all relevant treatment technologies is developed where the treatment plant is represented as a sequence of treatment tasks in the columns of the superstructure and alternative technologies placed in rows. A representative superstructure is shown in Figure 2. Moreover in this step, for each treatment technology system specific data are collected and used to calculate the design parameters (volumes, utility consumptions etc.) as well as performances (contaminant removals, sludge production etc.) by using a systematic data collection procedure developed by integrating the procedures given by ATV design standards, Tchobanoglous (2003), WEF (2010) and Henze et al. (2008).

Different individual sources of uncertainty are evaluated in this study, moving away from lumped uncertainty safety factors. In the second step, the domain of uncertainty is defined with respect to the selected parameters. A number of future scenarios are generated by sampling the uncertain space uniformly using Latin Hypercube Sampling (LHS). The mathematical formulation of the optimization problem as a Mixed Integer (Non)Linear Programming (MI(N)LP) problem is done in the third step where also the deterministic problem is solved by using GAMS. The optimization problem consists of the generic process interval model (Figure 2) represented by mass input-output models, process constraints, structural constraints, effluent limit constraints and cost models together with the objective function. The detailed mathematical formulation can be found elsewhere (Bozkurt et al., 2013).

In the next step, the deterministic problem is solved for the scenarios generated in the second step with respect to the uncertain data. The solution results in a distribution of optimal networks and objective function values which are then analysed to understand the effect of uncertainty on the decision making procedure. In the last step of the framework, the optimization problem is formulated as a stochastic problem and solved to find the optimal treatment network under uncertainty by using sample average approximation (SAA) (Birge & Louveaux, 1997).

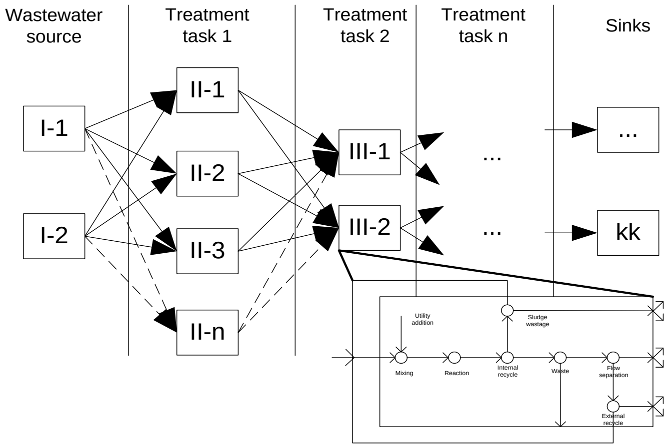

Figure 2. A representative superstructure and the generic process interval

CASE STUDY

The application of the superstructure based optimization framework is highlighted in this section with a case study. The problem is defined as retrofitting of an existing WWTP (Benchmark Simulation Model no.2 plant (Alex et al., 2008)) by treating the reject water stream resulting from the sludge treatment units with innovative nitrogen removal technologies. The objective function covers the Total Annualized Cost (TAC) which is to be minimized in compliance with the emission limits defined by EU Urban Wastewater Treatment Directive. Moreover, different scenarios cover more strict effluent limitations in terms of total nitrogen.

The superstructure developed for the case study problem is presented in Figure 3. The process intervals represented in grey (PC for primary clarifier, AS for the activated sludge unit) are the already existing treatment processes for primary and secondary treatment tasks together with the sludge treatment units (Thick for the sludge thickener, AD for anaerobic sludge stabilization and Dewat for the sludge dewatering unit) placed in between the source (WW) and sink intervals (Water and Sludge). For retrofitting purposes, a new task (Reject water treatment) is added to the superstructure and alternative innovative nitrogen removal technologies are placed there. First alternative is a single partial nitrification process (SHARON) followed by two combined partial nitrification and ammonium oxidation processes being two-stage and single stage, respectively (Shar/Anammox-1 and Shar/Anammox-2). The last alternative (Demon), which stands for Deammonification, is another efficient ammonium removal technology. The systematic data collection procedure is followed to design the treatment technologies prior to placing them in the process intervals. The uncertain domain is defined by defining the uncertainty with respect to cost parameters and effluent total nitrogen limitation. Accordingly, the parameters alpha, beta and fouling factor (Eq. 1, Tchobanoglous, 2003) are considered uncertain which defines the relation between actual (AOTR) and standard oxygen transfer rate (SOTR) together with standard oxygen transfer efficiency, price of electricity and total nitrogen effluent limitation.

$$AOTR = SOTR\left(\frac{\beta * C_{\bar{s},T,H} - C_L}{C_{s,20}}\right)(1.024^{T-20})(\alpha)(F) \qquad (1)$$

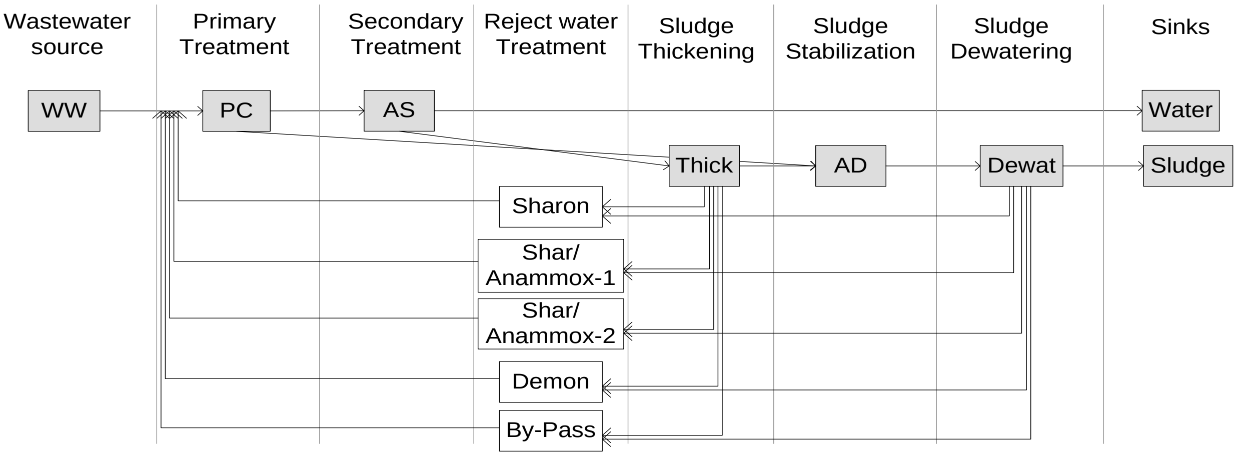

Figure 3. Case study superstructure including alternative side-stream nitrogen removal technologies

The results of the case study will be discussed in more details in the presentation.

CONCLUDING REMARKS

A superstructure based optimization methodology is developed which is used to deal with the early stage WWTP design/retrofit problem under uncertainty. The framework is applied to represent and identify optimal side-stream nitrogen removal technologies. The uncertainty analysis is performed to check different possible network configurations and objective function values under different sources of uncertainty. The presented framework with its models and database comprises a tool which is expected to assist the decision making by generating novel ideas for the WWTP process selection problem. The future work will focus on further expansion of the superstructure and its database and applying it to different case studies.

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(P48) Optimization methodology for enhancement the biogas production of anaerobic digestion of agro-wastes

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Abstract

This study aims to develop an optimization model for anaerobic co-digestion of agro-industrial wastes including highly problematic wastes for increasing the production of biogas as a source of renewable energy. In this study we are reporting a new experimental procedure and calculation tool for choosing the optimal blends of different wastes under specific operating conditions to assure maximal economical profit from anaerobic digestion. The optimization tool considers operational and economical constraints. Excel solver used to predict the optimal blends, where, the target function maximizes the methane production taking into account the cost of the waste and several restrictions. The target function considering the fitted parameters, obtained from the fitting of the Gompertz model to the bio-kinetic results. We tested waste from olive mill, cheese whey, slaughterhouse and biodiesel industry. This study offer an easy approach for co-digestion of complex agro-industrial waste mixtures.

Keywords
Optimization; Anaerobic; Methane; Biodegradation rate; Agro-industrial; Co-digestion

INTRODUCTION

The processing and manufacturing of the agriculture products and crops (vegetables, fruits, meat and dairy) leads to increasingly large quantities of very strong wastes, which are considered serious environmental problem due to the high organic load and the high content of microbial growth-inhibiting compounds. However, agro-industrial waste is considered an excellent resource for biogas production due to the high organic content that can be converted by anaerobic treatment to methane gas.

Commercial anaerobic digestion processes are often operated at well below their optimal performance due to a variety of factors (Alastair J. 2008). Alvarez and Liden's (2008) study shows that a combined treatment of different waste types like manure, slaughterhouse, fruit and vegetable waste in a mesophilic co-digestion process provides the possibility of treating waste that cannot be successfully treated separately. Co-digestion is a technology increasingly used for simultaneous treatment of different solid and liquid organic wastes (Bouallagui et al., 2009). Furthermore, the biogas yield, and therefore the energy output, has been found to be increased by co-digestion due to the positive synergistic effect established in the digestion medium and the supply of missing nutrients and buffering capacity by the co-substrates, a fact that increases the economic viability of biogas plants. Neves et al. (2009) shows that methane production was enhanced by the addition of oily wastes to the co-digestion processes of manure and food waste. This kind of waste has high methane potential (based on theoretical calculation). In comparison with other substances, fat, oil and grease (FOG) waste is considered a desirable substrate to be treated in anaerobic digestion processes (Angelidaki and Sanders, 2004). In addition to waste streams of the food industry, wastewater from dairies and slaughterhouses (Cammarota, Freire 2006) and olive mill wastewater (OMW) (D'Annibale, 2006) contain high levels of fats and complex organic compounds that are slowly-biodegradable.

The main issue for co-digestion process lies on balancing several parameters in the co-substrate mixture:

macro- and micronutrients, C:N ratio, pH, inhibitors/toxic compounds, biodegradable organic matter and dry matter (Hartmann et al., 2003). Alvarez et al. (2010) used linear programming method to set up different blends aimed at maximising the total substrate biodegradation potential (L CH4/kg VS) or the biokinetic potential (L CH_4/kg VS d) and found that linear programming is a powerful, useful and easy-to-use tool to estimate methane production in co-digestion units where different substrates can be fed.

The aim of this study is to develop experimental procedure and calculation tool for choosing the optimal blends from different wastes under specific operating conditions to assure maximal economical profit from anaerobic digestion. The optimization tool considers constraints, such as operational parameters, economic, structural and administrative of the anaerobic system.

METHODS

Batch assays were carried out in 100 mL plastic syringes with 20 ml active volume. All tests were performed in triplicate assays under the operating conditions of 37°C and 1 g granular anaerobic biomass from UASB treating citrus wastewater industry. These batch systems were used to carry out the experimental approach to evaluate the methane production of the studied four wastes: olive mill wastewater (OMW), cheese whey (CW), slaughterhouse solid waste (SSW) and biodiesel waste (BW). The cumulative methane production was measured for each waste at different initial VS (Fig 1). The Methane potential (Pmax), maximum methane production rate (Rmax) and the lag phase time (λ) were determined by fitting the modified Gompertz model (Eq 1) to the continuous detected cumulative methane production:

Eq 1:

$$P = P_{max}\left\{-\exp\left[\frac{R_{max}.e}{P_{max}}(\lambda - t) + 1\right]\right\}$$

Excel solver was used for predicting the optimal blends from different wastes. The target function (Eq 3) maximizes the equivalent “income” of methane production from anaerobic degradation, considering the cost of the waste in addition to several defined restrictions. The target function takes into account the equations of waste’s methane potential, bio-kinetics parameter and the lag phase that were obtained by Halden model (Eq2):

Eq 2:

$$r_s = \frac{r_{s,\max} \cdot VS_i}{k_s + VS_i + \frac{VS_i^2}{k_i}}$$

Eq 3:

$$\$ = \sum_{1}^{i} x_i\left(f * P_i * VS_i + CO_i\right)$$

r_s (either P or R); i- Waste index; x_i- Daily waste feed (ton/day): f- Methane cost (\$/L CH_4) VS_i- Initial waste VS (kg/ton); CO_i- Waste cost (including handling and transportation) (\$); P_i- methane potential (L CH_4/Kg/d).

RESULTS AND DISCUSSION

Experimental and estimated methane production potentials, rates and lag phase time: These experiments were carried out to determine the biodegradability, to predict the methane maximal potential, the maximal rate of methane production per initial organic VS and the lag phase time for each waste. Modified Gompertz model with Polymath software was fitted to the experimental continuous detected cumulative methane production.

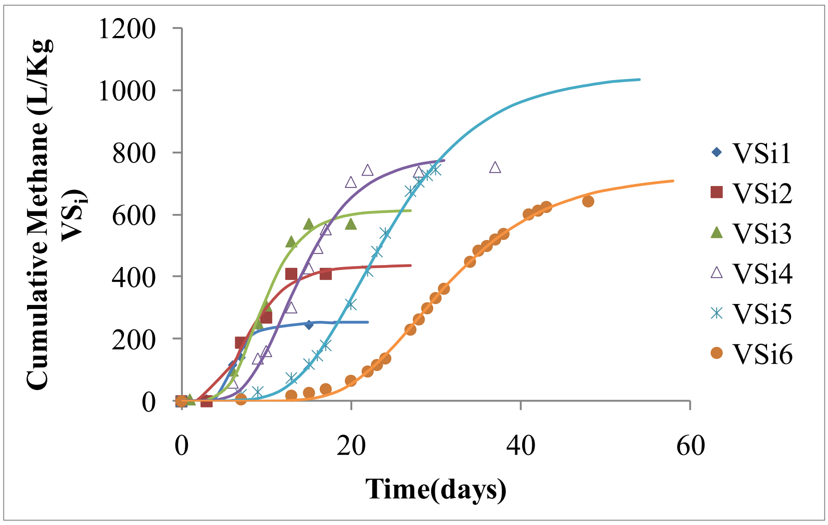

Fig. 1.Cumulative methane production for six different initial VS concentrations (1, 1.9, 3.8, 9.5, 15.2, 30.5 g/Kg) of SSW in batch systems at 37 °C. The solid lines represent the fitted Gompertz equation to the experimental

The fitted parameters of Gompertz model for each VSi value were fitted to either Halden model (for methane potential and methane production rate), and to modified Gompertz model for lag phase as can be seen in figure 2.

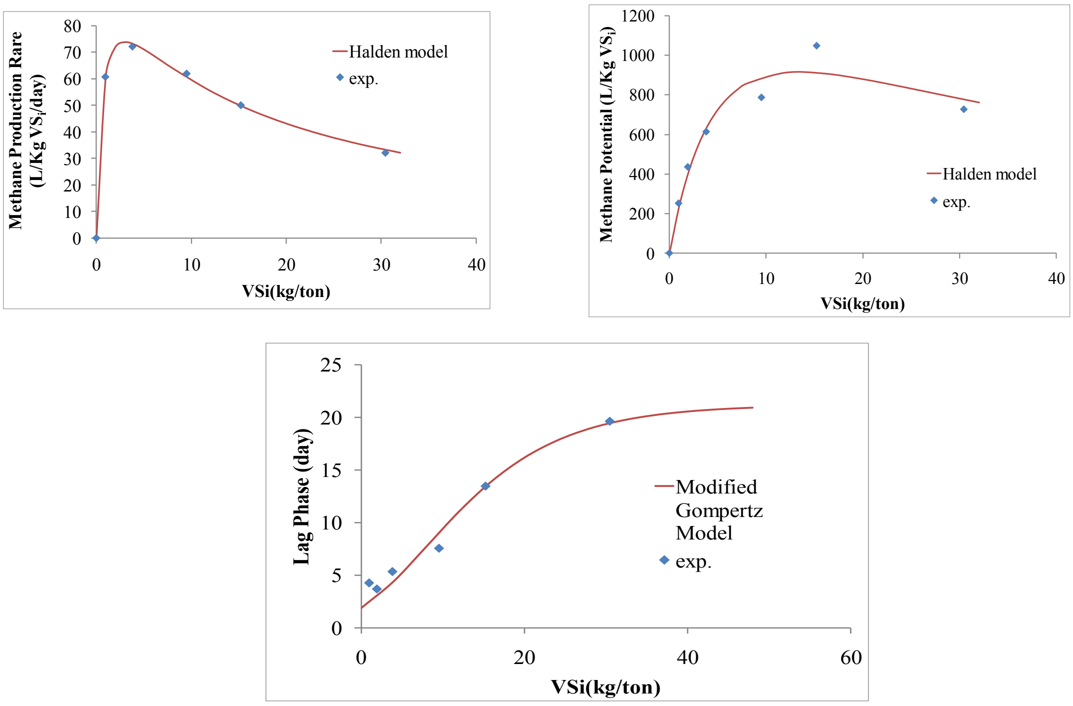

Figure 2: A- maximum methane production rate (Rmax), B- The Methane potential (Pmax) and C- the lag phase time (λ)

The target function (eq 3) takes into account the equations of waste's methane potential, bio-kinetics parameter and the lag phase that were obtained by Halden model or modified Gompertz equation. Excel solver was used for predicting the optimal blends from different wastes, where, the target function (Eq 3) maximizes the equivalent "income" of methane production from anaerobic degradation, considering the cost of the waste in addition to fulfilling several restrictions. The constrains can be the C/N, ammonia concentration, organic loading rate hydraulic retention time and other parameters. Table 1 shows the estimated potential mixture and the experimental results of one studied scenario. This scenario was defined for a digester of 1000 m^3 volume, maximal flow rate of 50 tons/d of a mixture of the four studied wastes. The optimal blend (based on the linear optimization) was compared against another two random blends. The results are presented in Table 1.

Table 1: Model validation of a feed blend for a reactor of 1000 m3 (HRT=15d)

	OMW	CW	SSW	BW	Experimental results (m3 CH4/d)	Income (US $/d)
Optimal blend	54.54	9.79	2.33	0	88.2	112
Random blend 1	10.5	18.3	61.2	10	84.76	107.7
Random blend 2	30.5	10.3	51.2	10	46.43	58.97

The results presented in Table 1 indicating that the simple model can predict the optimal blend and mixture of different wastes based on one simple experiment of the accumulated methane production at 3-5 different initial VS concentration of each waste. The following fitting procedure by Gompertz model and linear optimization provides the optimal blend for maximal income when considering known constrains.

ACKNOWLEDGEMENTS

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(P49) Energy optimization of the wastewater treatment plant in Castiglione T.se (NW of Italy)

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Abstract

The energy consumption represents a significant part of the operative cost of a wastewater treatment plant but, with a correct project and a careful management model, there are important possibilities for limitation. The proposed analysis concerns all the energetic aspects of the plant in Castiglione T.se (NW of Italy) that is the largest biological municipal wastewater treatment plant in Italy. The study takes into account every phase of the wastewater treatment scheme, in order to obtain specific electricity consumptions starting from a survey of the electrical devices operating in the plant: data from tele-control system, or direct readings and measurements in field have been used. Regarding the obtained results, the phase that uses the highest amount of energy is the biological wastewater oxidation, because of the high electricity consumption for the air compression and immission in the treatment tanks. Afterward the energy efficiency (by considering the obtained performances) of the used devices has been calculated, and compared with literature and best practices indications. For the whole plant an energy balance has been performed, and some energy optimization solutions to decrease the corresponding cost have been suggested.

Keywords

Energy consumption, energy optimization, wastewater treatment plant, biological oxidation.

Background

The wastewater treatment plant (WWTP) in Castiglione T.se, dedicated to the Torino metropolitan area, is the largest biological treatment plant in Italy: it is operating on a flow of more than 200 Mm3 per year, with service to a population corresponding to around 2.2 million of equivalent persons. The WWTP, besides to the wastewater treatment line, is equipped with a complete sludge treatment system.

Wastewater line. This line includes four parallel modules; the whole treatment process, for each module, can be divided in the following operating stages:

- primary treatment: screening, deodorization, grit and grease removal, primary sedimentation;
- secondary treatment: pre-denitrification, biological treatment (BOD oxidation and nitrification), secondary sedimentation;
- tertiary treatment: phosphorus removal, chlorination, final filtration.

Sludge line. The line receives and it is able to treat the primary and biological sludge trough the stages of pre-thickening, anaerobic digestion, sludge dewatering. From the biogas it is very important a possibility of energy recovery, in the year 2012 more than 12 million cubic metres of gas (70% methane) were obtained. The produced biogas is sent to two cogenerative engines, to produce electricity (able to satisfy one half of the requirement of the wastewater line) and heat, that is used to satisfy part of the internal energy needs of the plant (digestion, drying, space heating).

Data collection

In order to define in detail the actual energetic scenario, first of all it was required to evaluate the electrical consumption, and so an inventory of the electrical apparatus of the plant has been established. In the considered wastewater treatment plant, for the preparation of this inventory the informations obtained from the plant tele-control system, that allows a complete and real time overview of the plant, were used. Afterwards, direct current measurements were performed by using electric meters in field, and also some power data were collected from the nominal indications, or from the technical apparatus sheets; to evaluate energy consumptions from actual powers the operating times of the different devices were provided by the Company SMAT (*Società Metropolitana Acque Torino*), that manages the plant.

Methodology and results

The considered electrical apparatus were then grouped into categories, with reference to the treatment phase where they operate and, on the basis of the collected data, the energy consumption for each phase of treatment was calculated.

As is shown in Figure 1, the phase that requires the highest part of the electricity uptake is the biological oxidation: this requirement is linked to the energy used by the blowers that are employed use to introduce the air flow in the system; it is corresponding to the 51.6% of the total energy consumption.

Hence, on the basis of this result, it was considered as an important aspect the evaluation of the efficiency of the blowers; the study about these machines led to an estimation of an electrical efficiency that was found approximately 70 %, indicating a proper functioning of those devices. Another relevant percentage of consumption is due to the operation of sludge anaerobic digestion; in fact the produced biogas is not enough to cover the energy requirement for this phase, so it is necessary to purchase methane from external grid; this external uptake, destinated to two engines and also employed for boilers, was evaluated in different periods of the year.

To allow a comparison with others WWTPs, specific energy consumption indices were calculated: with reference to the values found out in literature for smaller Italian WWTPs, the plant has a lower specific consumption, as can be justified from scale effect: in fact larger plants that treat a major flux of wastewater and serve more population, has lower specific energy consumption compared to smaller plants.

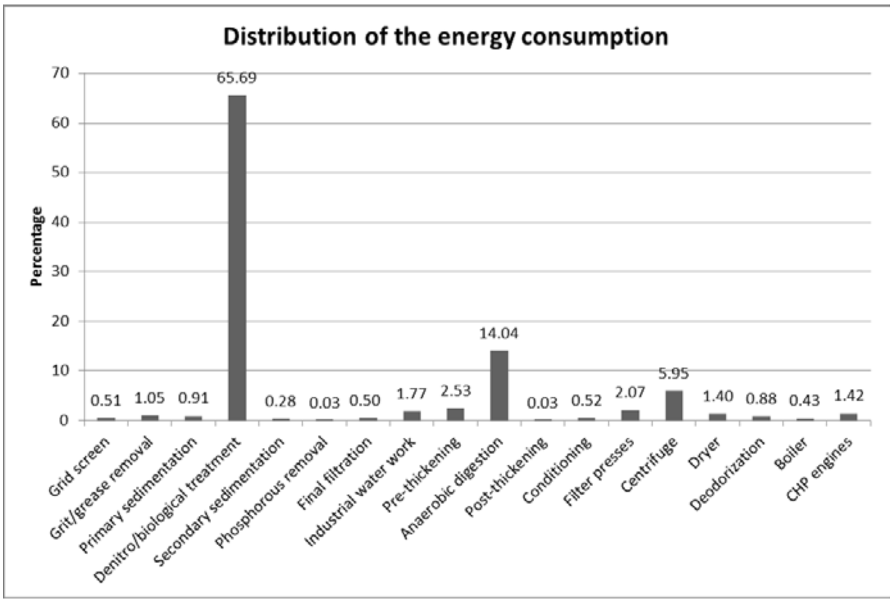

Figure 1. Distribution of the energy consumption.

Energy balance

The more significant part of the required electricity is purchased from the external grid (43%), while the electricity that is produced by two cogenerative engines fed with biogas covers the 39% of the total energy required by the WWTP; external grid methane that is combusted in other two engines is required for a 16% of the total consumption. Since the 2011, a photovoltaic system, with an area of 43000 square metres, gives a little contribution to the electricity requirement (1.8%).

In Figure 2 the energy balance of the system is represented. With regard to the thermal energy, the heat that is produced in the plant with the combustion of biogas is not sufficient to meet the needs of the system; so it is necessary to externally purchase natural gas, from the grid. Part of this methane is sent to two cogeneration engines, part to a boiler that is used to produce heat required for heating system of the building and the offices; a remaining part is sent to a boiler, where it is used to produce heating medium for the sludge drying. Moreover, the fumes that are produced in the driers are condensed, with recovery of hot water used to warm the digesters.

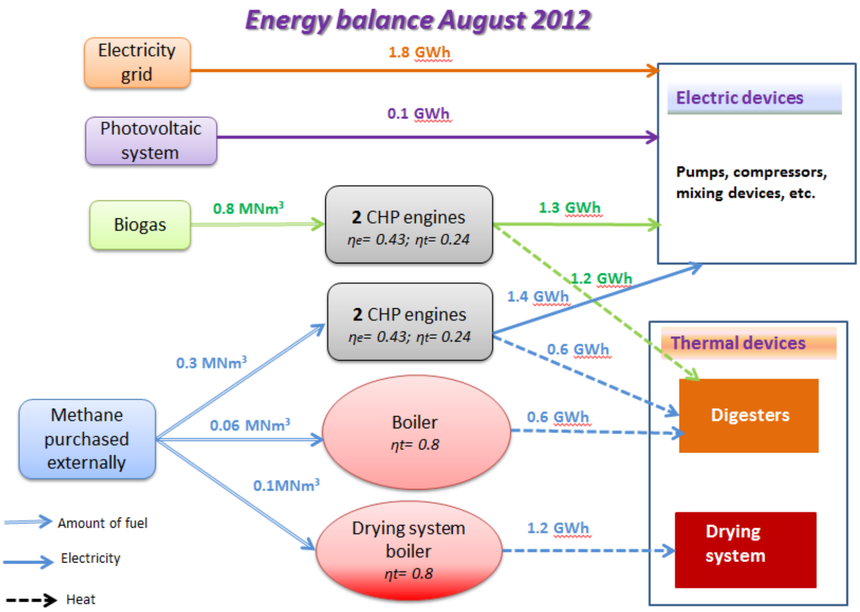

Figure 2. Energy balance of the month of August, 2012

On the basis of the quantity of fuel that for each month is purchased by SMAT in the year 2012, and of the characteristic efficiency of the engines and of the boilers employed in the system with reference to the sludge line, it was possible to calculate the amount of energy that is produced by each device by using the relationship: $P = G \cdot PCI \cdot \eta$ [KWh/month] where P is the specific power of each engine, G is the gas consumption [m^3/month], PCI is the lower heating value [KWh/m^3] and η is the performance.

Unfortunately, for the moment it was not possible to calculate the amount of heat destined to space heating as in the plant there are not meters to evaluate the heat flow. For this reason it was chosen to represent in Figure 2 the energy balance of the month of August, when the heating is not in operation.

The obtained result for the production of electricity from cogeneration with methane was compared with the data of the monthly electricity consumption recorded by SMAT in the year 2012. Moreover, taking in account the amount of biogas produced, the methane purchased and their energetic values, it was possible to check the values of the electrical efficiency of the gas engines, that were found to be approximately 43%, in accordance with the technical sheets.

Another useful comparison was made between the data of field measured electricity consumption (transformed in terms of kWh/year) and the total electricity consumption forecasted by the Company for the year 2013.

The consumptions calculated on the basis of the field inventory were equal to 65.04 GWh/y meanwhile those estimated by SMAT are 65.61 GWh/y. This good correspondence validates the sound of the obtained results of the study; small differences between the values may be due to the fact that it was not possible to survey the totality of the electrical devices and also to the fact that the electricity required to light the plant was not taken in account.

Energy optimization

The energy inventory analysis is a starting point and aims to evaluate possible solutions to improve efficiency of the plant, without compromising the quality of the treatment. To decrease the energy consumption it is possible to operate with structural solutions as plant modifications of the treatment scheme (normally leading to more expensive industrial devices), or operating solutions, as optimization of existing operational units; these less expensive systems can allow a pay-back of the cost in few years.

In the case of Castiglione T.se, as we have seen the aeration is the most expensive phase in term of energy consumption, hence the optimization of this phase would prevent energy and air waste.

Normally, in the WWTPs the aeration is controlled by measuring the dissolved oxygen in the tanks with linear controller, but in account of the fact that the biological process is not linear, and there are important variations in the quality of the incoming flow, the method are too simplified and unstable. To overcome this limit, there are innovative systems based on the fuzzy logic that allows to know the real time concentration of the ammonia; by adapting the process with a continuous and automatic adjustment of the set point of the dissolved oxygen it is possible to guarantee an higher stability. Currently this system is applied only on a module of the WWTP in Castiglione, but it could be extended to all modules in order to achieve a good energy saving.

A further efficiency increasing solution concerns the optimization of the anaerobic digestion for the energy recovery. The proposed improvement actions are the dynamic pre-thickening and thermal pretreatment of the sludge. The traditional thickening use a gravity sedimenter, but new dynamic thickening system and use of centrifuges could reduce the volume of the sludge, with a consequent reduction of the energy that is required to heat it inside the digesters. Another applicable proposal is the thermal pretreatment that acts with a cellular lysis; this fact increases the degradability of the substance and leads to the possibility to decrease the hydraulic retention times. A limit of this pretreatment could be the energy consumption to raise the temperature of the system, but by using a pretreatment al low temperature (lower than 100°C) this problem could be avoided.

Conclusions

The obtained results show a good performance of the wastewater treatment plant in Castiglione T.se, and the comparison with the data of energy consumption estimated for the current year by the Company that manages the plant validates the goodness of the conducted study. There are some possible solution for the energy optimization that are here presented, and that could be studied in more detail. It’s important to stay update with technological innovations and to respect the Italian regulations for the wastewater discharge: in fact an energy optimization is required to reduce the energy consumption without compromising the quality of the treatment destined to environmental protection.

(P50) Heat recovery from a WWTP treating high-concentrated wastewater

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Abstract

This contribution assesses the heat recovery potential from a biological wastewater treatment plant (WWTP) treating manure. Based on previous knowledge, additional physical considerations and dedicated experiments, a heat balance was set up to calculate the temperature profile of the aeration basin and the associated heat recovery potential over a one-year period. The technical and economic potential for heat recovery by means of heat pumps was subsequently assessed.

Keywords
biological nitrogen removal; energy balance; experimental work; heat pumps, heat recovery; modelling, simulation

INTRODUCTION

The increasing scarcity of fossil energy resources, giving rise to high energy prices, as well as the need for reducing greenhouse gas emissions related to climate change, have made renewable energy an important issue in our society. Given that the energy consumption for heating buildings makes up a significant fraction of the total energy bill of industrialized countries, (Gong et al., 2008), heat recovery has gained increasing interest. This is in particular true for heat recovery from wastewater. Possible options in this respect include heat recovery from wastewater in homes (Frijns et al., 2013), heat recovery from sewers and heat recovery at wastewater treatment plants (WWTPs), either from the biological wastewater treatment tanks or from the WWTP effluent. It is clear that the potential heat recovery increases with increasing heat production during biological conversion, i.e. for wastewater containing high concentrations of organic matter (COD) and/or nitrogen.

This study addresses the heat recovery from an aeration basin of a WWTP treating manure. A heat balance has been set up to calculate the temperature profile of the aeration basin and the associated heat recovery potential over a one-year period. This model has been based on previous knowledge, additional physical considerations and dedicated experiments concerning the foam characteristics and heat resistance on this type of WWTPs. The technical and economic potential for heat recovery by means of heat pumps has subsequently been assessed. Particular attention has been paid to the optimal heat pump design in terms of capacity and configuration, maximizing the heat recovery efficiency while taking into account the associated payback time and time in operation.

MATERIALS AND METHODS

Heat balance – temperature model

Under steady state conditions, the heat balance for a completely mixed aeration basin (assuming that the water temperature is uniform over the basin and equals the outlet temperature) is given by

$$\Delta H = \rho_w c_{pw} Q_w (T_i - T_w) \qquad [J.s^{-1} = W] \qquad \text{Eq. 1}$$

expressing that the net heat exchange over the basin (ΔH) equals the enthalpy change between the influent and the effluent streams, where ρ_w ($kg.m^{-3}$) denotes the density of the wastewater, c_{pw} its specific heat capacity ($J.kg^{-1}.K^{-1}$), Q_w ($m^3.s^{-1}$) the wastewater flow rate, T_i (K) the influent temperature and T_w (K) the waste water temperature. The net heat exchange equals the heat input through solar radiation (H_{sr}), aerator power input (H_p) and biological reactions (H_b) as well as the heat losses through atmospheric radiation (H_{ar}), surface evaporation (H_{ev}), surface convection (H_c), surface aeration (H_{ae}) and convection and conduction through the tank bottom and wall (H_{tw}), as described by the model of Talati and Stenstrom (1990) and Sedory and Stenstrom (1995), which was applied to predict temperature changes in an aerated lagoon treating industrial wastewater by Gillot and Vanrolleghem (2003). In this study, the model was applied to simulate the possible heat recovery form high-concentrated influent streams. For this purpose, new expressions were derived to quantify heat losses through surface convection (H_c) and through surface evaporation (H_{ev}), based on first principles and therefore expected to be more generally valid than the expressions applied in the abovementioned references. Besides, the effect of a foam layer on the aeration tank was taken into account as well, affecting the terms H_{ar}, H_{ev} and H_c. Finally, also the possible heat extraction through heat pumps (H_{hp}) was added to the model, resulting in

$$\square H = H_{sr} + H_p + H_b - H_{ar} - H_{ev} - H_c - H_{ae} - H_{tw} - H_{hp} \qquad [J.s^{-1} = W] \qquad \text{Eq. 2}$$

Experimental set-up

The aeration basin was simulated by a tube (outer diameter = 0.110 m; inner diameter = 0.105 m; height = 1.5 meter) which was well insulated such that it could be assumed that heat loss only took place through the surface. Two tubes were operated in parallel, in one of which mineral oil was added as an anti-foaming agent. In the other tube, foam was formed due to aeration up to a foam level of 0.17 m. All tests were carried out using wastewater from a pig manure WWTP (Trevi N.V.). Previous to each test, the wastewater was heated to over 303 K, to stimulate biological activity and thus create a significant temperature difference in the basin compared to the environment. Aeration was provided by aquarium pumps, the aeration flow rate was kept constant at 76 L.h^{-1}, unless mentioned otherwise.

Wastewater treatment plant under study – scenario analysis

Simulations were carried out describing an existing pig manure treatment facility. The aeration basin had a volume of approximately 1700 m³, treating an influent of pig manure of 58 m³.day^{-1}, characterized by a COD concentration of 30 kg.m^{-3}. A foam layer with thickness of 0.17 m was implemented in the model. The installed heat pumps were assumed to have a COP of 3.

RESULTS AND DISCUSSION

Experimental work

Once air is blown through the aeration basin, micro–organisms can carry out their metabolic activity. Due to mixing, aeration and biological conversions, a foam layer is formed at the water surface. Even though this foam is known to have an insulating effect and as such represents a heat resistance, more precise knowledge in this respect has been lacking. In this study, dedicated experiments have been performed regarding the temperature profile within the foam layer and the influence of the aeration flow rate.

Temperature profile within foam layer. A linearity test was conducted to determine whether the temperature of the foam layer changes linear with the foam thickness. The results of this test are displayed in Figure 1. It can be seen that the value of the temperature gradient in the foam was almost constant. This indicates that the temperature profile in the foam layer is linear, at least in steady state. It implies that the insulating capacity of the foam layer increases in proportion to its thickness. As a result, the foam layer can be modelled as an insulating layer with conductive heat loss, characterized by a thermal conductivity coefficient ($\square_{foam}$). The linearity of the temperature proifles also indicates that the foam layer is not disturbed by rising gas bubbles. Most probably the air bubbles do not rise through the foam layer but are attached at the bottom of the foam layer. *Influence of aeration flow rate.* Experiments were carried out to investigate the effect of the aeration flow rate (ranging from 40 L.h^{-1} to 110 L.h^{-1}) on the heat resistance, under atmospheric as well as laboratory conditions, with and without foam layer (results not shown). It was concluded that the effect of the aeration flow rate on the total heat resistance is negligible.

Thermal conductivity coefficient of the foam layer. Given that the aeration flow rate did not have an additional influence, the thermal conductivity coefficient of the foam layer λ_{foam} could be calculated from the experimental data from the tests with foam at the surface as

$$\lambda_{foam} = \frac{1}{A\frac{\Delta T}{d}} \cdot \Phi = \frac{1}{A\frac{\Delta T}{d}} \cdot V \cdot \rho_W \cdot c_{pW} \frac{\left(T(t) - T(t_0)\right)}{t - t_0} \qquad [W.m^{-2}.K^{-1}] \qquad \text{Eq. 3}$$

with Φ [W] the heat flow through the foam layer, A [m^2] the surface of the aeration tank, $\Delta t/d$ [$K.m^{-1}$] the slope of the graph obtained in the linearity test (Figure 1), V [m^3] the aeration tank volume, T [K] the temperature of the aeration tank, t and t_0 [s] the start and end time of data registration, respectively. Eq. 4 assumes that heat loss during these tests only takes place through the surface and as such needs to pass through the foam layer. The average value of the thermal conductivity coefficient (λ_{foam}) was determined as 13 $W.m^{-2}.K^{-1}$ and implemented in the model.

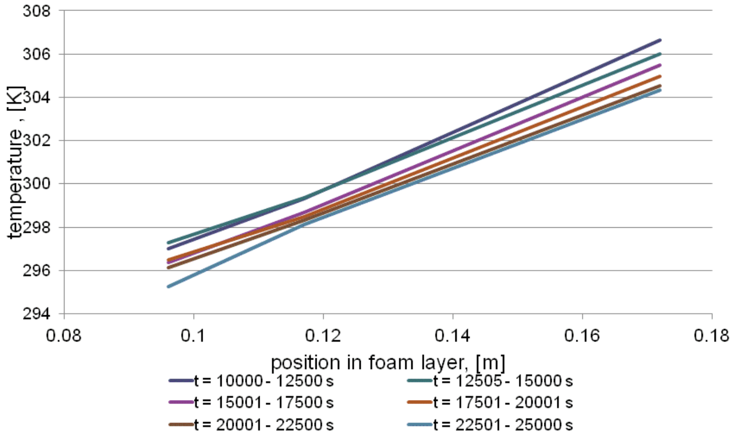

Figure 1. Temperature profile within foam layer, based on measurements at positions 0.096 m, 0.117 m and 0.172 m, at different time instants.

Simulation study

Heat recovery potential. The simulated temperature profile over 1 year is displayed in Figure 2. The heat surplus in the aeration tank or the heat recovery potential is defined as the maximum amount of heat which could be recovered through an ideal heat pump which extracts all heat in case the temperature in the aeration basin exceeds a predefined critical temperature (T_{crit}). This heat surplus is proportional to the area enclosed in Figure 2 by the temperature T and the critical temperature T_{crit}, for $T > T_{crit}$. The lower the critical temperature, the more heat can be recovered. On the other hand, the critical temperature needs to be high enough to ensure sufficient biological activity. Based on these considerations, T_{crit} was set to 20°C (298.15K) in this study. This corresponds to a yearly heat surplus of 1078 MWh in the aeration tank.

Heat recovery with a single heat pump. In reality, the heat extraction by a heat pump will be limited by its power. A single heat pump was considered with a variable heat extraction capacity, ranging between 50% and 100% of its maximum power. The optimal maximum heat pump power was determined through model simulation using a time step of half an hour, i.e. taking a decision whether or not to switch on the heat pump every half an hour, based on the available heat at that moment. Figure 3 summarizes the results. The yearly heat recovery first increases and then decreases with increasing maximum heat pump power. Smaller heat pumps will recover heat also during the winter months but are not able to recover all heat in summer. Large heat pumps on the other hand, will be put into operation mainly during the peak (summer) months, but are not suitable for heat recovery during the winter months due to overdimensioning. Figure 4 shows the corresponding time the heat pump is in operation in terms of its maximum power. From Figure 3, the optimal maximum heat pump power is determined as 200 kW. The corresponding maximum yearly heat recovery amounts to 2.93 10^{12} J per year or 815 MWh per year, being 76% of the theoretical heat recovery potential.

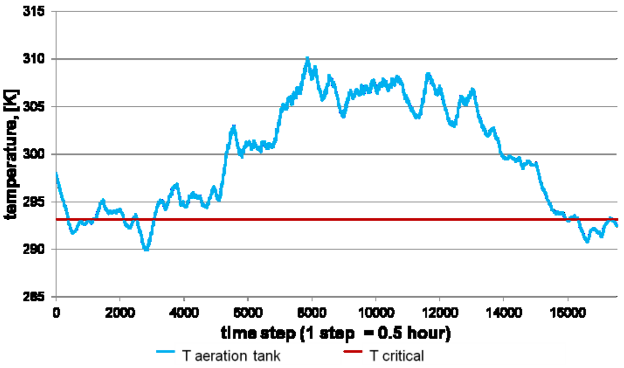

Figure 2. Temperature profile of the aeration tank over 1 year (time step =0 corresponds to 1 January) compared to critical temperature

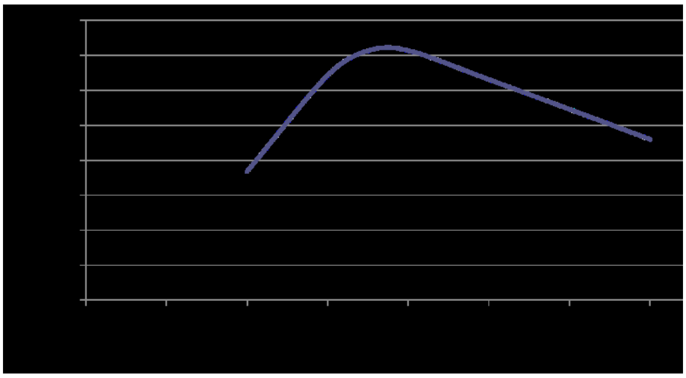

Figure 3. Yearly heat recovery in terms of maximum heat pump power – assuming 1 heat pump with variable power (50 - 100% of maximum power)

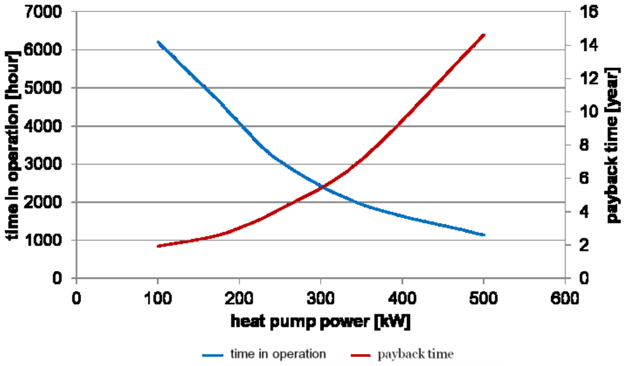

Figure 4. Time in operation per year and payback time in terms of maximum heat pump power – assuming 1 heat pump with variable power (50-100% of max. power)

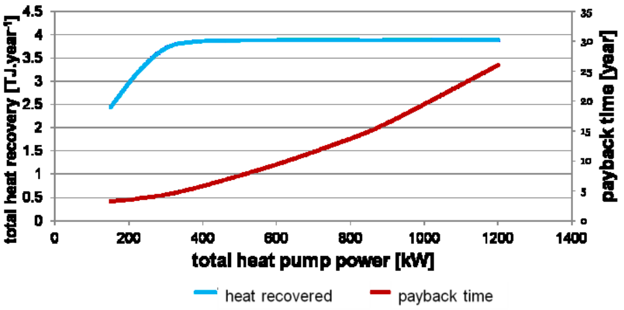

Figure 5. Yearly heat recovery and payback time in terms of total heat pump power – assuming 2 heat pumps with variable power

Economical evaluation. Installing a heat pump implies investment and maintenance costs ($C_{investment}$, and $C_{maintenance}$, respectively), which increase with increasing heat pump power. The operating costs ($C_{operation}$) and the energy savings realized due the reduction in fossil fuel consumption ($C_{savings}$) are proportional with the amount of heat recovered (Figure 3). The resulting payback time

$$t_{payback} = \frac{C_{investment}}{C_{savings} - C_{operation} - C_{maintenance}} \quad \text{[year]} \qquad \text{Eq. 4}$$

is displayed in Figure 4 in terms of maximum heat pump power. It can be seen that a heat pump of 200 kW will be operational for 4075 hours per year and has a payback time of about 3 years.

Heat recovery with two heat pumps. In view of obtaining a higher energy amount of heat recovery compared to the theoretical potential 1078 MWh per year, a scenario with two heat pumps was evaluated. The capacity of the heat pumps was set such that the maximum power of the largest heat pump was double of the maximum power of the smallest heat pump, both heat pumps having a variable heat extraction capacity, ranging between 50% and 100% of their maximum power. In this sense, the power ranges of both heat pumps are complementary. Figure 5 shows the total yearly heat recovery in terms of the total power of the two heat pumps installed. It was found that, for a total heat pump power above 400 kW, the total heat recoved remains constant at about 3.78 10^{12} J per year or 1050 MWh per year, being over 97% of the theoretical heat recovery potential. It was concluded that installing two heat pumps with capacities of 150 kW and 300 kW was the best choice. The time in operation of these pumps amounted to 3551 and 2923 hours per year, respectively (results not shown). The corresponding payback time was calculated as 6.7 years which is, even though higher than when installing a single heat pump, still economically attractive.

CONCLUSIONS

The heat recovery potential from a manure WWTP was assessed

- A heat balance has been set up, based on first principles and considering the effect of a foam layer on the aeration tank
- The temperature profile through the foam layer was experimentally determined to follow a linear profile, characterized by an apparent thermal conductivity coefficient of 13 $W.m^{-2}.K^{-1}$
- The potential heat recovery through one or more heat pumps was assessed from a technical and economical perspective

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Efficient Technologies

(Wedneday, 25 June 2014, Aula T2, Polo Zanotto)

(K10) Comparison of small treatment systems: UASB-ponds, UASB-horizontal wetlands and vertical wetlands

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Abstract

The paper presents a comparison between three simple sewage treatment lines involving natural processes: (a) UASB reactor – three maturation ponds in series – coarse rock filter; (b) UASB reactor – horizontal subsurface-flow constructed wetland; (c) vertical-flow constructed wetlands (French system). The evaluation was based on several years of practical experience with three small full-scale plants receiving the same influent wastewater in the city of Belo Horizonte, Brazil. The comparison included interpretation of monitoring data (organic matter, solids, nitrogen, phosphorus, coliforms and helminth eggs), together with an evaluation of practical operational aspects. Each system has their own specificities, and no generalization can be made on the best option. The overall conclusion is that the three lines are suitable for sewage treatment in small communities in warm-climate regions.

Keywords

Domestic sewage; horizontal subsurface-flow wetlands; maturation ponds; UASB reactor; vertical-flow wetlands

INTRODUCTION

Natural wastewater treatment processes are a very good alternative for the treatment of domestic sewage generated in small communities, due to their conceptual simplicity and low operation and maintenance costs. The major variants of extensive systems are stabilization ponds and constructed wetlands. Although not a natural treatment process, UASB (Upflow Anaerobic Sludge Blanket) reactors are also simple, and are widely used in some countries as the first stage in the treatment line. Generalizations on what is the best treatment system should be avoided, due to the fact that there is no single solution for all situations, and the decision lies on a multitude of factors, comprising land requirements, effluent quality requirements, performance in terms of organic matter, nutrients and pathogen removal, construction costs and operation and maintenance costs.

The present paper presents an investigation on the performance and behaviour of the following treatment lines over several years, all of them involving a natural system and receiving the same influent: (a) UASB reactor – three maturation ponds in series – coarse rock filter; (b) UASB reactor – horizontal subsurface-flow constructed wetland; (c) Vertical-flow constructed wetlands (French system).

Since most of the papers comparing treatment systems deal with plants receiving different wastewaters in different locations, this papers aims at making a comparison with simple treatment lines fed by the same sanitary sewage. The data used and the basis for the analysis came from Costa et al (2013), Dias et al (2013), Lana et al (2013) and Manjate et al (2013), in which individual evaluations of each system were presented.

METHODS

The experiments were undertaken at the Centre for Research and Training in Sanitation UFMG-Copasa, which receives sanitary sewage from the city of Belo Horizonte, Brazil (latitude 19°53’ S). Belo Horizonte is located in Cfa or Cwa humid subtropical climate according to Köppen classification, with a mean annual temperature of 22.1^{o}C and mean annual rainfall of 1540 mm/year. There are basically two seasons in the region: April to September (dry and cool, with mean temperatures of 20.9 ^{o}C and mean rainfall of 33 mm/month), and October to March (wet and warm, with mean temperatures of 23.4 °C and mean rainfall of 254 mm/month). After preliminary treatment (coarse and medium screens followed by grit removal) the wastewater is directed to the treatment units. The influent is comprised mainly from domestic sewage generated in the large city of Belo Horizonte (2.5 million inhabitants), with only a small fraction of industrial wastewater.

The system comprising UASB reactor and ponds was designed for a population equivalent around 220 inhabitants, and had the following characteristics: (a) UASB reactor: volume = 14.2 m^3, height = 4.5 m, diameter = 2.0 m; (b) maturation ponds: three ponds in series, each with length = 25.00 m and width = 5.25 m; (c) coarse rock filter occupying the final 1/3 of the third pond, with length = 8.44 m; width = 5.25 m and grain size between 32 and 150 mm. The results presented here are from May 2002 to February 2013 (almost 11 years). During the period, the influent flow varied, with a mean value of 33.0 m^3/d. In addition, the ponds depth was changed in order to investigate its influence on the system behaviour, with values ranging from 0.40 to 0.80 m. As a result, the hydraulic retention times (HRT) varied. In ponds 1 and 2 HRT varied between 2.0 and 6.0 days (range between 10 and 90 percentile). In Pond 3 HRT was lower (range between 0.8 and 2.5 days) because the pond was shallower and 1/3 of its volume was taken up by the coarse rock filter. The rock filter operated with hydraulic loading rates between 1.0 and 1.5 m^3/ m^3.d.

The treatment system with the horizontal subsurface flow wetland was also preceded by a UASB reactor. The wetland unit was designed for a population equivalent of 50 inhabitants and received a mean flow of 8.0 m^3/d. The medium was steel slag with d_{10} = 19 mm, non-uniformity coefficient d_{60}/d_{10}=1.2 and porosity = 0.40. The height of the bed was 0.40 m, and the design water depth was 0.30 m. The bed was cultivated with cattail (*Typha latifolia*). The dimensions of the unit were: length = 24.1 m; width = 3.0 m; length/width ratio = 8.0; surface area = 72.3 m^2; wet volume V = 21.7 m^3; surface hydraulic loading rate = 0.11 m^3/m^2.d; hydraulic retention time (V.porosity/Q) = 1.1 d. The operational period covered here is from September 2007 to August 2011 (four years).

The system with vertical-flow constructed wetlands received raw sewage after only preliminary treatment (there was no UASB reactor in the line) from a population equivalent of 90 inhabitants. There were three units in parallel (according to the first stage of the French system). The bed was planted with Tifton 85 (*Cynodon* spp), and each unit had a length of 9.3 m and a width of 3.1 m, with the filter bed consisting of an upper layer of gravel (2.4 – 12.5mm) with 0.40 m height, an intermediary layer of 0.15 m of gravel (4.8 – 25mm) and a drainage layer of 0.15 m of coarse gravel (19 – 50mm). The filters started operation in 2009, and were intermittently fed by pulse flooding alternated with drainage and rest periods, with different feeding strategies in the period. The results presented here are from January 2012 to October 2012, in which each unit was fed on weekly cycles with raw sewage for 2.5 days and rested for 4.5 days, with a mean inflow of 13.4 m^3/d, with one batch of 560L every one hour (mean hydraulic loading rate HLR of 0.45 m^3/m^2.d in the working bed and 0.15 m^3/m^2.d in the whole system).

RESULTS

Table 1 presents the mean values of the main quality parameters. Because of space limitations here, full descriptive statistics are not presented, and results from intermediate sampling points (ponds 2 and 3) are also supressed. Although the influent wastewater was the same, its mean concentration changed during the monitoring period of each system, what justifies different mean values for each treatment system. Table 2 shows the mean removal efficiencies at each stage of the treatment lines, while Figure 1 depicts the overall efficiencies obtained by the three systems.

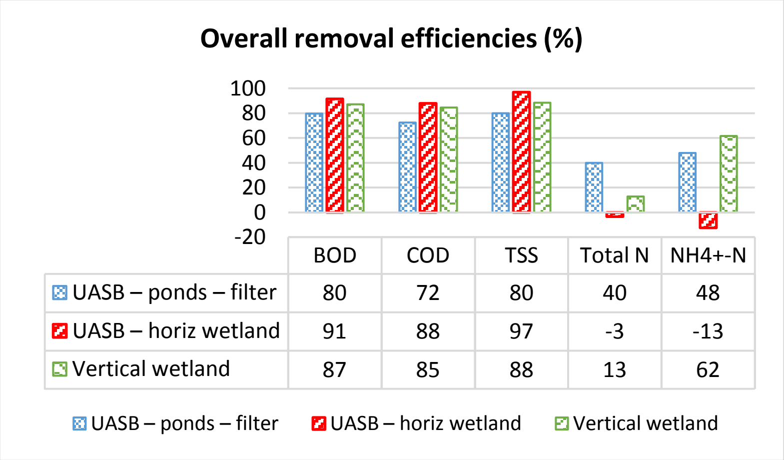
Table 1. Mean concentration values of the main quality parameters

Treatment line	UASB – three ponds in series – coarse filter				UASB – horizontal wetland			Vertical wetland	
Period	May 2002 - Feb 2013				Sep 2007 - Aug 2011			Jan 2012 - Oct 2012	
Parameter	Influent	UASB	Pond 1	Coarse filter	Influent	UASB	Horizontal wetland	Influent	Vertical wetland
BOD	235	78	60	48	293	83	25	279	36
COD	373	161	147	103	414	179	50	465	71
TSS	194	74	68	39	296	51	9	293	34
Total N	30	35	27	18	29	32	30	31	27
NH_4^+-N	23	29	21	12	24	29	27	26	10
NO_2^-N	0.001	0.07	0.18	0.76	0.02	0.02	0.02	0.01	0.2
NO_3^-N	0.28	0.20	0.20	0.16	0.03	0.05	0.16	0.1	12.6
Total P	1.7	1.7	2.0	2.0	-	3.2	2.3	3.9	2.1
E. coli	2.46×10^8	4.61×10^7	4.03×10^5	4.50×10^2	-	4.87×10^6	9.59×10^4	1.33×10^8	1.33×10^7
Helm. eggs	-	-	-	0	-	-	-	61	1

Units: mg/L, except *E. coli* (MPN/100mL) and helminth eggs (eggs/L); *E. coli* - geometric mean; (-) data not available

Table 2. Mean removal efficiencies at each stage of the three treatment lines

System	UASB – three ponds in series – coarse filter			UASB – horizontal wetland		Vertical wetland
Parameter	UASB	Pond 1	Ponds 2-3 + filter	UASB	Horizontal wetland	Vertical wetland
BOD	67	23	20	72	70	87
COD	57	9	30	57	72	85
TSS	62	8	43	83	82	88
Total N	-17	23	33	-10	6	13
NH_4^+-N	-26	28	43	-21	7	62
Total P	0	-18	0	-	28	46
E. coli	81	99,1	99,9	-	98	90



	BOD	COD	TSS	Total N	NH4+-N
▨ UASB – ponds – filter	80	72	80	40	48
▨ UASB – horiz wetland	91	88	97	-3	-13
▨ Vertical wetland	87	85	88	13	62

Figure 1. Overall mean removal efficiencies from the three treatment lines

From the tables and figures, the following points regarding the performance of the treatment units and systems can be made (comments confined to the operational conditions and loading rates applied to the units): (a) the performance of the UASB reactor was according to what is reported in the literature; (b) the treatment line with the best performance in terms of organic matter and suspended solids removal was UASB + horizontal subsurface flow wetland, followed by the vertical flow wetland; (c) total nitrogen and ammonia were partially removed at the UASB + ponds system and in the vertical flow wetland, and there was virtually no removal at the UASB + horizontal subsurface flow wetland system; (d) phosphorus removal was not high in any of the treatment lines; (e) the system with the maturation ponds was able to produce an effluent with excellent bacteriological quality (*E. coli* < 10^3 MPN/100mL; almost 6 log units removal) and zero helminth eggs counting (100% efficiency), and this was the main reason for having the three ponds in series.

FINAL REMARKS

The general comparison between the three treatment lines is presented in tabular format, including, not only the performance evaluation shown previously, but also an additional assessment in terms of implementation and operational aspects. No cost data were available to enter the analysis.

Item	UASB – three ponds in series – coarse filter	UASB – horizontal subsurface flow wetland	Vertical flow wetland
Organic matter removal	Good	Excellent	Very good
Suspended solids removal	Good	Excellent	Very good
Nitrogen removal	Fair. Removal mechanisms not clearly identified.	Negligible. Major removal mechanisms, including uptake by plants, not relevant.	Poor. Occurrence of nitrification and some denitrification. Uptake by plants was small.
Ammonia removal	Fair. Removal mechanisms not clearly identified.	Negligible. Major removal mechanisms, including uptake by plants, not relevant.	Good. Important nitrification. Uptake by plants was small.
Phosphorus removal	Negligible	Fair. Uptake by plants was small.	Fair. Uptake by plants was small.
Coliform removal	Excellent	Fair	Poor
Helminth eggs removal	Excellent	*(not tested)*	Good
Units in the liquid line	One UASB reactor, three ponds, one rock filter	One UASB reactor, one wetland	Three wetland units in parallel
Units in the sludge line	Sludge drying bed for UASB waste sludge	Sludge drying bed for UASB waste sludge	None
Per capita land requirements (*)	1.8 m^2 per inhabitant	1.5 m^2 per inhabitant	1.0 m^2 per inhabitant
Sludge handling	Withdrawal of waste sludge from UASB reactor (low production) and dewatering in drying beds. No removal	Withdrawal of waste sludge from UASB reactor (low production) and	No need for sludge removal after 5 years of operation. No sludge handling.

	of sludge from ponds during 11 years of operation. Mean accumulation rates of 0.020 and 0.004 m^3/person.year in ponds 1 and 2.	dewatering in drying beds	
Plant management	No plants in the system	Cutting of cattail every 3 to 4 months. Mean growth rate between 0.5 and 1.5 cm/d.	Cutting of tifton every 3 to 4 months
Clogging of wetland units	No units to clog.	Clogging leading to surface flow appeared after around 3 years of operation; no deterioration of effluent quality	No important clogging
Biogas production	Gas produced in the UASB reactor (potential for energy recovery)	Gas produced in the UASB reactor (potential for energy recovery)	No biogas production
Mal odours	Potential for odour release in UASB reactor (but not observed)	Potential for odour release in UASB reactor (but not observed)	Not observed
Mosquitoes	Occasional appearance in the ponds, without major implications (control by Nile tilapia fish)	Not observed	Not observed

(*) land requirements by the treatment units alone (not including space between units, urbanization, laboratories etc)

As seen by the above comparison, there is no overall best system, and the three options have each their own applicability, advantages and limitations, and can be successfully applied for sewage treatment of small communities. The selection among them must be based on a general evaluation, emphasizing those aspects which are more relevant for each application.

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REFERENCES – not shown here, due to space limitations; to be shown in the full paper.

(P51) Integrating the selection of PHA storing biomass and nitrogen removal via nitrite in the main wastewater treatment line

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Abstract

A novel scheme was developed for the treatment of low strength wastewater integrating the nitritation/denitritation and the selection of polyhydroxyalkanoates (PHA) storing biomass. An aerobic-feast and anoxic-famine regime was adopted feeding biowaste fermented liquidduring the aerobic phase, while denitritation was accomplished by the internally stored polyhydroxyalkanoates (PHAs). The SBR was operated at a nitrogen loading rate of 0.081±0.01 $kgN \cdot m^{-3} \cdot d^{-1}$. The average nitrogen removal was 45±14%. In the presence of volatile fatty acids (VFAs) and relatively low dissolved oxygen ($DO=1.5\ mg \cdot L^{-1}$) there was a lag phase of approximately 40 minutes after which ammonium oxidation was observed. The aerobic depletion of VFA was followed by an increase of sAUR from 0.41 to 3.23 $mgN \cdot gVSS^{-1} \cdot h^{-1}$.When DO was increased (6 $mg \cdot L^{-1}$), the sAUR and sNUR increased to 3.79±0.24 $mgN \cdot gVSS^{-1} \cdot h^{-1}$and4.89±0.44 $mgN \cdot gVSS^{-1} \cdot h^{-1}$,respectively. The PHA accumulation capacity was examined using pulse feed ofbiowaste fermented liquid in a fed batch reactor. After 8 h the PHA content was 23% ($gPHA \cdot gTSS^{-1}$).

Keywords:denitritation; polyhydroxyalkanoates; biowaste fermentation liquid; selection; accumulation; nitrogen removal; one stage process

Introduction

Polyhydroxyalkanoates (PHAs) are biodegradable and biobased polymers, well-known for their application in bioplastics. PHAs have attracted attention due to their thermoplastic and elastomeric properties and the possibility of producing them from renewable resources (Gumel et al., 2013). Microorganisms produce PHA as an energy and carbon reserve that can be used when food is limited. An aerobic feast and famine regime is the most appropriate scheme that is widely applied for the selection of PHA storing biomass (Jiang et al., 2009), since it creates favourable conditions for microorganisms capable of storing short chain fatty acids (SCFAs) as PHA. The SCFAs are taken up very fast by PHA accumulating bacteria during the feast phase and can be utilized to gain a competitive advantage during the famine phase (Dionisi et al., 2004). The carbon source that is added can consist of fermented sewage sludge or biowaste, which is rich in volatile fatty acids (VFAs) and can be produced at low cost within the wastewater treatment plant (WWTP)through fermentation (Katsou et al., 2014). During the feast conditions the PHA content of bacteria increases, while during the famine conditions it is consumed. The feast and famine regime can induce the bacteria to store external substrates as internal storage compounds, which they can consume to gain a more balanced growth. Studies on the sequencing batch reactor (SBR) process for wastewater treatment have shown that the build-up of electron donors as storage compounds is of great importance for nitrogen removal (Third et al., 2003). Storage compounds can serve as internal carbon sources for post-anoxic denitrification. However, the length of the phases (feast–aerobic and famine–anoxic) should be adjusted to ensure the 'maintenance' of the synthesized PHAs under aerobic conditions and their depletion in the anoxic phase. Nitritation-denitritation can be a sustainable alternative for Nremovalsince the oxygen demand of the process is 25% lower compared to the conventional nitrification/denitrification process (Ma et al., 2009).

In this work, a novel scheme was developed for the treatment of low strength wastewater, where nitritation/denitritation was integrated with the selection of PHA storing biomass. In this scheme the feast phase took place under aerobic conditions and the famine phase under anoxic conditions.

Material and Methods

The SBR was a Plexiglas reactorhaving a working volume of 20 L and a hydraulic retention time (HRT) of 15±1 h. During the start-up, the SBR was operated without any biomass wasting for 10 days (MLVSS increased up to 2 $g \cdot L^{-1}$); while in the subsequent normal operation activated sludge was wasted to achieve an SRT of 25 days (MLVSS~2.5 $g \cdot L^{-1}$). The sequence of the SBR cycle consisted of fill, aerobic reaction, anoxic reaction, settle, and decant.The aerobic and anoxic reaction length varied, depending on the nitritation/denitritation rates observed, from 130-160 min and from 40-50 min, respectively.Two different types of external carbon were added to enhance denitritation and the selection of PHA storing biomass;the fermentation liquid originating from the organic fraction of municipal solid waste (OFMSW FL) and fermentation liquid produced from primary sludge mixed withOFMSW(PS&OFMSW FL). The latter carbon source simulated the case of a food waste disposers application.

The low strength wastewater was fed into the SBR. The feast conditions were established in aerobic environment, by feeding the reactor with fermentation liquid. The oxidation of ammonium to nitrite occurred during the aerobic feast conditions, while denitritation occurred under the famine, anoxic conditions. Furthermore, the selection of PHA storing biomass took place under the established feast and famine regime. In situ and ex situ biomass activity tests were carried out to evaluate the rate of nitrogen removal and VFA uptake.A separate batchreactor was used for the accumulation of PHA. Biomass (1-2 L) was collected from the ‘parent SBR’ reactor at the end of the anoxic phase and was transferred in the ‘accumulation’ reactor. The batch reactor was equipped with an oxygen meter, a pH probe and a temperature meter.Biowaste FL was spiked into the biomass in a pulse mode based on the profile of the oxygen uptake rate (OUR) which was automatically recorded using a Martina device. PHA extraction was performed following the method described byLyberatos et al. (2013).

The SBR operation was divided into three periods based on the applied strategy.

- Period I: carbon source (OFMSW FL) was added in the beginning of the aerobic and the anoxic reaction phase. The DO during the aerobic reaction phase was first maintained at 1.5$mg \cdot L^{-1}$ and afterwards at 2.5 $mg \cdot L^{-1}$.
- Period II: OFSMW FL was added at the beginning of the aerobic phase (only 1 spike), while denitritation was driven by the stored PHA during the famine (anoxic) phase. Hence, denitritation was driven by the stored PHA during the famine phase. Furthermore, the duration of the aerobic period was increase by 23% compared to period 1. The DO target was initially set at 6 $mg \cdot L^{-1}$ to ensurea complete aerobic environment, favouring anefficient nitritation and production of nitrites. Then the DO was reduced to 1.5-3.0 $mg \cdot L^{-1}$
- Period III: PS&OFMSW FL was applied as carbon source in the beginning of the aerobic reaction phase, following the same strategy as in Period II. The DO was maintained at 2.0-3.0 $mg \cdot L^{-1}$

The PHA accumulation capacity of biomass was evaluated in batch tests, where the fermentation liquid was fed in a pulse mode. 1 g·SCFA L^{-1} of OFMSW FL was added as carbon source with a ratio C/N/P of 100/10.3/0.97.

Results and Discussion

The volumetric nitrogen rate (vNLR) was 0.081±0.01 kgN·m^{-3}·d^{-1}. The main characteristics of the wastewater and the external carbon source that were fed are summarized in Table 1. In all three experimental periods, complete accumulation of nitrite was ensured as the biomass with which the SBR was inoculated had been previously acclimatized to the via nitrite process. Furthermore, the low DO (1.5mg·L^{-1})that was maintained in the first days of period I favoured the development of ammonium oxidizing bacteria (AOB).

Table 1. Characteristics of wastewater and external carbon source used in the different periods

Parameter	Wastewater and carbon source	OFMSW FL	PS&OFMSW FL
pH	7.26 ± 0.27	5.00 ± 0.52	5.21 ± 0.12
COD (mg·L^{-1})	408.9 ± 87.5	21497 ± 1535	10500 ± 177
sCOD (mg·L^{-1})	129.2 ± 53.2	18075 ± 248	1230 ± 57
TN (mg·L^{-1})	52.12 ± 0.12	959 ± 4	580 ± 5
PO_4-P (mg·L^{-1})	5.24 ± 1.66	90.8 ± 1.1	122.3 ± 1.8
Acetic acid (mgCOD·L^{-1})	-	2717 ± 1082	1584 ± 285
Propionic acid (mgCOD·L^{-1})	-	560 ± 256	766 ± 231
Butyric acid (mgCOD·L^{-1})	-	2790 ± 1391	445 ± 125
C5-C7(mgCOD·L^{-1})	-	1365 ± 700	372 ± 109
C/N/P	100/13/1.3	100/10.3/0.97	100/12.7/2.7

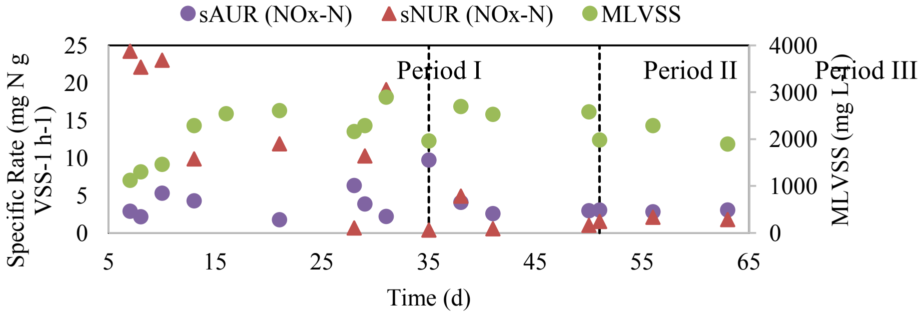

Figure 1. sAUR and sNURduring the operation of the SBR

Figure 1 shows thespecific ammonium uptake rate (sAUR), the specific nitrite uptake rate (sNUR) and the MLVSS concentration variation with the time of operation for the three experimental periods. The sAUR was significantly affected by the presence of SCFAs and the fact that the SBR treated low strength wastewater. At low DO level (1.5mg·L^{-1}), the profile of nitration presented a ‘lag phase’ for the first40 min. This lag period coincides with the time that is required for the SCFA uptake as it is clearly shown in the ex situ experiments of the time profile of the various nitrogen forms and of SCFAs (Figure 2). For example, in period II and at DO=1.5 mg·L^{-1}, the aerobic depletion of SCFA was followed by an increase of sAUR from 0.41 to 3.23 mgN·gVSS^{-1}·h^{-1}. When the DO was increased to 2.5 mg·L^{-1}the lag phase of nitritation decreased to only 10 min. As shown in Figure 1, the sAUR increased in days 28 and 35 due to a lack of carbon in the system which provided the nitrifiers with a competitive advantage over heterotrophic biomass. The average nitrogen removal achieved in period I was 68±14%. The denitritation rate in period I was significant (sNUR=15.8±7.1mgN·gVSS^{-1}·h^{-1}) since the OFMSW FL was also added in the anoxic phase providing suitable carbon source. In period II, a higher duration of the aerobic phase resulted in the availability of more nitrite for the subsequent denitritation process, resulting in enhanced degradation of PHA. The average sNUR=5.69±2.71mgN·gVSS^{-1}·h^{-1}was significantly lower compared to the respective one obtained in the previous period.However, it was much higher than the endogenous one. This rate is attributed to the internally stored PHA. The average nitrogen removal rate was 41±11%.Finally, in period III similar sAUR was observed as in period II, while the sNUR was slightly higher. The efficiency of system in terms of nitrogen removal was 44±22%. The latter reveals the importance of the stable presence of nitrites for effective nitrogen removal and PHA selection.

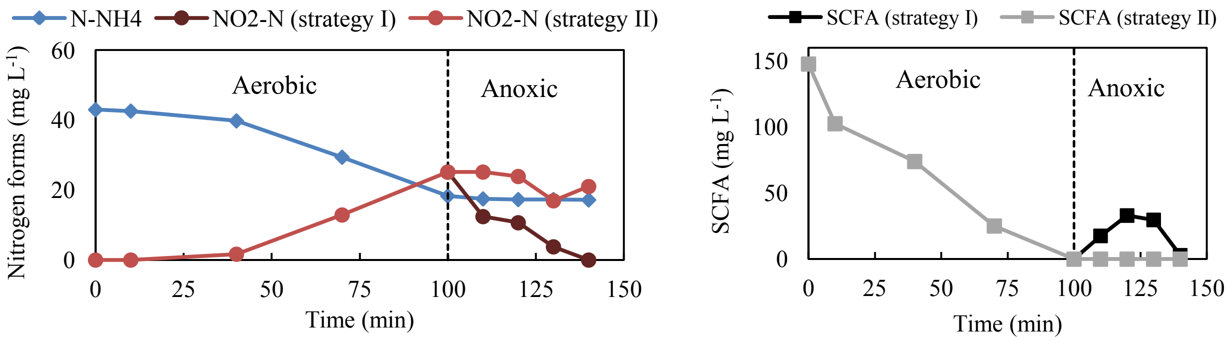

Figure 2. Ex situ(a)nitrogen and (b) SCFA time profile obtained following carbon source spiking during both the aerobic and the anoxic phase (strategy I) and spiking only in the aerobic phase (Strategy 2)

In the batch accumulation tests, PHA content that was obtained after 8 hof accumulation was 23% with a PHA storage rate of q_{PHA}=6.7 mgCOD·gCOD^{-1}h^{-1}and a SCFA uptake rate of –q_{SCFA}=88.6 mgCOD·gCOD^{-1}h^{-1}. The observed yields in terms of PHA storage and growth were $Y_{PHA/TCOD}$=0.15gCOD/gCOD, $Y_{X/TCOD}$=0.43gCOD/gCODrespectively. Therefore, from the total amount of SCFA that is taken up, 15% is attributed to PHA accumulation. In Figure 3, the contribution of each process to the total SCFA uptake is presented. The COD of the carbon source is partially biodegradable.Thus, part of the non-SCFA (i.e. slowly biodegradable particulate COD) can be consumed for growth resulting in lower PHA yields. Therefore, it is important to ensure a good efficiency of the anaerobic fermentation process and the solid/liquid separation of the fermentation liquid before its use in the selection / accumulation process.Finally, the energy requirements of the SBR applying the aerobic (feast) – anoxic (famine) scheme were estimated and compared with the typical aerobic feast and famine regime for the PHA selection of the PHA storing biomass(Table 2). ‘Our process’ – case 1, exhibits 25% higher air demand compared to case 2, where only nitrogen removal is performed in the SBR. However, in ‘case 1’ only one stage reactor is required for the processes that take place in cases 2 and 3 in two separate reactors.

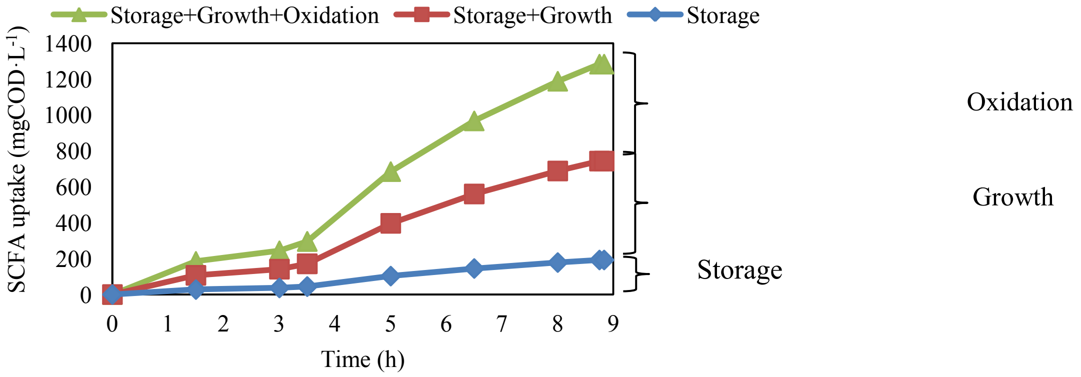

Figure 3. Contribution of COD uptaken to the PHA storage, growth and oxidation.

Thus, ‘our proposed scheme’ results in ~50% less air requirements compared to the conventional process. Additionally, the selection of PHA storing biomass under feast (aerobic) / famine (anoxic) conditions requires less air compared to the typical feast / famine regime carried out under continuous aerobic conditions (scenario 3).

Table 2. Air demandfor alternative schemes applied forN removal and the selection of PHA storing biomass

Parameter	Case 1‘Our process’ Nitrogen removal and PHA selection in one single reactor	Case 2 SBR for nitrogen removal nitritation/denitritation	Case 3 SBR for the selection of PHA storing biomass
Time of aerobic period/ cycle (h)	2.67	2.67	3.5
Time of feast aerobic/cycle (h)	0.4-0.5	-	-
Aerobic feast period / cycle (%)	10 – 12	-	10 – 15
Time of anoxic phase (h)	0.83	0.83	-
MLVSS (g/L)	2.5	2.5	2.5
Energy (kWh/m^{3}d)	**0.42**	**0.32**	**0.56**

Conclusions

A novel process was developed that integrates the selection of PHA storing biomass, and nitrogen removal via nitrite in an SBR. Furthermore, denitrification was accomplished through the internally stored PHA. The rates were higher than the ones attributed to endogenous respiration, butlower than the respective sNURaccomplished with the addition of fermentation liquid during the anoxic reaction phase. The increased competition between the heterotrophic and autotrophic bacteria in the aerobic phase for the DO in the presence of SCFA is a drawback of the examined scheme, resulting in limited sAUR.

Acknowledgments

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(P52) Integrating concepts for energy and resource recovery from municipal wastewater with LCA

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Abstract
Energy and resource recovery from raw municipal wastewater is a pre-requisite for an efficient and sustainable wastewater treatment in the future. This paper evaluates several processes for upgrading existing wastewater treatment plants or new concepts towards energy positive and resource efficient wastewater treatment in their life-cyle impacts on the energy balance. In addition, future challenges for integrating both energy and resource recovery in wastewater treatment schemes are identified and discussed.

Keywords
Wastewater treatment; energy recovery; phosphorus recovery; LCA

INTRODUCTION

Raw municipal wastewater contains significant amounts of resources both in energy and material terms, originating mainly from human excreta. The theoretical chemical energy potential of organic matter measured as chemical oxygen demand (COD) has been estimated to 4 kWh/kg COD (Heidrich et al. 2010). In addition, valuable plant nutrients such as phosphorus and nitrogen are found in high amounts in municipal wastewater, amounting to 1.8 g P and 11 g N per person equivalent (pe) and day on average (ATV 2000). In total, the annual energy and nutrients potential in municipal wastewater can thus be calculated to 175 kWh of chemical energy potential (assuming 120 g COD/(pe*d)(ATV 2000)) and 0.66 kg P and 4 kg N per year. Other materials that could potentially be recovered from raw wastewater include cellulosic material.

On the other hand, major demands of energy and chemicals are required to remove organic matter and nutrients from wastewater in wastewater treatment plants (WWTP). The efficient integration of WWTP processes for increasing the recovery of energy and nutrients from wastewater is thus a major target for future concepts of wastewater treatment, finally targeting an energy-positive process with maximum recovery of non-renewable resources such as mineral P or energy-intensive N fertilizers. In the following, different available options for upgrading conventional WWTPs for energy and resource recovery are evaluated with life-cycle based tools, and the benefits and challenges of their integration in future concepts for municipal wastewater treatment are discussed.

EXAMPLES FOR ENERGY AND RESOURCE RECOVERY FROM WASTEWATER

Upgrading sludge treatment with thermal hydrolysis

In a conventional WWTP, a high amount of organic matter ends up in primary and excess sludge from the activated sludge process. The recovery of the embedded energy in sludge is done in anaerobic digestion, producing biogas which can be valorized in central heat and power (CHP) plants. To increase the degradation of the organic matter of the sludge in the digestor, a thermal pre-treatment at high temperature (up to 160°C in thermal hydrolysis) can be implemented for excess sludge. This process can be driven by off-gas heat from the CHP plant and may also be combined with upstream dewatering to reduce heat demand. A combination of sludge digestion, dewatering, thermal hydrolysis, and second digestion (DLD) can further increase the biogas production considerably and decrease the heat demand of the hydrolysis unit. In an LCA of the full-scale WWTP of Braunschweig, both options have been assessed based on process data of pilot trials for biogas yield and supplier data for the hydrolysis process (KWB 2012). It could be shown that thermal hydrolysis will reduce the net energy demand of the system by 21%, whereas DLD even saves 62% of current net energy demand (**Figure 16**). Based on these promising results, a DLD system is currently in planning for implementation at WWTP Braunschweig.

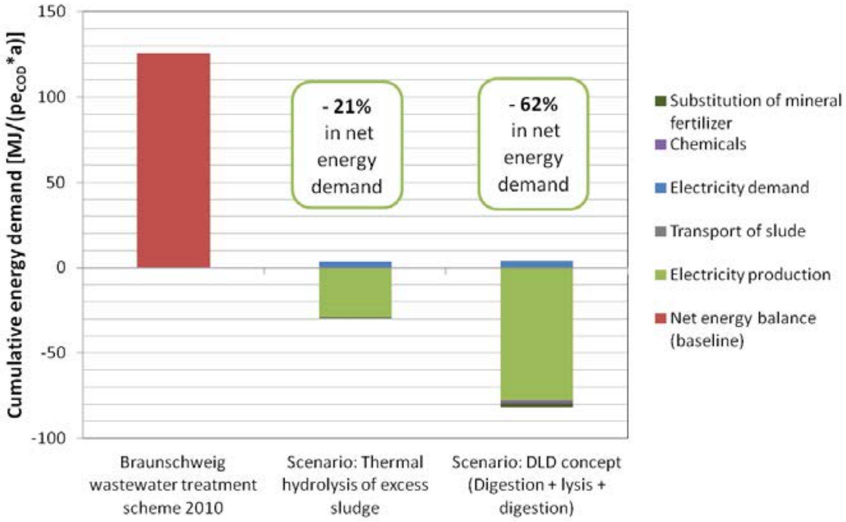

Figure 16: Impact of implementation of thermal hydrolysis on holistic energy balance of WWTP Braunschweig

Enhancing energetic valorization of sludge in incineration with improved dewatering

Another route for energy recovery from organic matter in sewage sludge is available with incineration of dewatered sludge, either in mono-incineration facilities or in co-incineration in power plants or cement kilns. However, the remaining water content in the dewatered sludge has a significant impact on the heating value and finally the energy that can be recovered via sludge incineration. Recently, the process of hydrothermal carbonisation (HTC) has been proposed as a potential alternative for improved dewatering of sewage sludge. Through heating of the sludge to > 180°C for a longer time (150 min), superior dewatering up to 65% total solids (TS) can be reached in final dewatering. Taking into account both the heat demand of the process and the additional biogas yield from the highly-loaded liquor, HTC can improve the energy balance of sludge treatment considerably in comparison to dewatering in centrifuges or filter press (**Figure 17**).

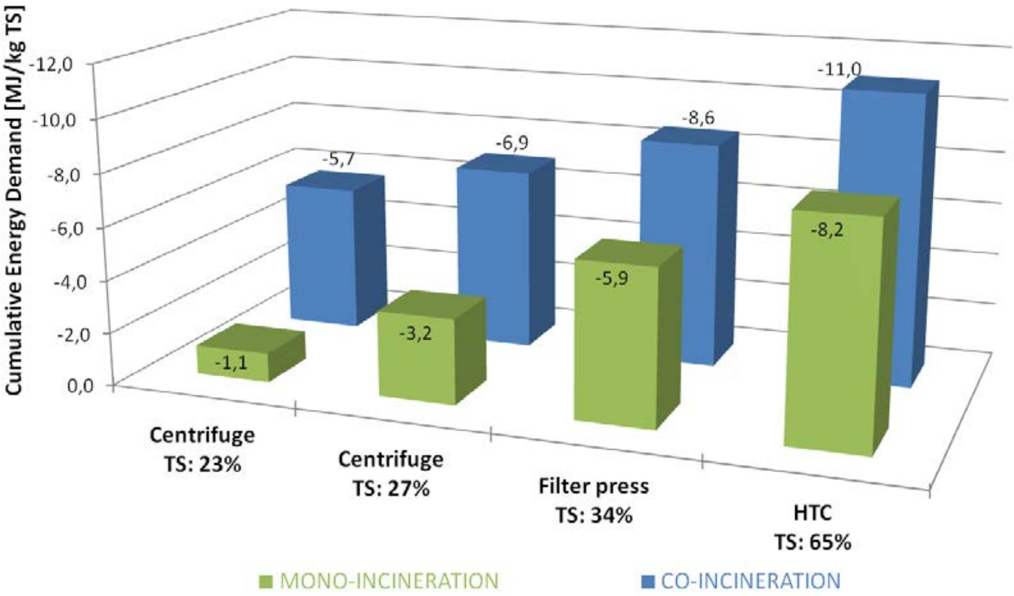

Figure 17: Net energy balance of sludge treatment (digestion + dewatering) and energetic disposal in mono-incineration or co-incineration for model WWTP (500 000 pe) (Remy et al. 2013)

These results also show that sludge disposal in mono-incineration has a distinctively lower energy recovery than in co-incineration (power plants), especially for sludge with high water content which requires high amounts of fuel oil in mono-incinerators or pre-drying with available waste heat. However, mono-incineration of sludge has other benefits in terms of phosphorus recovery and pollutant control, so that the optimisation of mono-incineration facilities in net energy balance should be a major target in the future to enable simultaneous recovery of energy and phosphorus.

Nutrient recovery from sewage sludge

Phosphorus as a non-renewable and essential nutrient can be recovered from sewage sludge through different routes, i.e. from sludge or sludge liquor, from the ash of mono-incineration, or via land application of sludge. The latter form is still practiced widely throughout Europe and can be an effective way of nutrient recycling, if sludge quality (e.g. content of heavy metals, organic pollutants) is sufficiently good and nutrient availability is high. Against the background of unknown effects of emerging pollutants and long-term application on soil quality, land application of sewage sludge has been banned in some countries (NL, CH), requiring new routes for nutrient recovery. P recovery through struvite (MAP) precipitation in sludge liquor has been shown to be both economically feasible and environmentally beneficial (**Figure 18**) through mineral fertilizer substitution and advantageous side effects of improved dewatering of sludge and mitigation of operational problems in WWTP with biological phosphorus removal. As the P content in the sludge liquor is only 5-15% of the total P load in the sludge, the MAP route is limited in its P recovery potential. For full P recovery, P has to be solubilized from sludge through acid leaching with high chemical demand and mobilisation of heavy metals, or it can be recovered from ashes of mono-incineration. Taking into account the low energy recovery in existing mono-incineration facilities discussed above, an existing trade-off between full P recovery and optimized energy balance can be identified here. Again, the optimisation of energy recovery in mono-incineration should be targeted to provide both energy and resource efficiency for future routes of sewage sludge disposal. A life-cycle based evaluation of all available processes for P recovery from sewage sludge is required to identify these trade-offs, which will be carried out in the on-going EU project P-REX (www.p-rex.eu).

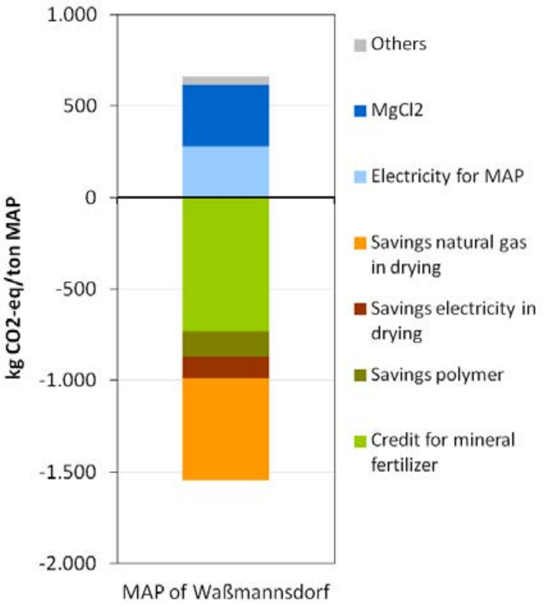

Figure 18: Carbon footprint of MAP recovered in WWTP Berlin-Waßmannsdorf

New concepts for wastewater treatment

Conventional WWTP with activated sludge process require a high amount of electricity for aeration, mineralizing a considerable part of the organic matter or transfering it into bacterial biomass in excess sludge. Thus, only around 10% (15-20 kWh/(pe*a)) of the theoretical energy potential in raw wastewater are recovered today in activated sludge WWTP via anaerobic digestion of sewage sludge and biogas valorization in CHP plants. To overcome this dilemma, new concepts for wastewater treatment are being developed which improve the overall energy balance of WWTPs by reducing the energy demand for treatment and increasing the energy recovery at the same time, finally targeting energy-neutral or even energy-positive WWTP without compromising the treatment performance in terms of effluent quality.

A promising new concept builds up upon advanced primary treatment, extracting as much organics as possible with physico-chemical processes to maximize sludge production and minimize energy demand for biological treatment. This concept consists of coagulation and flocculation of raw wastewater, followed by low-energy microsieve filtration (100 µm) to separate the sludge. However, post-treatment will be required to remove nitrogen and guarantee effluent quality in terms of COD, N, and P concentration. Pilot trials of microsieve filtration with real wastewater proved that is is possible to extract 70-80% of COD from raw wastewater (Remy et al. 2014). Holistic energy balances of respective treatment schemes, based on industrial scale pilot trials and including post-treatment in biofilter for nitrification and denitrification with external carbon source show that these new concepts are superior to a reference activated sludge process in net energy balance, reaching a comparable effluent quality (**Figure 19**). Although energy demand for chemicals production has been taken into account, microsieve filtration and subsequent biofilter have a positive net energy balance, making this scheme finally an "energy-positive" WWTP. Following this proof of concept, it is planned to demonstrate the performance and energy balance of this new concept in a full-scale WWTP of smaller size (2000 pe) as a next step.

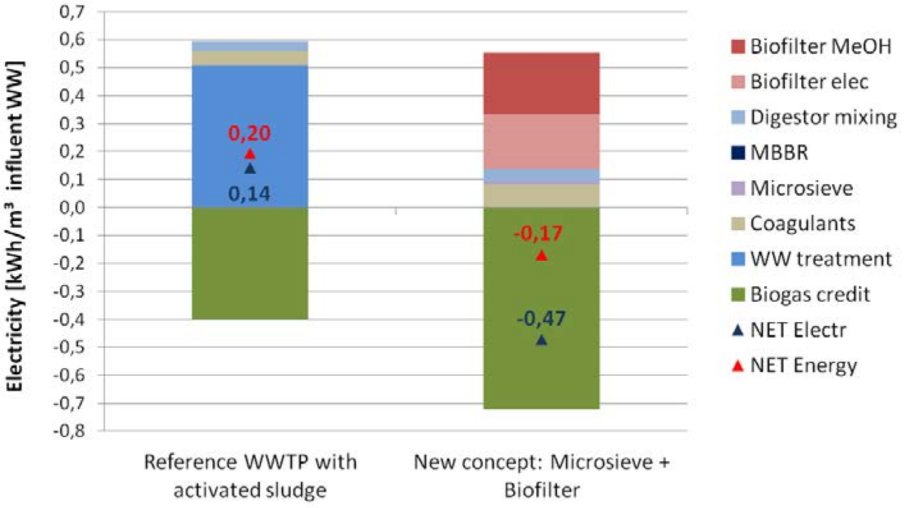

Figure 19: Energy balance for reference WWTP and new treatment scheme with comparable effluent quality (100 mg/L COD, 18 mg/L N, 2 mg/L P)

CONCLUSION

The presentation and final paper will further discuss the benefits and challenges of integrating energy and resource recovery in existing and new concepts for wastewater treatment schemes to provide an overview of available processes and identify research needs for a sustainable and ecoefficient wastewater treatment plant of the future.

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(P53) Alternative Membrane Bioreactor treatment lines with high energy efficiency

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Abstract

Energy consumption remains the key factor for the improvement of MBR performance. This paper presents a study comparing four alternative hybrid membrane bioreactor treatment trains based on the assumption that only dry weather peak flow is treated by the membranes, the wet weather flow being diverted towards more conventional process units, thus reducing the required membrane area and the associated air scouring flow. Criteria for comparison include civil work and membrane costs, energy costs and environmental impacts simulated by Life Cycle Analysis. The results demonstrated a high potential for energy savings up to 40 % of these alternative MBR treatment lines, which in most cases are associated however to higher environmental impacts.

Keywords
energy consumption, hybrid systems, LCA analysis, membrane bioreactors, wastewater treatment

INTRODUCTION

Membrane bioreactors (MBRs) are now widely used in wastewater treatment but despite the advantages over conventional activated sludge (smaller footprint, high effluent quality) they still suffer from higher operational costs mainly due to higher energy consumption. One of the main energy consumers is the air required for membrane scouring to limit the fouling (Barillon et al., 2013).

To ensure a high quality effluent during wet weather conditions, MBR installations are most of the time designed on wet weather peak flow, assuming that membranes can handle a higher flow during a limited amount of time. In other words, membrane surface ensures that the whole effluent flow rate, based on wet weather peak flow, is treated by the MBR, resulting in the fact that, during dry weather, the membrane surface will not be used at its full capacity. Such flexibility is necessary as wastewater flow variations are very high, in particular for combined sewer systems. As a consequence of varying fluxes, the calculation of membrane area is a matter of how much risk can be taken. Obviously, the larger the membrane area is, the lower the risk. Moreover, the design generally comprises a spare treatment line in case of failure of one of the treatment lines. The associated capital and operating costs for aerating the membranes are an important disadvantage.

Driven by refurbishment considerations and especially by the opportunity of reusing existing buildings and infrastructure, alternative hybrid MBR configurations were proposed (Krzeminski et al, 2012; Frechen, 2010), where part of the wastewater is treated in a conventional activated sludge system and part is treated by the MBR. Diverting part of the flow from the MBR towards other less expensive process units would enable to reduce the membrane area and to operate the MBR under more constant conditions closer to the design and would significantly reduce the energy demand. This is indeed particularly important in the case of MBR facilities operated at lower loads, less than 50% of the nominal design, as the resulting specific energy consumption becomes relatively high due to the important fraction of fixed energy.

A case study, comparing four alternative hybrid MBR configurations to conventional MBR in terms of capital (civil and membranes) and energy costs, was undertaken for a large wastewater treatment plant as a reference. Life cycle analyses were also carried out for the selected trains to assess their environmental impact.

MATERIAL AND METHODS

A reference wastewater treatment plant (WWTP) of 150,000 p.e. with a ratio “wet weather peak flow (WWPF) / dry weather peak flow (DWPF)” of 3 and a ratio “dry weather peak flow / dry weather flow” of 1.5 is considered to compare all the selected treatment trains. Flow rate during wet weather equals 31,380 m^3/h and the WWTP is designed for C, N and P removal with a mass load of 9,200 kg BDO_5/d.

Five selected treatment trains are considered: (i) conventional MBR, (ii) MBR with primary settling tank in serial, (iii) MBR with primary settling tank in parallel (only used in case of wet weather), (iv) MBR with additional clarifier and (v) MBR and conventional activated sludge (CAS) in parallel.

Membranes are hollow fibre type and are intermittently scoured by an air flow calculated on the following sequence: 10/30 aeration during 80 % of the time and 10/10 aeration during 20 % of the time. The nominal air flow for the membrane scouring is set to 0.4 $L.m^2_{membrane}.h^{-1}$.

In configuration (v), the presence of biomass in the second treatment line (CAS) requires a minimum influent flow for this line, even during dry weather. Consequently, the membrane surface is not sized on the basis of the dry weather peak flow but on the basis of a lower flow, taking into account the flow required by the CAS. The distribution percentage between both lines is set to 70 % (MBR) – 30 % (CAS) during dry weather and 50 %– 50 % during wet weather.

In the MBR treatment lines, MLSS concentration is set to 6 g/L in the aerobic tank and 8 g/L in the membrane tanks, corresponding to a recirculation rate of 300 % of the annual average dry weather flow. Exception was made for configuration (iv) with a MLSS concentration of 4 g/L in the aerobic tank in order to keep the sedimentation properties of the sludge in the clarifier during wet weather periods. In the CAS treatment line, MLSS concentration is set to 4 g/L.

In this comparative study, CAPEX comprise civil works the initial cost of the membranes installed in the membrane tanks while OPEX only comprise the energy costs for pumping, for biology aeration and membrane scouring.

An assessment of the environmental impact of each one of the selected configurations is done through a life cycle analysis (LCA). SimaPro© software v7.3.3, developed by Pre Consultant, was used. The selected calculations methods are ReCiPe v1.07 in the Europe hierarchist version and Usetox Recommended v1.01. Twelve impact categories are considered in the present study. They are included in the eighteen impacts proposed by ReCiPe method and the three impacts proposed by Usetox method.

RESULTS AND CONCLUSIONS

As shown in Table 1, configurations (ii) and (iii), with a primary settling tank, have lower CAPEX due to the fact that membranes were sized on the DWPF and not on the WWPF. Configuration (iv) presents significantly higher CAPEX as the MLSS concentration in the biological reactors should not exceed 4 g/L to ensure the sludge sedimentation in the clarifier. As a consequence, the volume of the biological tanks have to be increased, resulting in higher footprint. In configuration (v) the gain in the membrane surface, designed on the basis of 70 % of the flow is counterbalanced by the CAPEX related to the independent CAS treatment line.

In all cases, energy consumption is reduced, from 20 to 40%, thanks to the decrease of energy consumption for air scouring. In configurations (ii) and (iii), the higher percentage of energy reduction is related to the decrease in organic load from the primary settling tank.

Table 1: Comparison of capital (civil work and membranes) and energy costs for the selected alternative hybrid MBR trains with conventional MBR.

Configurations	Energy reduction / conv. MBR	CAPEX / conv. MBR	Reasons for improvement	Drawbacks
(ii) MBR with primary settling tank in serial	40 %	- 30 %	Lower influent flow, lower pollutant load	Lower quality of effluent overflow during wet weather (only decantation)
(iii) MBR with primary settling tank in parallel	30 %	- 35 %	Lower influent flow, lower pollutant load	
(iv) MBR with additional clarifier	20 %	+ 55 %	Lower influent flow	Lower quality of effluent during wet weather (clarification)
(v) MBR and CAS in parallel	20 %	+ 10 %	Lower influent flow	

If the quality of effluent can be decreased during wet weather, the addition of a primary settling tank, configurations (ii) and (iii), is beneficial to both CAPEX and energy consumption. Mitigation of decanted water with permeate could be a way to limit the impact on the environment. In addition, this type of treatment implies to take into account the primary sludge and to design an appropriate sludge treatment line, including an anaerobic digestion unit for instance.

In configurations (iv) and (v) reduction of energy consumption is still significant, up to 20 %, but CAPEX are higher. These configurations would be recommended for plant refurbishment.

The selected treatment lines, even if they appear relevant in terms of energy reduction, may result in a greater environmental impact, especially in configurations (ii) and (iii) where the wet weather effluent is only decanted. Life cycle analysis is a means for establishing a hierarchy in these configurations, by selecting the most sustainable ones.

Figure 1 is a comparative radar graph with configuration (i) as a reference. LCA simulations show that the two configurations equipped with primary settlers to treat storm water present a higher impact in terms of eutrophication due to the effluent quality (N and P removal efficiency) and a non-negligible impact in terms of toxicity (human and freshwater toxicity). Configurations (iv) and (v) have a smaller environmental footprint than the conventional MBR plant except for toxicity impacts slightly higher than the reference because of the discharge in water of a higher quantity of micro pollutants. However, the other impacts are reduced thanks to the energy consumption reduction, which is the first goal of these configurations.

The CAS plant exhibits a smallest environmental footprint except for the ecotoxicity impact. The reduced footprint is easily explained by the fact that the energy consumption is reduced, the acid citric consumption is null and the effluent quality, in terms of nitrogen and phosphorous is equal to the conventional MBR plant. Nevertheless, the lower efficiency regarding the micropollutants removal of this configuration implies a significant impact in terms of freshwater ecotoxicity.

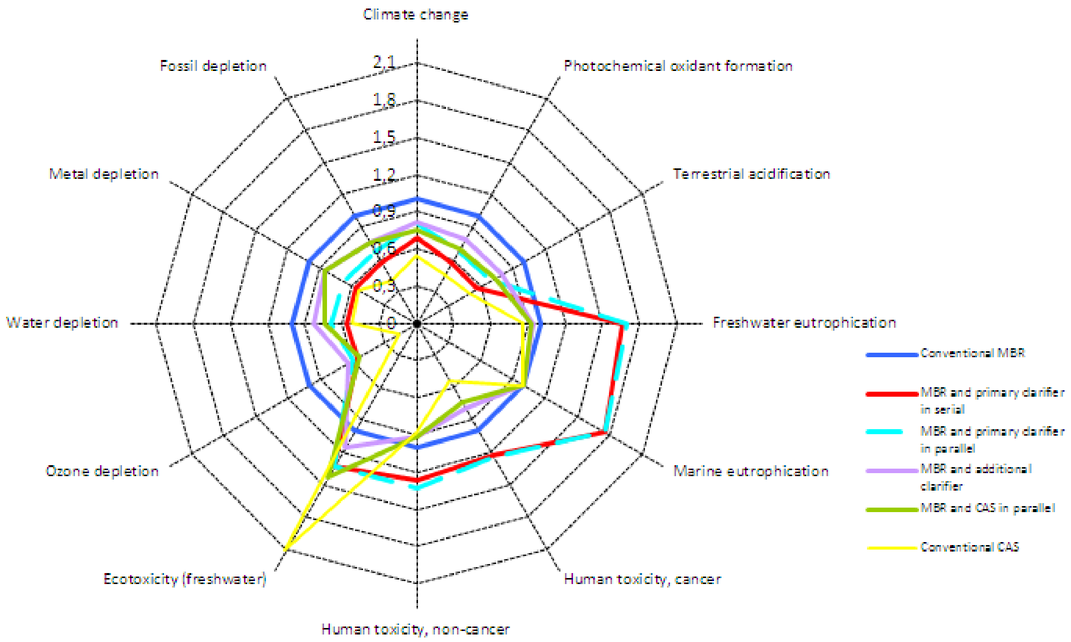

Figure 1: Comparison of the resulting impacts from LCA analysis for the 4 selected alternative MBR trains and conventional CAS. Reference: conventional MBR

This comparative study demonstrated the potential in terms of energy reduction of alternative hybrid MBR treatment lines based on a design of membranes on dry weather peak flow. The results also highlighted that the counterpart of high energy savings is an increase of the environmental impact of the hybrid treatment train. The implementation of these alternative treatment lines will be possible if discussions are conducted on the usage of the treated effluent: industrial water, re-use,… and if derogations are given for the discharge of a lower effluent quality during rain events.

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Efficient Technologies - Energy Efficiency and Novel Biological Processes

(Wedneday, 25 June 2014, Aula T2, Polo Zanotto)

(P54) The Study on the Energy Potential Flow Analysis for the Energy balanced Sewage Treatment Plant

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Abstract

To improve the independent, generation of electric power by utilizing the organics in sewage influent, an analysis was made of the behaviour of organics within the plant, together with electric power consumption, in the form of energy flow. The energy potential was calculated from COD, and the behaviour in each process was studied. About 10% of the energy potential could be recovered by power generation with digestion gas, but most of the energy potential was lost in mineralization in the aeration tank and incinerator. Methods that could be used to raise electric power independence were evaluated in terms of "Required COD" for independence. 1500 mg/L of COD is required even at 100% recovery of solids. However, 800 mg/L of COD will be calculated if the specific energy consumption could be reduced by 50% to 0.25kWh/m3 by promoting energy saving.

Keywords

Energy Flow Analysis, Energy Potential, Organic Matter, Sewage Treatment plant

Introduction

In Japan, since the Great East Japan Earthquake, concern about possible insufficient supplies of electric power has led to studies on the feasibility of energy recovery and the promotion of further power saving in sewage treatment plants.

For the purpose of improving electric power independence through utilization of organics in sewage influent in Japan, power consumption and the behaviour of organics in treatment plants (recovery, mineralization) was analyzed as energy flows. This was done to identify issues related to organics consumption and measures for improvement of independence

Material and Methods

To better understand the behaviour of organics in Sewage treatment plants, the Performance Evaluation System (Fukushima and Somiya, 2009) was applied for a model plant, and an energy flow analysis was conducted on the basis of changes in water quality and electric power consumption in each process. With a view toward introducing digestion gas power generation assumed, the thermal energy of methane (CH_4) was converted to the energy (electric power) on the basis of the methane amount per 1 g of COD, and 3.49kWh/kg COD (CORNEL et al, 2012) was used for calculation.

Results and Discussion

Changes in the energy potential in each treatment process are presented together with the electric power consumption (shown as negative values) in Figure 1. (Left: sewage treatment, Right: sludge treatment). The energy potential of the organics in the sewage influent was reduced by about 30% due to primary sludge withdrawal (recovery) and by 50% through mineralization in the aeration tank. In the digestion tank, 60% (about 10% of the potential of the influent sewage) was recovered in the form of digestion gas. Digested sludge was mixed with centrifugally thickened sludge and dewatered for final mineralization in the incinerator. The total electric power consumption of the sewage treatment plant is about 25,000 kWh/day (pecific energy consumption: 0.53kWh/m3), and 90% of the energy potential (60,000 kWh/day) of organics in the influent sewage, other than the 10% recovered in the form of digestion gas, is lost. It was, therefore, estimated that energy equivalent to about 40% of the consumption came from the additional energy applied.

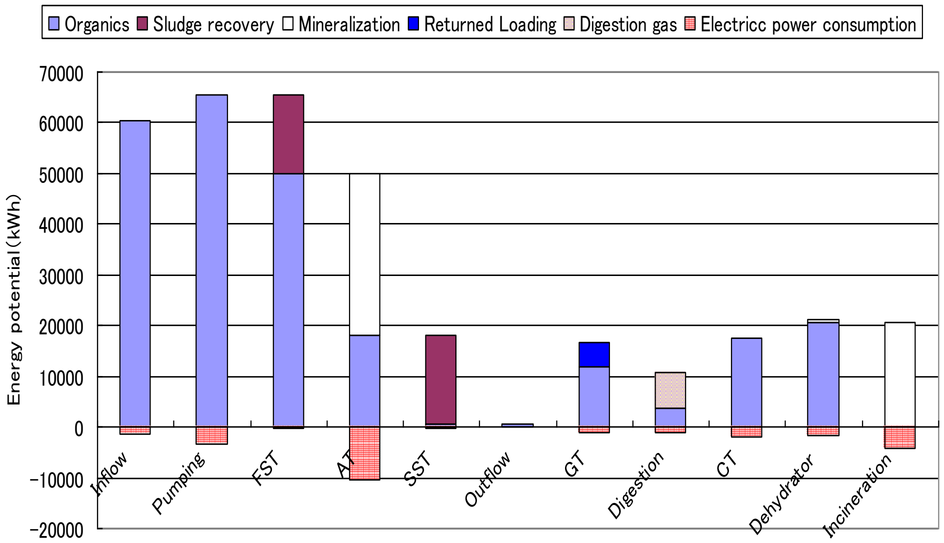

Figure 1. Change in the sewage treatment plant of the energy potential

In this context, the improved electric-power self-supply ratio enabled by a decrease of the consumption rate due to an increase in the organics recovery rate and by promoting energy saving was calculated as “COD concentration necessary (required COD) for independence.”

Required COD (mg/L) = Consumption rate /3.49 x electric power recovery ratio

With a normal specific energy consumption of 0.5kWh/ m3, 1500 mg/L of COD will be required even at 100% recovery of solids, which means that the possibility of energy independence is very low. However, 800 mg/L of COD is calculated if the power consumption rate could be reduced by 50% to 0.25kWh/m3 by promoting energy saving. This indicates an increased possibility of energy independence.

Conclusions

Using the performance evaluation system (PES) of sewage treatment plant for overall evaluation of the effluent quality and energy consumption we examined the behaviour in the sewage treatment plant by energy analysis. Furthermore, we examined some electric power independence improvement measures with an index of the Required COD for independence. The result is summarized below:

1) Approximately 10% of the energy potential of organics in sewage influent could be recovered through power generation with digestion gas. Most of the potential was lost due to mineralization in the aeration tank and incinerator.

2) Electric power independence is difficult to achieve at the normal specific energy consumption, but the possibility of doing so can be expected to rise through positive recovery of organics and promotion of energy saving.

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(S39) Energy efficient WWTPs: simulation and validation of a decision support system through modelling

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Abstract

Mathematical modelling has been tested as a decision support system to management of a biological WWTP, aimed at optimizing energetic efficiency. A conventional activated sludge plant has been studied and the ASM1 mathematical model has been implemented, calibrated and validated, by using West® 2012, DHI software. Optimal operating strategies, under different operating conditions, such as variable influent loading, have been defined. Also, indicators concerning energy efficiency and effluent quality have been defined and quantified.

Keywords

WWTP simulation, modelling, EDSS, effluent quality, energy efficiency

INTRODUCTION

Wastewater treatment plants (WWTPs) must ensure effluent quality standards under variable influent loading and different operating conditions. Olsson (2006) showed that the use of appropriate instrumentation, control and automation (ICA) tools may improve energy and depurative efficiency up to 30%. To this aim, mathematical models are frequently used for the simulation of biological processes (Gernaey et al., 2004) and several advanced control strategies have been designed using both model based (Demey et al., 2001) and soft computing techniques, such as artificial neural networks and fuzzy logic (Ruano et al., 2010).

Dynamic simulation of WWTPs based on mathematical models offers several benefits, such as the predetermination of organic matter and nutrient removal efficiency for different scenarios, such as, for example, substantial changes of influent loading and quality. Simulations have been performed on a pilot-scale, continuous-flow conventional activated sludge (CAS) plant, fed on real wastewater, aiming at achieving the maximum energy efficiency under different loading conditions. The experimentation is part of a wider project, coordinated by ENEA (section UTVALAMB IDR - Water Resource Management, based in Bologna) in collaboration with the multi-utility Hera SpA (Bologna) and Politecnico di Milano, aiming at developing automation and control of WWTP based on simple, cheap and reliable probes, measuring dissolved oxygen, pH and redox potential. These indirect signals will be used to implement PI controllers (and, in the near future, fuzzy-logic based controllers) acting on air flow and internal and external recycle flow-rates.

MATERIALS AND METHODS

Pilot plant

Figure 1 and 2 show a schematic and the front view of the pilot plant, located inside the area of the municipal WWTP in Trebbo di Reno (Bologna). The plant is composed of a pre-denitrification tank (95 L), an oxidation tank (162 L), a secondary sedimentation tank (85 L). Mechanical equipment includes a stirrer, a variable-flow blower connected to a fine bubble membrane diffuser, three peristaltic pumps: one is used for influent loading (460 l/d), and the other two for internal (760 l/d) and external (430 l/d) recycle flows. The plant was fed with real wastewater, taken downstream of the full-scale micro-screen and was provided with probes to measure pH, ORP, NH_4^+-N, NO_3^--N in the anoxic tank and pH, ORP, DO,

NH_4^+-N, NO_3^--N and TSS in the aeration tank. Data are acquired and stored by a data logger stand-alone dataTaker DT 80, at a frequency of 1 per minute.

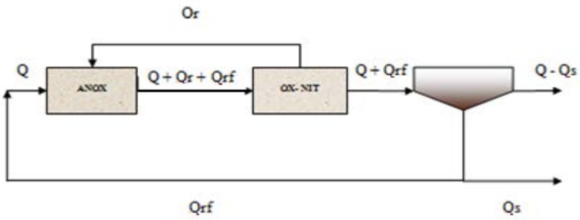


Fig. 1: CAS *block diagram*

Fig. 2: *pilot plant front view*

Modeling and respirometry

The ASM1 dynamic model of the plant has been implemented in WEST DHI 2012 (Vanhooren et al., 2003), following the protocol defined in Petersen et al. (2002). Respirometric tests for biomass and wastewater characterisation were carried out with M.A.R.TIN.A (Multiple Reprogrammable TitratioN Analyser) (Artiga et al., 2005), a titration biosensor that allows to measure the bacterial activity in sludge samples, at constant DO and pH (thus, it is a pH and DO-stat titration).

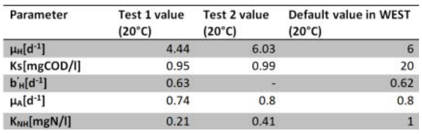
Analyses

Wastewater was sampled at a frequency of 1 sample/h by an automatic sampler, ISCO 6712. Six data sets of 24 h were collected and the daily variability has been expressed as arithmetic means and 95% confidence range. DO, pH and ORP were continuously measured by two modular multi-parameter measuring systems WTW IQ SENSOR NET. Occasionally, COD, ammonium, nitrate, nitrite and TKN have also been measured by chemical analyses according to Standard Methods (APHA, 1995).

RESULTS

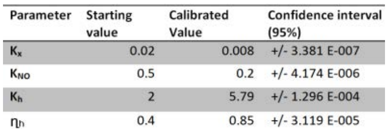
Simulation and control logic implementation

The kinetic parameters measured with respirometric tests are reported in Table 1, while Table 2 and Table 3 report the calibrated parameters concerning the anoxic and the aerobic tank, respectively.



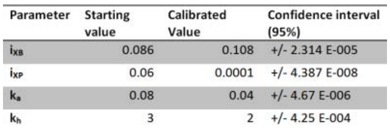
Parameter	Test 1 value (20°C)	Test 2 value (20°C)	Default value in WEST (20°C)
μ_H[d^{-1}]	4.44	6.03	6
Ks[mgCOD/l]	0.95	0.99	20
b'_H[d^{-1}]	0.63	-	0.62
μ_A[d^{-1}]	0.74	0.8	0.8
K_{NH}[mgN/l]	0.21	0.41	1

Table 1: kinetic parameters



Parameter	Starting value	Calibrated Value	Confidence interval (95%)
K_x	0.02	0.008	+/- 3.381 E-007
K_{NO}	0.5	0.2	+/- 4.174 E-006
K_h	2	5.79	+/- 1.296 E-004
η_h	0.4	0.85	+/- 3.119 E-005

Table 2: parameters calibrated for the anoxic tank



Parameter	Starting value	Calibrated Value	Confidence interval (95%)
i_{XB}	0.086	0.108	+/- 2.314 E-005
i_{XP}	0.06	0.0001	+/- 4.387 E-008
k_a	0.08	0.04	+/- 4.67 E-006
k_h	3	2	+/- 4.25 E-004

Table 3: parameters calibrated for the aerobic tank

Improvements of water quality in the tanks and in the effluent were evaluated with different control strategies and the corresponding simulation results are shown in Figures 3 and 4.

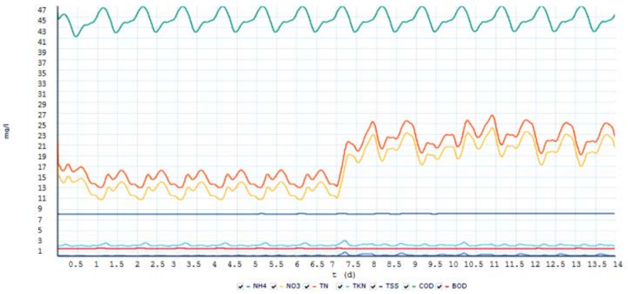


Fig 3: pollutant concentration in effluent (*open loop simulation)*

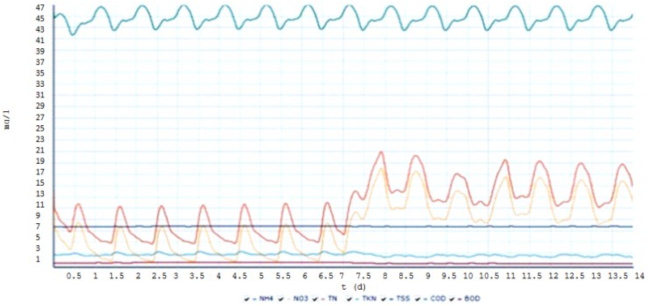


Fig 4: pollutant concentration in effluent (*cascade control simulation)*

Fifteen control logics have been defined and simulated (Di Cosmo, 2012). One of the most significant is the cascade control of dissolved oxygen in the aerobic tank. The implementation of the cascade controller with DO variable minimizes aeration requirements, thus improving energy savings (Yoo and Liu, 2011).

If the ammonia concentration is too high, then DO set-point increases and vice versa. Normally, one sets the minimum and maximum rate of change of the DO set-point; however optimization may push the value of ammonia set-point up, but below ammonia effluent allowable concentration limit for discharge. A first PI controller fixes the ammonia set-point at 1 to 1.5 mg/l while the second PI controller has a variable DO set-point with a hysteresis cycle between 0 to 2.5 mg/l as a function of NH_4^+-N concentration in the aerobic tank. This allows setting the aeration so that the nitrification process produces the maximum allowable effluent ammonia concentration, while effluent nitrate concentration is reduced consequently (Figure 4). The parameters of the controllers used are shown in Tables 4 and 5.

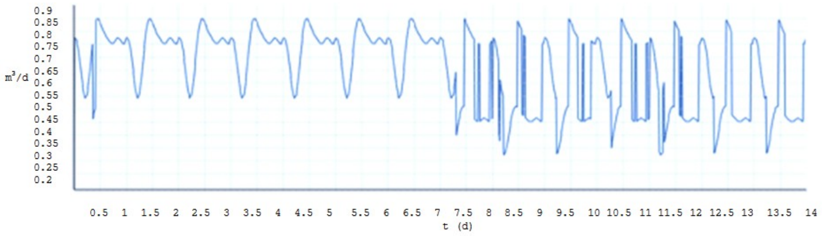
Controller Type	PI	Unit
Proportional Gain (K_p)	250	$m^3(g(-COD))^{-1}d^{-1}$
Integral time constant (t_i)	10	minutes
Controlled variable	S_0 in aerobic tank	
Set point	2-1-0.5	mg/l
Manipulated Variable (VM)	K_La	d^{-1}
VM max value	300	d^{-1}

Table 4: parameter for *Oxygen PI controller*

Controller Type	PI	Unit
Proportional Gain (K_p)	-10	$m^3(g(-N))^{-1}d^{-1}$
Integral time constant (t_i)	50	minutes
Controlled variable	S_{NH} in aerobic tank	
Set point	1.5-1	mg/l
Manipulated Variable (VM)	y_s controller DO	mg/l

Table 5: parameter for ammonia *PI controller*

This controller is also associated with the variation of internal and external recirculation, maintaining a constant proportion with the influent flow-rate. A further analysis involved the use of a strategy to support critical transitional phases, during which nitrate may build up in the anoxic tank, for example when internal recirculation is too high compared to the available biodegradable carbon, adversely affecting the denitrification process. The modulation of the internal recirculation flow allows stabilizing nitrate concentrations in the anoxic tank around a set point of 2 mg/l. An ON | OFF controller sets the internal recirculation flow rate to the 80% of the influent flow rate, if measured nitrate (SNO3) increases over the set point, else it increases it to 165%. Figure 5 displays the flow profile of the internal recirculation and the values of nitrate in the anoxic tank, with a set-point around a value of 2 mg/l.



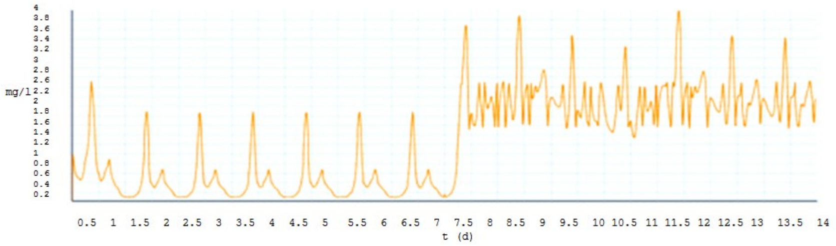


Fig. 5: *Trend of the internal recirculation flow (in m^3/d, above) and corresponding trend in the concentration of nitrate in the anoxic tank (in mg/l, below).*

The results show that these strategies can improve both energy savings and effluent quality. Following the Benchmark approach (Copp, 1999) several indicators have been considered and calculated (Figure 6). First of all, the Effluent Quality Index and the percentage, over time, when total nitrogen exceeded the effluent threshold value established for sensitive areas. The latter was tested as an evaluation index, because the facility is not located in a sensitive area. The calculation included the value of kLa in the aeration tank within 14 days of simulation, as this parameter is related to the intensity of aeration and, hence, to the power used by the air-blowers. Energy costs have been evaluated at a price of 0.14 €/kWh, with an oxygen transfer rate of 1.8 kgO/kWh.

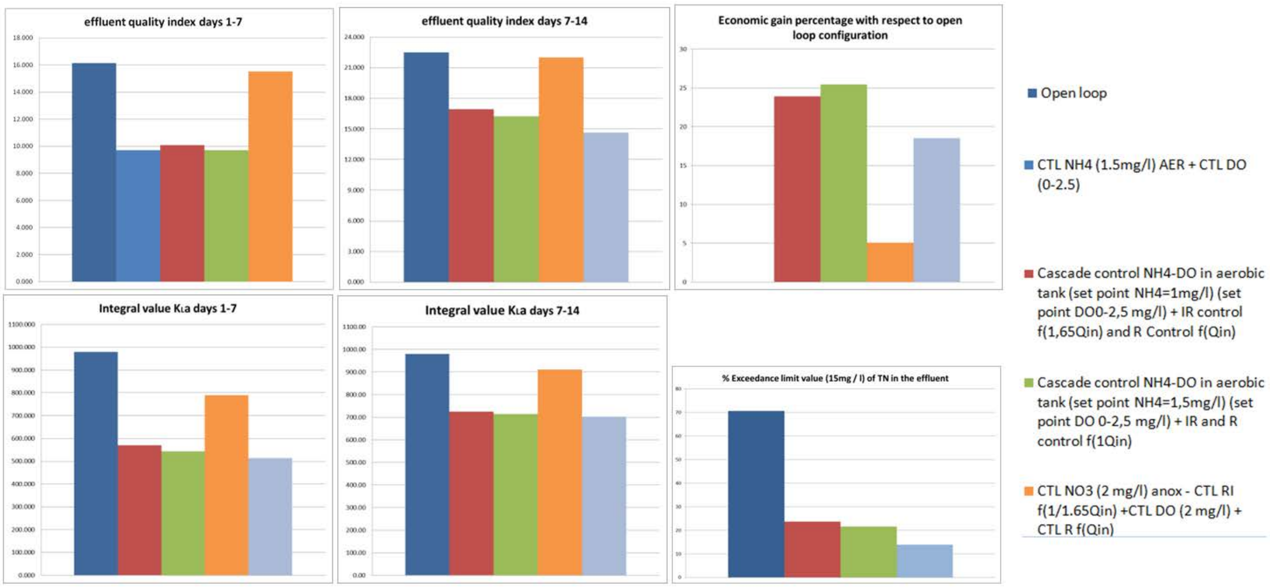


Fig. 6: *Results of the economic evaluations using different qualitative control strategies.*

CONCLUSIONS

The adverse effects of the very high daily variability of the wastewater characteristics on the performance of the biological processes in the WWTP could be counteracted by control strategies In particular, the NH_4-DO cascade control proved very efficient in improving the energy and quality performance of the biological processes when nitrate is measured in the anoxic tank as the controlled variable and this is associated with an active control of the internal recirculation.

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(S40) The influence of the external factors on the catabolic pathways in the mixed-culture fermentation

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Abstract

It is anticipated that by changing the parameters of the anaerobic digestion process it will be possible to produce, based on volatile fatty acid platform, desired chemical compound from sewage sludge and agricultural or municipal by-products/wastes. The aim of the project is to investigate the impact of several different external factors (temperature, substrate composition and concentration, pH, and C/N ratio) on catabolic pathways during the anaerobic mixed-culture fermentation. In the future perspective, the expected results will have a great positive impact on the development of highly efficient mixed-culture fermentations in order to produce high value biochemicals.

Keywords

Anaerobic digestion; volatile fatty acids; mixed culture fermentation;

INTRODUCTION

Mixed-culture fermentation is a common process but it is still considered as a “black box”. Currently, biofuels and biochemicals derived from agricultural and municipal wastes are not widely available, despite the numerous benefits they could bring to the society in the form of energy/chemicals security, job market expansion, and greenhouse gas abatement. In response to these challenges, the proposed project aims at identifying different possibilities to generate new products as well as discover new ones. Understanding the impact of several factors on this complex but widely occurring process will significantly extent knowledge about it. In a longer perspective, it will help utilizing various waste streams generated by nowadays societies.

Anaerobic digestion is a biological process where most organic matter (carbohydrates, lipids, proteins) except for lignin components, in the absence of oxygen, is degraded into methane and carbon dioxide. The process consists of series of reactions and it is a natural process which takes places in several anaerobic environments. In anaerobic digestion processes can be divided into (Gujer and Zehnder, 1983; Angelidaki et al., 2003).

The most suitable raw material for sustainable processing is biomass. Biomass can be considered as one of the most sustainable resource for organic fuels, chemicals, and materials. Growing plants consume CO_2 - therefore biomass-based products can be included in photosynthesis carbon cycle reaching almost CO_2-neutral lifecycle. Moreover, the biological processes are mostly carried out in aqueous environment and the effluents are non-toxic to the environment and easy to discharge. In some cases, the effluents can be even valuable by-products (Demirbas, 2006). Biomass resources occur in variety of ways, such as woody and herbaceous species, wood wastes, bagasse, agriculture and industrial residues, waste paper, municipal solid wastes, sawdust, biosolids, grass, waste from food processing, animal wastes, aquatic plants and algae, and so on.

DISCUSSION

Typically, anaerobic digestion provides renewable energy source (biomethane) and it also delivers highly efficient natural fertilizer (Angelidaki et al., 2003). Biological conversion such as anaerobic digestion that converts wet biomass waste into biogas is a well-established technology (Holm-Nielsen et al., 2009), whereas conversion of biomass waste to high-value biochemicals is only in the exploratory research phase. The main advantage of the mixed-culture fermentation is that it consists of stable microbial population (as the one typically found in nature), another is that less pure substrates or even waste (e.g. wastewater, manure, etc.) could be potentially used as a substrates (Rodriguez et al., 2006). Agriculture by-products and waste streams are being produce in vast amounts; its utilization into useful products would bring great advantage. First of all it would decrease the amount of waste generated, secondly it would provide sustainable products (in contrast to fossil fuels based product) cutting down green-house gasses emission.

The process consists of series of reactions. Potential compounds obtained through mixed culture fermentations are: mixture of volatile fatty acids, alcohols or lactate - a possible building blocks for other processes (Rodriguez et al., 2006). The most possible options using volatile fatty acids (VFAs) platform is presented on Fig. 1.

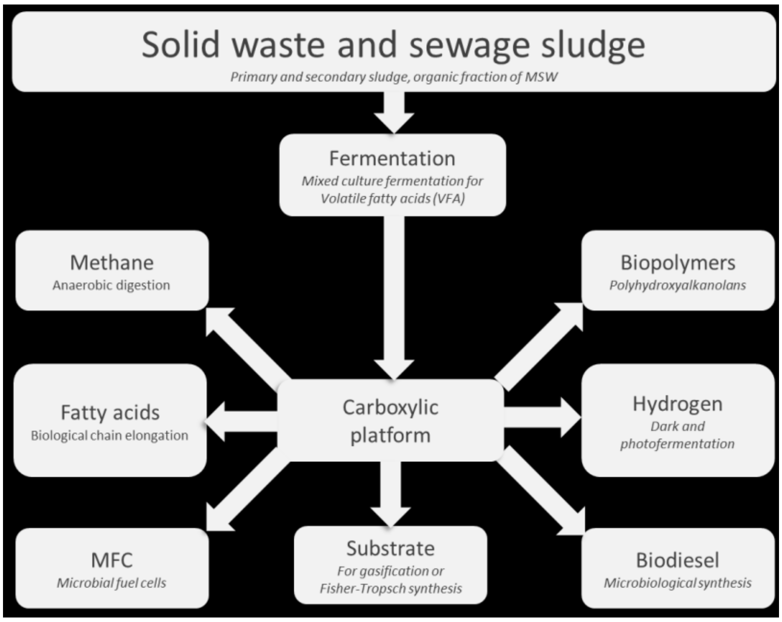

Figure 1. Carboxylic platform for wastewater treatment plant.

CONCLUSIONS

Ultimately, the achieved results in the project will be a great foundation for development of the biorefinery facilities fed with waste. It will bring closer a society run by sustainable processes where the waste streams are minimized and where the environmental protection and sustainable development is a priority.

Acknowledgment

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(S41) Metabolic behaviour of Tetrasphaera and Accumulibacter populations in enhanced biological phosphorus removal

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Abstract

While *Tetrasphaera* and *Accumulibacter* are both abundant polyphosphate accumulating organisms in full-scale enhanced biological phosphorus removal (EBPR) systems, little is known about the metabolic behaviour and ecological niche that each organism exhibits in mixed culture communities. An enriched culture of*Tetrasphaera* and *Accumulibacter*was obtained using casein hydrolysate as sole carbon source. This culture was able to achieve a high phosphorus removal efficiency (>99%), where both groups of organisms stored polyphosphate. Microautoradiography and fluorescence *in situ* hybridisation (MAR-FISH) was used to characterize the substrate uptake of the culture. Glucose and amino acids were taken up by three of the probe defined populations (Tet1-266, Tet2-174, and Tet3-654) while *Accumulibacter* were not able to uptake any of the substrates.This study will improve our understanding of EBPR and enable novel process optimisation strategies.

Keywords

Tetrasphaera-related bacteria, Candidatus*Accumulibacter*phosphatis, enhanced biological phosphorus removal (EBPR).

INTRODUCTION

The enhanced biological phosphorus removal (EBPR) process is an efficient, relatively inexpensive and environmentally sustainable option for phosphorus (P) removal in wastewater treatment plants (WWTP). *Accumulibacter*is the most widely known polyphosphate accumulating organism (PAO), able to accumulate large amounts of polyphosphate (poly-P) aerobically after taking up organic substrates anaerobically. Besides *Accumulibacter*, *Tetrasphaera*-related organisms are also putative PAOs that can take up phosphate aerobically and store it intracellularly as polyphosphate,while assimilating different organic substrates under anaerobic conditions(Kong et al., 2005; Nguyenet al., 2011). *Tetrasphaera* were also reported to ferment glucose anaerobically, to synthesise glycogen as a storage polymer for aerobic growth and replenishment oftheir intracellular polyphosphate reserves (Kristiansen et al., 2013). Quantitative FISH analyses reveal that *Tetrasphaera*are usually present in a higher abundance than *Accumulibacter*, in full-scale EBPR systems up to 30% of the total biomass in EBPRs in Denmark (Kong et al., 2005; Nguyenet al., 2011; Mielczarek et al., 2013) and in the interval of 20-30% in Portuguese EBPR plants(Lanham et al., 2013). Nevertheless, little is known about the P removal efficiency of *Tetrasphaera*-related organisms in EBPR systems or their metabolic behaviour, as it is difficult to distinguish their activity from *Accumulibacter*, particularly in full-scale systems. A better understanding of their ecophysiology is needed to understand their function, improving our understanding of the EBPR process and our ability to optimize it.

MATERIALS AND METHODS

A sequencingbatch reactor (SBR) with 0.5L working volume was inoculated with sludge from a WWTP in Setubal, Portugal. The SBR was operated with 8h cycles, including an anaerobic phase (4h), a settling/decant phase (1h) and an aerobic phase (3h) with a HRT of 16h.A synthetic medium containing casein hydrolysateas the sole carbon source was fed anaerobically. The pH and temperature were controlled at ≤7.1 and 20ºC, respectively.

The performance of the reactor was assessed through chemical and biological methods. Chemical analyses included phosphate(colorimetry), VFAs and glycogen (high-performance liquid chromatography), polyhydroxyalkanoates(PHAs -gas chromatography), total organic carbon (TOC – Shimadzu),and ammonium (potentiometric sensor) throughout the anaerobic/aerobic phases, and total suspended solids and volatile suspended solids at the end of each aerobic phase (Standard Methods).Fluorescence *in situ*hybridisation (FISH)was performed at the end of the anaerobic and aerobic phases using the probes developed by Nguyen et al. (2011) for *Tetrasphaera*,besides the classical probes for *Accumulibacter*. Microautoradiography combined with FISH (MAR-FISH)wasperformed as detailed in Nguyenet al., (2011) to investigate the substrate uptake of probe-defined members of the genus *Tetrasphaera* and *Accumulibacter*.

RESULTS AND CONCLUSIONS

As shown in Figure 1, casein hydrolysatewas taken up during the anaerobic phase,which was accompanied by P release and glycogen hydrolysis. In the subsequent aerobic phase, the culture was able to use a currently unidentified internal storage product for biomass growth and for replenishing the polyphosphate and glycogen pools. A very low PHA production and consequently consumption was detected in the anaerobic and aerobic phase. A high P removal efficiency was maintained in the SBR (>99%). This mixed culture also showed a high intracellular P content, accounting for 10% of the TSS concentration.

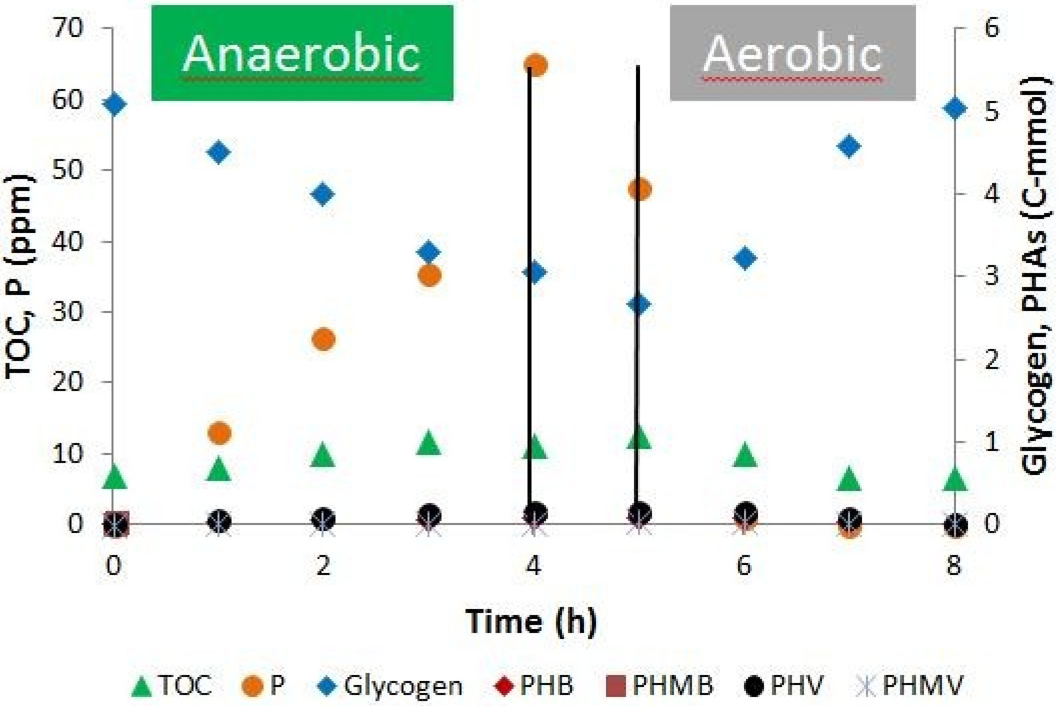

Figure 1. Typicalcycle study during SBR operation. Between the solid lines, the settling and decant phases occur.

Upon comparing the results from the *Tetrasphaera* culture with typical *Accumulibacter* parameters,the culture displayed comparable levels of intracellular P, glycogendegradation and P release,while much lower PHA production was found (Table 1). The storage compound being utilised by this culture is currently under investigation.

Table 5. Results from a typical cycle study during SBR operation comparing it to typical results from

studies with *Accumulibacter* performed by Smolders et al. 1994 (a) and Oehmen et al. 2005 (b).

Parameter	SBR Culture	*Accumulibacter* **Acetate**	 **Propionate**
P (% of TSS)	10	7-17	7-17
PHAs(C-mmol/C-mmol substrate)	0.04	1.33^{a}	1.22^{b}
Glycogen(C-mmol/C-mmol substrate)	0.33	0.5^{a}	0.33^{b}
Prelease(Pmmol/C-mmol substrate)	0.2-0.3	0.5^{a}	0.4^{b}

From FISH analysis, all 4 previously described groups of *Tetrasphaera*(Nguyenet al., 2011) were present in the biomass, as well as *Accumulibacter*Type I and II.As shown in Figure 2, the *Tetrasphaera*showed different morphologies, including filaments and thin filaments, some cocci in tetrads and short rods. Methylene blue staining showed the presence of polyphosphate inside *Tetrasphaera*and *Accumulibacter*cells (data not shown). Thus, both microbial groups were likely contributing towards P removal, a situation that is similar to full-scale EBPR plants.

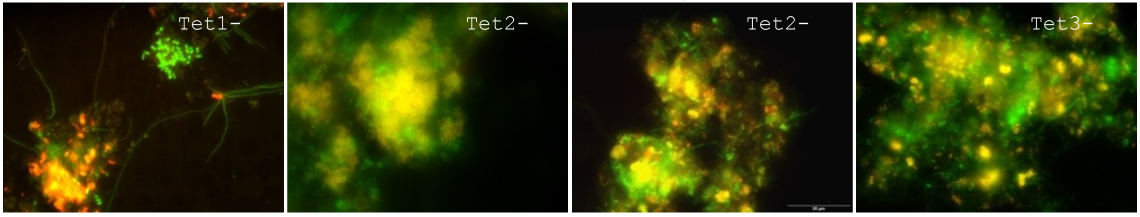

Figure 2. FISH images of *Tetrasphaera*-PAO in SBR sludge. EUBmix is in green while Tet1-226, Tet2-174, Tet2-892 and Tet3-654 are in yellow. The sample was taken on Day 233 after inoculation.

Batch testswere carried out with different labelled carbon sources (glucose, acetate, ,glutamate, aspartate and glycine) using the microautoradiography-FISH (MAR-FISH)techniquein order to assess the substrates that are being taken up by each group of organisms.Glucose and amino acids (aspartate, glutamate and glycine) had a very similar uptake pattern for three of the probe-defined *Tetrasphaera* populations (Tet1-266, Tet2-174, and Tet3-654). *Accumulibacter* were unable to take up any of the substrates, despite positive signals in the flocs from other bacteria detected (Table 2).This information will be correlated with batch tests with individual substrates evaluating the organic carbon, P, PHA and glycogen dynamics.

Table 6.*Accumulibacter* and *Tetrasphaera* MAR-FISH result summary from anaerobic incubation with 6 substrates (Yes: > 90% of cell can uptake substrate; ND: could not quantify.)

Probes	Acetate	Glucose	Glutamate	Aspartate	Glycine
Accumulibacter	No	No	<10% positive	No	No
Tet1-266	No	Yes	Yes	Yes	Yes
Tet2-892	No	Yes	<10% positive	No	50% positive
Tet2-174	< 20%	Yes	Yes	Yes	Yes
Tet3-654	No	Yes	Yes	Yes	Yes

The results of this work will enable the establishment of a link between the different PAO microbial groups and how they co-exist in the same system, their preferred carbon sources and the associated metabolism. This knowledge will set the ground for a deeper understanding of the performance of these populations in full-scale plants, improving our understanding of the EBPR process and the ability to optimize it.

ACKNOWLEDGEMENTS

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Innovative case studies

(Wedneday, 25 June 2014, Aula T2, Polo Zanotto)

(I5) Wastewater Disinfection with Performic Acid: Full-scale Comparisons with Chlorine and Peracetic Acid

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Abstract
In this work a new disinfection system based on the on-site production and use of performic acid (PFA) has been studied in different full scale wastewater treatment plants (WWTPs). Its suitability as disinfectant in this field was originally tested in previous experimentations performed at two municipal WWTPs. In order to compare its effectiveness and impact with those of peracetic acid and chlorine hypochlorite (chemical disinfection systems more widely used in this field), further experiments were performed from 2011 to 2013 at WWTPs designed for equivalent inhabitants ranging from 32,000 to 160,000. The results clearly show that PFA is a reliable alternative to chlorine compounds in relations to both disinfection effectiveness and quality impact. Besides a greater disinfection power as compared to PAA has been observed. In relation to the main investigated qualitative parameters, no differences between treated and untreated effluents and no ecotoxicological effects have emerged.

Keywords
disinfection, performic acid, wastewater, peracetic acid, chlorine hypochlorite

INTRODUCTION

The choice of the most suitable disinfection system in different wastewater treatments should occur through the evaluation of effectiveness, efficiency and impacts on effluent characteristics. However this represents a delicate phase, because each alternative implies both advantages and disadvantages requiring a contextualization of interferences. Moreover the effectiveness reported by literature often refers to microorganisms and conditions other than those of interest.

Given the tendency to progressively reduce chlorine use in wastewater disinfection practices moreover, the alternatives at our disposal have further decreased. Our work aimed to confirm the effectiveness of a new disinfection method, recently studied in this application field (Gehr et al., 2009; Ragazzo et al. 2013), comparing its behaviour with that of other chemical disinfectant compounds traditionally used in wastewater: chlorine hypochlorite (HYP) and peracetic acid (PAA).

The method, developed by Kemira Oyj, is based on producing a disinfection solution containing performic acid (PFA), by mixing formic acid (FA) and hydrogen peroxide (H_2O_2). Due to its instability, the disinfectant solution is produced on site just before its dosage.

METHODS

The PFA disinfection method was studied in full scale plants in various phases from 2006 to 2013; most experiments took place during spring and summer seasons, when the main municipal WWTPs have to undergo compulsory disinfection.

The WWTPs, situated in the North East of Italy, range from 32,000 to 160,000 equivalent inhabitants (e.i.) and function through a conventional sequence of sewage treatments. The final effluents are discharged into sensitive areas near the Adriatic coast. Most of the plants routinely used in the past PAA or HYP as disinfectants.

In the first step – during 11 months between 2006 and 2011 - the reliability of PFA for wastewater disinfection was proven at two WWTPs under different conditions of flow and organic load (Ragazzo et al. 2013). In the second step until 2013, to compare its behaviour with that observed when using PAA and HYP, further investigations were performed in other similar WWTPs. In the WWTPs using PAA and

HYP, the useful conditions for comparisons were obtained by adjusting management and controls; the usual dosages ensuring the regulatory limit respect were maintained.

In all cases the disinfectant dosages were flow-paced.

In this paper for PFA, only the performances obtained from 2011 to 2013 are dealt with and discussed. Table 1 summarizes all the trials hereafter discussed and their relative operational conditions.

Table 1 | Summary of Full Scale Experiments Operational Conditions - Average (minimum-maximum)

WWTPs	**Disinf.**	**Year**	**Flow rate m^3/d**	**Disinfectant Dosage mg/L**	**Retention Time min**
WWTP_1	PFA	2011	3,190 (1,790-4,700)	1.0 (0.6-1.2)	11 (6-19)
WWTP_2	PFA	2012	21,460 (10,020-32,310)	0.8 (0.6-1.4)	19 (14-30)
WWTP_3	PFA	2013	12,860 (8,550-17,650)	0.5 (0.5-0.6)	25 (19-36)
WWTP_4	HYP	2008	9,270 (5,640-14,300)	2.5 (0.9-4.9)	23 (10-42)
WWTP_2	HYP	2011	24,400 (15,900-30,500)	2.7 (1.9-3.2)	20 (15-30)
WWTP_1	HYP	2012	3,470 (1,420-4,750)	3.7 (3.2-4.2)	13 (6-31)
WWTP_2	PAA	2006	32,900 (23,600-43,700)	1.5 (0.9-2.1)	16 (12-20)
WWTP_5	PAA	2013	10,130 (7,940-15,470)	1.1 (0.7-1.4)	42 (22-70)

WWTP: Wastewater Treatment Plant; PFA: performic acid; HYP: chlorine–hypochlorite; PAA: peracetic acid.

The PFA solution is produced according to the following exothermic reaction:

$HCOOH + H_2O_2 \leftrightarrow HCOOOH + H_2O$

by mixing FA (70–80 wt %) and H_2O_2 (50 wt %) in the presence of sulphuric acid as catalyst.

In the production unit Desinfix, the disinfection solution at equilibrium contains PFA, at average concentration of 13,5 wt %, FA, water and H_2O_2. It has been demonstrated that PFA, alone or in combination with H_2O_2, is responsible for disinfection (Gehr et al. 2009). For HYP and PAA we used the commercial solutions with theoretical concentrations of 12% and 15% by weight respectively.

In all the experiments the disinfection effectiveness was tested by collecting representative sequential composite samples at disinfection inlet and outlet, using sterile bottles provided with sodium thiosulphate as quenching.

The main physical-chemical parameters analysed were: temperature, pH, Total Organic Carbon (TOC), turbidity, total suspended solids, ammonia, bromate, aldehydes, Volatile Organic Compounds screening and the disinfectant residual concentrations. The PFA toxicological effects (Acute Toxicity (EC_{50}) with *V. fischeri*) were also investigated.

The disinfection effectiveness was evaluated against *Escherichia coli* and Faecal enterococci, in terms of log bacterial reduction and CT conditions, where C is the dosed disinfectant concentration (mg/L) and T the contact time (min).

RESULTS AND DISCUSSION

The main characteristics of the effluents at the disinfection inlet are summarised in Table 2.
The working conditions in terms of bacterial concentration, physical interfering parameters – total suspended solid, turbidity – and reducing compounds were always comparable, with the only exception of WWTP_2 where also appreciable concentrations of ammonia were observed.

Table 2 | Chemical and Microbiological Characteristics of the Wastewater Effluent at Disinfection Inlet - Average (minimum - maximum)

Disinfectant *System*	**PFA**			**PAA**		**HYP**		
WWTPs	**1**	**2**	**3**	**2**	**5**	**4**	**2**	**1**
TSS [mg/L]	10 (<10-17)	10 (<10-16)	10 (<10-17)	10 (<10-18)	10 (<10-10)	<10 (<10-15)	10 (<10-17)	<10 (<10-<10)
Turbidity [NTU]	3.8 (1.1-7.6)	3.9 (1.3-15)	n.t.	4.2 (1.9-10.4)	n.t.	2.2 (0.9-4.6)	3.8 (1.5-8.2)	n.t.
N-NH$_4$ [mg/L]	0.61 (0.02-3.6)	4.3 (0.2-13.4)	0.2 (<0.2-0.2)	0.66 (0.20-1.20)	n.t.	0.30 (0.13-0.90)	2.66 (1.9-3.2)	1.4 (<0.2-3.1)
EC [Log (CFU/100mL)]	4.5 (3.8-5.6)	4.8 (4.0-5.5)	4.4 (3.0-5.3)	4.7 (4.3-5.3)	4.1 (3.3-5.2)	4.3 (3.5-5.0)	4.8 (4.3-6.2)	4.8 (4.2-5.3)
FC [Log (CFU/100mL)]	3.5 (1.9-4.3)	3.3 (2.7-4.2)	3.2 (2.7-3.9)	3.5 (3.2-4.3)	3.2 (2.7-4.2)	3.6 (2.7-4.5)	3.5 (2.6-4.6)	3.7 (2.3-4.2)

PFA: performic acid; PAA: peracetic acid; HYP: chlorine–hypochlorite; WWTP: Wastewater Treatment Plant; CFU: colony forming units; n.t.: not tested parameter.

An overall view of all the results obtained with PFA, PAA and HYP in terms of bacterial log reduction versus CT conditions is shown in Fig. 1.

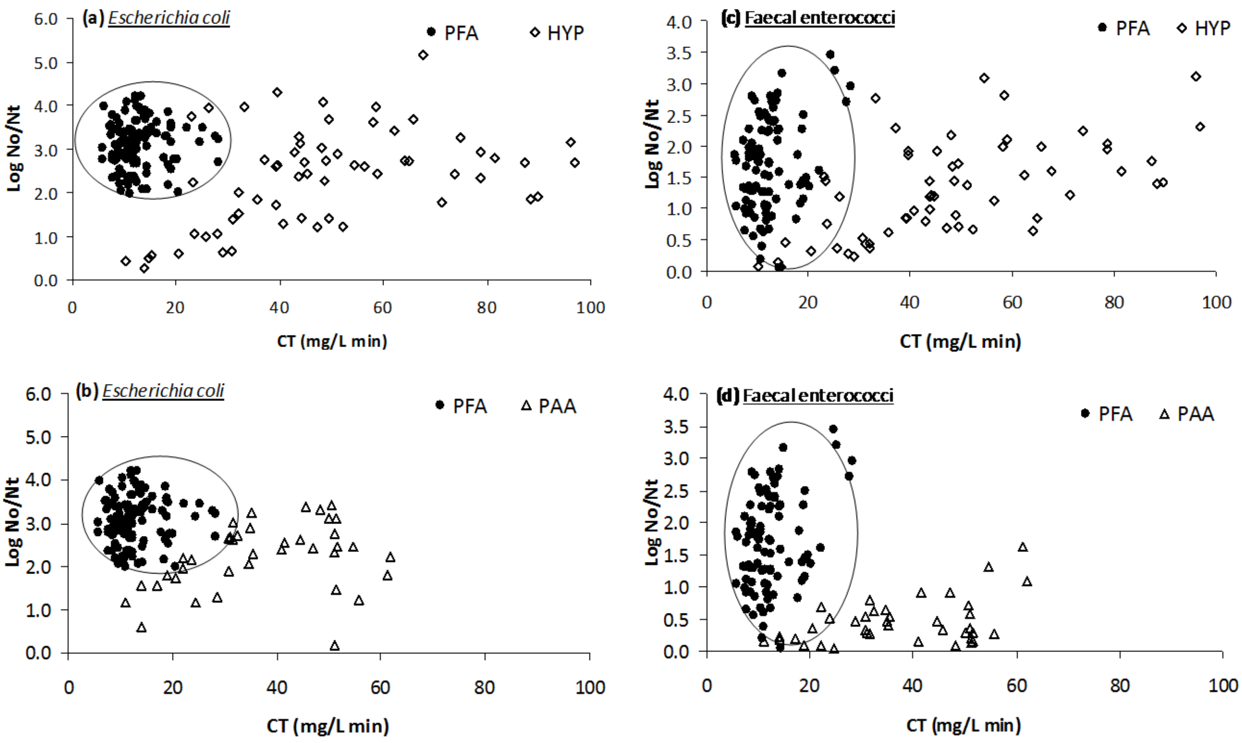

Figure 1 | Log reduction vs. CT conditions (disinfectant concentration x contact time) in all the experimentations. PFA: performic acid, PAA: peracetic acid, HYP: chlorine hypochlorite.

What is evident is the higher efficacy of PFA compared to those of PAA and HYP for all the faecal microorganisms tested; in fact even at lower operative CT conditions the system reaches *E. coli* reductions always higher than those obtained with PAA and similar to those obtained with HYP. The PFA higher effectiveness was even more evident against Enterococci, which anyway showed a lower sensitivity towards all the disinfectants as compared to *E. coli*, thus confirming their higher suitability to represent the pathogen behaviour.

The low performance of HYP can be due to the low dosages and ammonia presence, which caused it to disinfect mainly as combined compound.

In order to focus comparisons among the different disinfectants, the data were elaborated in terms of exceedance probability and some results for *E. coli* are reported in Table 3. The probabilities of exceeding 3 Log reduction is significant and similar for PFA and HYP, very low for PAA.

Table 3 | Probability of exceeding 3 Log units reduction for *Escherichia coli*

WWTPs		PFA	HYP	PAA
WWTP_1	*Dosage ^{a} (mg/L) – Time ^{a} (min)*	*1.0 - 11*	*3.7 - 13*	---
	Exceedance probability	55 %	39 %	---
WWTP_2	*Dosage ^{a} (mg/L) – Time ^{a} (min)*	*0.8 - 19*	*2.7 - 20*	*1.5 - 16*
	Exceedance probability	51 %	61 %	neg.
WWTP_3	*Dosage ^{a} (mg/L) – Time ^{a} (min)*	*0.5 - 25*	---	---

	Exceedance probability	60 %	---	---
WWTP_4	*Dosage [a] (mg/L) – Time [a] (min)*	---	---	*1.1 - 42*
	Exceedance probability	---	---	26 %

WWTP: Wastewater Treatment Plant; PFA: performic acid; HYP: chlorine–hypochlorite; PAA: peracetic acid;

[a] Average value; neg.: probability < 0%

In a similar assessment for Enterococci instead, the differences among the disinfectants were more evident: while PAA never reached 2 Log reduction, the probabilities of exceeding this value were 30% and 20 % for PFA and HYP respectively.

The overall effectiveness registered for the disinfectants against Enterococci is shown in Fig. 2

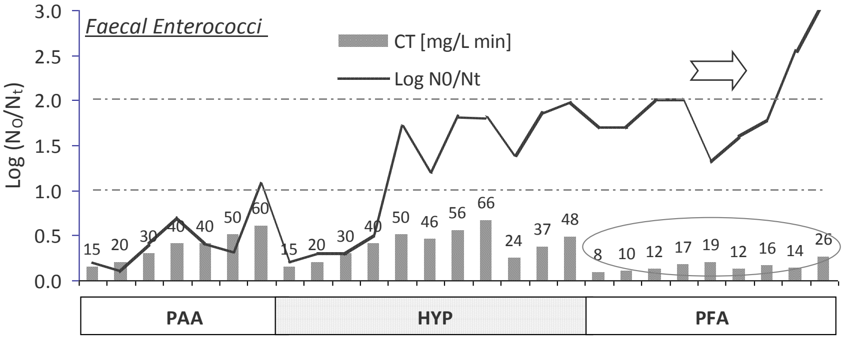

Figure 2 | Enterococci Log reduction and CT conditions (disinfectant concentration x contact time) in all the experimentations. PFA: performic acid, PAA: peracetic acid, HYP: chlorine hypochlorite.

Regarding the PFA quality impact on effluents characteristics, all the measurements carried out throughout the whole period of experimentation show the absence of significant differences between treated and untreated effluents.

The lack of PFA strong oxidising effect on organic carbon, which could mean a low tendency to lead to by-products, was confirmed in these experiments as well. The TOC and formate concentrations at the disinfection outlet were not significantly different ($p>0.05$) from those expected from the PFA dosages applied.

In 2012 at WWTP_2 the Trihalomethane Formation Potential (THMFP) was measured to evaluate the PFA ability to change the organic matter structure, making it more reactive to chlorine attack. This could be an indirect way to assess partial organic oxidations by PFA: no significant variations on THMs production were revealed between the disinfection inlet and outlet.

On the other hand, the head-space gas chromatographic mass spectrum did not reveal appreciable changes in volatile organic substances (Ragazzo et al. 2013).

For compounds such as ketones, phthalates, bromates, aldehydes and phenols no appreciable changes between treated and untreated effluents were observed.

Despite the persistence of formate in the wastewater effluent, similar results were observed for eco-toxicological effect in terms of *Vibrio fischeri* light suppression (Ragazzo et al. 2013).

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(I6) Intermittent aeration process through the OSCAR® controller: full scale applications and mathematical modelling

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Abstract

The OSCAR® controller is an integrated hardware/software tool for real-time monitoring and process automation of wastewater treatment plants. By including different automation algorithms, OSCAR® allows for (i) reduction in electrical energy consumption, (ii) improved nitrogen removal efficiencies through the single-tank intermittent aeration process, (iii) reduction in sludge production. The paper shows inferences from two full-scale installations, with a potential capability of 10,000 PE and 100,000 PE, where OSCAR® has been successfully installed and operated since 2011 and 2012 respectively. As a consequence of to the real-time optimization, specific energy consumption for the bioprocess (kWh PE^{-1} d^{-1}) was dramatically reduced of some 66% in the smaller installation and roughly 28% in the larger installation, also reflecting in a significant increase of nitrogen removal efficiency (up to 90%) and a stable and continuous observance of effluent quality standards. At the same time, due to the slower-rate biomass growth under frequent anoxic conditions, the observed yield was reduced of some 27% in one installation and 38% in the other one, resulting in 6.8 and 11.9 kgTS PE_{COD}^{-1} y^{-1} respectively. Finally, the application of IWA-ASM 1 model under the OSCAR® operation is presented and discussed, showing a fairly good fitting of real-time monitoring over both short- and long-term.

Keywords
Intermittent aeration; real-time control; nitrogen removal; energy saving; sludge reduction; ASM1

INTRODUCTION

The single-tank intermittent aeration process was firstly proposed in ‘70s and is widely recognized as an effective and low-cost option for upgrading existing wastewater treatment plants which need to cope with operational costs minimization, lack of space for new process tanks and strict limitations on effluent nitrogen forms in the final discharge. Although several works have been reported in which process control is driven by real-time monitoring of indirect parameters such as pH and ORP (*inter alia* Hao and Huang, 1996, Paul *et al.*, 1998), the need for different control strategies based on direct measurement of nitrogen forms is more and more increasing, especially where both ammonia and total nitrogen have to cope with specific effluent quality standards.

The paper reports long-term inferences from two full-scale installations where the advanced controller OSCAR® has been installed for the intermittent aeration process. The positive impact on process performances is presented and discussed, with a special focus on effluent nitrogen, energy consumption and sludge production. Moreover, the mathematical modelization of one of the two plant under OSCAR® operation is presented.

MATERIALS AND METHODS

Experimental site

Plant A. The WWTP Baselga di Piné is located near Trento, North Eastern Italy. Although its nominal design capability is 10,000 PE, seasonal fluctuations are typically observed because of the touristic flows in the area. The flow-scheme includes pre-treatement units (3 mm rotating drum screen, grit chamber and oil removal), two activated sludge biotanks (900 m^3 each, equipped with fine bubble diffusers and two 2-speed rotatory blowers), two rectangular secondary settlers, disinfection with NaOCl and final discharge. The bioprocess tank are outdoor and, due to the high altitude (1000 m above sea level) and the Alpine climate, temperature in the bulk can drop down 3-4°C during Winter time. Since the start-up in 1982, the biological process has been regularly operated according to an extended aeration process, air supply being regulated according to a dissolved oxygen set point in each tank. Since May 2011, the OSCAR® controller has been installed, with one ISE-probe for on-line ammonia measurement and a submersible horizontal-axis mixer in each biological process compartment.

Plant B. The WWTP of Mantua was started-up in 1978 and has been afterwards extended in early '90s. The flow scheme includes: bar screens, grit chamber, five primary settling tanks, four activated sludge tanks (3 x 1250 m^3 and 1 x 2500 m^3), three secondary settlers, one chlorination basin for final disinfection. The bioprocess aeration is achieved through two rotatory blowers per tank, one at fixed-speed and one with frequency converter. In all biological process compartments dissolved oxygen, ammonia and nitrate are monitored in real-time by means of submerged probes and a central PLC-SCADA system. Since 2010, a time-base intermittent aeration process was operated. The OSCAR® controller was installed at first in only one of the 1250 m^3 tanks (May 2012), then it was extended to all the biological process compartments (since December 2012).

The qualitative and quantitative characterization of influent wastewater for both installations is shown in Table 1. Concerning the Mantua installation, a 30-40% removal efficiency of COD is typically observed downstream the primary clarification step, thus leading to a relatively low C/N ratio (4-5) entering the biological process, also due to the feedback from the dewatering of the anaerobically digested sludge.

Table 1. Influent wastewater characteristics

Parameter	**Unit**	**Baselga di Piné***	**Mantua**#
Average flowrate	$m^3 d^{-1}$	2208 ± 1085	26661 ± 4971
COD	$g m^{-3}$	326.0 ± 224.4	112.4 ± 95.1
BOD_5	$g m^{-3}$	121.6 ± 90.6	120.0 ± 143.6
TSS	$g m^{-3}$	181.2 ± 163.1	225.6 ± 199.2
TN	$g m^{-3}$	34.7 ± 13.0	18.9 ± 6.5
TP	$g m^{-3}$	3.4 ± 2.4	4.6 ± 3.8

* Monitoring period: January 2011 – December 2013, 24-hours grab samples collected weekly

#: Monitoring period: January 2012 – October 2013, 24-hours grab samples collected bi-weekly

Mathematical modelling – Plant layout and model calibration

In order to better evaluate the biological process behaviour under different operational conditions, the IWA-ASM1 included the T effect on biokinetics was calibrated and validated on the historical data-series collected at Baselga di Piné. The DHI-WEST® software platform was used, and Biomath protocol was chosen for calibration, according to Sin (2004).

RESULTS

Nitrogen removal

Nitrogen forms in effluent for both installations before and after the OSCAR® installations are summarized in Table 2.

Table 2. Influent wastewater characteristics

Parameter	Unit	Baselga di Piné*		Mantua$^{\#}$	
		Pre-OSCAR$^{®}$	**Post-OSCAR$^{®}$**	**Pre-OSCAR®**	**Post-OSCAR$^{®}$**
$N\text{-}NH_4^+$	g m^{-3}	0.4 ± 0.1	1.8 ± 1.0	2.6 ± 1.9	2.0 ± 2.2
$N\text{-}NO_2^-$	g m^{-3}	0.1 ± 0.2	0.1 ± 0.1	0.2 ± 0.1	0.5 ± 0.2
$N\text{-}NO_3^-$	g m^{-3}	10.5 ± 3.2	1.1 ± 1.4	10.7 ± 3.7	7.8 ± 4.2
TN	g m^{-3}	14.1 ± 3.1	4.1 ± 2.1	13.2 ± 4.2	10.0 ± 4.3

Concerning the smaller installation, the adoption of OSCAR$^{®}$ reflected in a slightly higher effluent ammonia concentration which however did not affect the stable respect of the local regulation ($N\text{-}NH_4^+$ ≤ 3 g m^{-3} when temperature is higher than 15°C). At the same moment, the introduction of optimized length anoxic phases lead to a dramatic increase in the denitrification performance, which take the effluent nitric nitrogen down to less than 2 g m^{-3} and the total nitrogen down to about 4 g m^{-3}. Similarly, in the Mantua installation where the low C/N set a challenge in steadily respecting the required effluent TN concentration (15 g m^{-3}), once the advanced controller was introduced effluent TN was successfully accomplished.

Energy saving and excess-sludge production

The effect of anoxic periods and, consequently, the use of nitrate as electron acceptor for C removal during the denitrification phase, reflected in a significant reduction in energy consumption and, to some extent, in a decrease of the observed yield, as shown in Table 3.

Table 3. Influent wastewater characteristics (data for the post-OSCAR$^{®}$ period take into account the energy consumption for submersible mixers)

Parameter	Unit	Baselga di Piné*		Mantua$^{\#}$	
		Pre-OSCAR$^{®}$	**Post-OSCAR$^{®}$**	**Pre-OSCAR®**	**Post-OSCAR$^{®}$**
EE consumption for the bioprocess	Wh PE_{COD}^{-3} d^{-1}	84.2	29.0	79.4	57.7
Sludge production	kgTS PE_{COD}^{-3} y^{-1}	9.3	6.8	19.1	11.9

In order to better compare the process performances before and after the installation of the real-time controller, energy consumption for the bioprocess and sludge production are expressed per PE. The Baselga installation, where longer anoxic phases where achieved especially during the low touristic loading season, achieved a 67% reduction in specific energy consumption and a 27% reduction in specific sludge production.

Modelization

Once calibrated under both steady- and dynamic-state, the ASM1 model was validated on three different data sets collected at the plant of Baselga di Piné. The overall output of model validation are listed in Table 4; examples from dynamic validation over one month and one day are shown in Figure 1.

Table 4. Influent wastewater characteristics

Main macro-pollutants in the effluent		**September 2012**	**December 2012**	**February 2013**
COD [g m^{-3}]	Measurement	26.9	19.47	24.42
	Model	21.2	14.07	18.01
N-NH_4^+ [g m^{-3}]	Measurement	1.1	1.3	1.2
	Model	0.9	1.4	1.1
N-NO_3^- [g m^{-3}]	Measurement	0.4	0.96	0.50
	Model	0.1	1.20	0.22
TSS [g m^{-3}]	Measurement	4.8	7.00	6.00
	Model	4.7	3.90	5.16

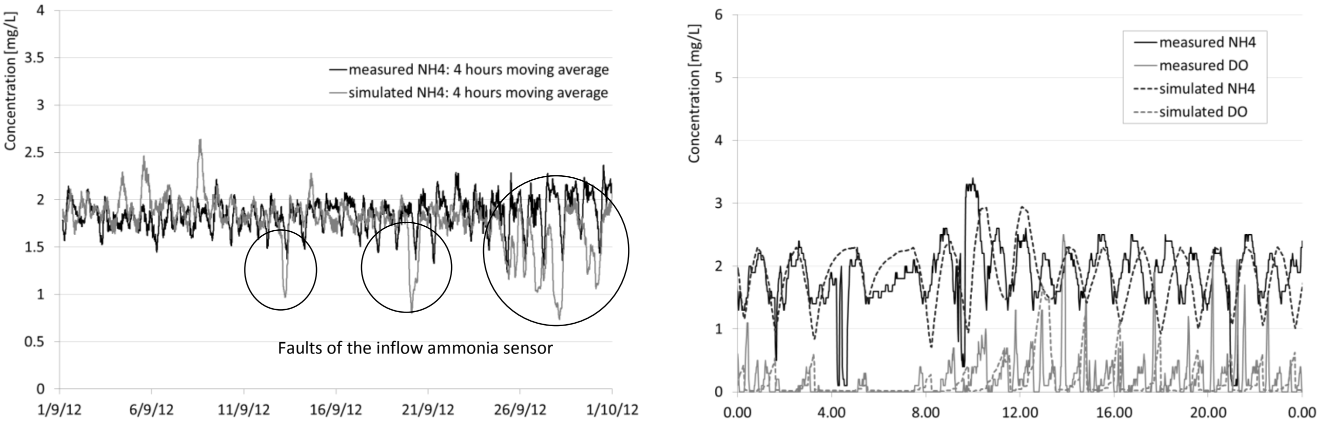

Figure 1. Long-term (30 days) and short-term validation for N-NH_4^+ (on the left) and N-NH_4^+ and dissolved oxygen in Line 1 (on the right). Circles in the left graph refer to faults in the influent ammonia probe

Over both long- and short-term periods the properly calibrated ASM1 showed a good fitting capacity of the real data. The presence of different on-line probes for process monitoring and control allows for relatively easy model calibration. This promotes the adoption of mathematical models as tool for decision-support in defining the operational strategies.

CONCLUSIONS

A relevant operational costs reduction has been demonstrated at full-scale in two largely different installations, after the introduction of the real-time OSCAR® controller in process automation and supervision. The introduction of anoxic phases had a direct positive effect on energy consumption for C and N removal and effluent quality. Moreover, the reduction of observed yield reflected in a reduced surplus sludge production. The available online measurements also permitted a successful application of ASM1, which was validated over both short- and long-term simulations.

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(I7) NEREDA® - An Emerging Technology for Sewage Treatment

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Abstract

Stringent environmental regulations and severe water pollution has divert the attention of stakeholders, water boards and ministries dealing with the water resources and environment to explore new technologies to make rivers and water bodies free from pollution. Recently an aerobic granular biomass based technology; named NEREDA® has been gaining wide publicity around the globe. It has several advantages such as less power requirement, no need of chemicals and its compactness due to high mixed liquor suspended solids (MLSS), significantly less capital and operational costs. NEREDA® can be regarded as an alternative to conventional aerobic technology for sewage and industrial wastewater treatment.

Recently NEREDA® technology has been installed at sewage treatment plants (STPs) in Europe and South Africa and few are under pipeline in parts of Latin America, Israel and India.

Keywords

Aerobic Granular Biomass, NEREDA®, Sustainability, N & P Removal

INTRODUCTION

Several modification of conventional activated sludge process (ASP) were made for efficient removal of carbon, nitrogen and phosphorous since its development. The problem of poor settling of sludge, high bulking and low nutrient removal frequently experienced in ASP systems. This has led to the development of advanced biological nutrient removal (BNR) systems for activated sludge. Several options are available these days such as sequencing batch reactor (SBR), moving bed bio-film reactor (MBBR), continuous fill intermittent decant type SBR (CFID), down flow hanging sponge reactor (DHS) and rotating biological contactors (RBC) (Khan, 2012). SBR and MBBR were now used at full scale level while DHS and RBC under laboratory/ pilot scale investigation. Results are promising; however, more studies are needed at pilot scale or demonstration level with actual environmental conditions. The most common problem encountered in the operation of these modified ASP system are foaming and bulking. The mixed liquor suspended solid (MLSS) flocs do not settle well or compact and flocs discharged in effluent in a bulking sludge.

Prof. Mark van Loosdrecht (2012 Lee Kuan Yew Water Prize winner), and his team at Delft University of Technology (TU Delft) investigated the formation of aerobic granules 1990s (Morgenroth et al.1997). The SBR is one of the modifications of ASP which can utilize on aerobic granular biomass to get rid of poor settling and bulking and sufficient number of pilots scale plants were installed for municipal and industrial wastewater (Khan, 2012). Aerobic granular biomass has several advantages over conventional activated sludge flocs that have been well-documented. These include good settling ability that leads to better biomass retention and higher biomass concentrations, provision of a structured matrix for biomass growth, and ability to withstand high load variations. These all lead to a compact reactor design that can reduce plant footprints significantly. Recently, the process has been engineered to suit commercial applications by DHV (now known as Royal HaskoningDHV) and has been commercially branded as Nereda® Technology.

FULL SCALE NEREDA® INSTALLATION

Nereda, a new biological wastewater technology, has been deployed at number of municipal waste water treatment plant (WWTP) in The Netherlands, to meet the high standards of sludge treatment, chemicals use and energy consumption. The Epe WWTP, using the Nereda wastewater technology, which flows up to 1,500m³ per hour, was commissioned in the middle of 2011. The plant was designed to meet the high influent COD load at temperature ranged 8 – 25°C. The plant, which has been operational for the last 16 months, has been under constant monitoring for its performance. During the monitoring, the Nereda wastewater technology exceeded its expectations and met the set stringent standards of effluent quality, sludge treatment, chemical use and power consumption. Electricity required by the plant, including sand filtration and sludge treatment, is comparatively less than that of any other similarly sized conventional treatment plant in the country. In addition, the system's effluent quality meets the country's set standards, which specifies that total nitrogen and phosphorous concentrations should be less than 5 and 0.3 mg per litre. Nereda is cost-effective and can save over 25% in investment and operational costs, when compared to other conventional systems. The system, which showed endurance and stability under strong varying influent load conditions and extreme influent pH fluctuations, can also remove Nitrogen from sludge even in wintry conditions.

Table 1. Treatment Performance of Epe WWTP

Parameter	**Influent** (mg/l)	**Effluent (Average)** (mg/l)
COD	879	27
BOD	333	< 2.0
TKN	77	1.4
NH_4-N	54	0.1
N-total		< 4.0
P-total	9.3	0.3
Suspended Solids	341	< 5.0

The high quality effluent could be obtained from Nereda treatment. Results of Eppe WWTP were summarized in Table 1.

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(I8) Optimization of the alternate cycles process in a municipal wastewater treatment plant

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Abstract

Alternate cycles process can be a solution, which requires minimal interventions, to improve nitrogen removal in medium-small municipal wastewater treatment plants. This study shows the benefits of the application of a control strategy based on ammonium and nitrate sensors compared to the timer control system in a municipal WWTP.

Treatment plant modeling was performed by using WEST software. Optimal values of the switching functions were assessed together with the minimum and the maximum length of the aerated and non aerated phases. The model was validated and the new control strategy was applied in the WWTP from October 2013. Benefits owing to the new control strategy are highlighted in this study. The new control simplifies the WWTP management, allows to manage periodic inhibitions of the nitrification process and to increase nitrogen removal. Moreover, it allowed to lower the DO in the oxidation tank and to change the average partition of the cycles from 55% mixing and 45% aeration to 70% mixing and 30% aeration, thus reducing the energy consumptions of the plant.

Keywords

Alternate cycles; intermittent aeration; energy saving; modelling; nitrogen removal; process control; wastewater.

INTRODUCTION

In the last decades, several strategies for the alternate cycles control have been applied. The main alternatives are: time control, control based on DO and ORP sensors (using a simple threshold control or analyzing the signal profiles to find bending points), and control based on ammonium and nitrate sensors (Paul et al., 1998; Lukasse et al,. 1999). The first solution is simple and economic, but needs continuous adjustments to be efficient and it does not take into account the quality of the treated effluent. The second one, even if the sensors are economic, has not always an optimal behaviour. As a matter of fact, it is proved (Lefevre et al., 1993) that a simple threshold control with DO and ORP sensors is not efficient, and the recognition of the inflection points is not always simple. As a consequence, the software control sometimes behaves like a timer or a threshold control (Battistoni et al., 2003; Cola et al., 2007; Battistoni et al., 2008; Eusebi et al., 2008; Nardelli et al., 2009). For example, for under-loaded conditions (during wet weather or during the night), the DO concentration may rise too fast and the control system is not always able to find bending points on the DO curve. Furthermore, the switch from one phase to another one only takes place when ammonium is exhausted, during aerated phase, and when nitrate is exhausted, during mixed phase. This behavior is not always optimal: a low concentration of the total nitrogen in the effluent flow can be reached even if there is not the total exhaustion of ammonium or nitrite

The control based on ammonium and nitrate sensors is expensive because of the high cost of the probes, but it allows to switch from one phase to another one according to the WWTP manager objectives without the need to reach total ammonium and total nitrate removal. Moreover, it is possible to directly monitor the concentration of the nitrogen compounds for which there are discharge limits.

This study shows the benefits of the application of a control strategy based on the ammonium and the nitrate sensors compared to the time control system.

The research was carried out in a conventional municipal wastewater treatment plant (30000 p.e., average flow 2 Mm^3/year), where alternate cycles are applied in two Carousel Passavant tanks. In each tank there are two surface aerators (Mammoth Rotor) and two low-speed mixers (ITT Flygt 4430.010/462). Furthermore, in the biological reactors there are SST and DO probes and at the exit of the reactors ammonium (AMTAX sc, HACH-LANGE) and nitrate (NITRATAX Plus sc., HACH-LANGE) probes were recently installed.

First, the WWTP process was modelled. In particular, benefits in terms of nitrogen removal efficiency and energy savings were highlighted switching from a timer control strategy of the alternate cycles to a control system based on the ammonium and nitrate probes. Optimal values of the switching functions were assessed together with the minimum and the maximum length of the aerated and non aerated phases. The model was validated and the new control strategy was applied in the WWTP. Benefits owing to the new control strategy are highlighted in this study.

MATERIALS AND METHODS

Treatment plant modeling was performed by using WEST software (DHI). The model selected is the ASM1_AN (Veys et al., 2010), because it enables to observe nitrite fluctuations for which there is a very low concentration discharge limit (0.6 $N\text{-}NO_2$ mg/l). The model outputs are, therefore, the trend of the ammonium, the nitrates, the nitrites and TN. A manual calibration was performed, as suggested by the STOWA protocol (Hulsbeek et al., 2002).

Chemical analysis (ammonium and total and filtered COD) were combined with BOD tests (performed with the Controller OxiTop OC110) as the STOWA protocol suggests to assess the COD fractionation (Roeleved P.J. and van Loosdrecht M.C.M., 2002). Samplings were performed in different periods of the year to obtain reliable results.

To simulate present conditions in the biological tanks, the available data (frequency of 15 days) from 2010 to 2013 were analyzed: flow rate, total COD, ammonium, total nitrogen, nitrite, nitrate and TSS concentrations in the WWTP influent and effluent. Moreover, in order to finer characterize the WWTP influent and effluent for the model calibration, a 24-hour monitoring was carried out. The following parameters were monitored: total and filtered COD, ammonium, nitrates and nitrites. The 24-hour monitoring experiment was repeated for the validation of the model.

RESULTS AND DISCUSSION

Calibration results are shown in Figure 1. After the model calibration, the timer control was replaced with the control based on the ammonium and nitrate probes values. Optimal settings for control were found, and a comparison between the two different control strategy was made. The results show that, using the new control, it is possible to reduce the TN effluent concentration (see Figure 3) and guarantee energy saving due to a lower average value of DO and a different partition of the cycles (see Figure 2): longer mixing steps and shorter aeration steps.

Moreover, Figure 2 highlights that while with the timer the cycle duration was constant, with the new control system it varied with the influent quality.

On October 1st 2013, the new control system was installed on the WWTP and, during the first trial period, cycles have run as follows: the aeration was always stopped at the optimal ammonium concentration switching value found by the model (0.5 mg $N\text{-}NH_4$/l), except during inhibition of nitrification. The mixing phase was correctly stopped at the optimal nitrate concentration found by the model (8 mg $N\text{-}NO_3$/l), with the exception of particular conditions characterized by a lack of biodegradable carbonaceous substance in inlet. The new control allows to reduce energy consumption, to higher TN efficiency removal, as shown in Table 1, and to deal with inhibition phenomena of nitrification, which sometimes occur in the WWTP.

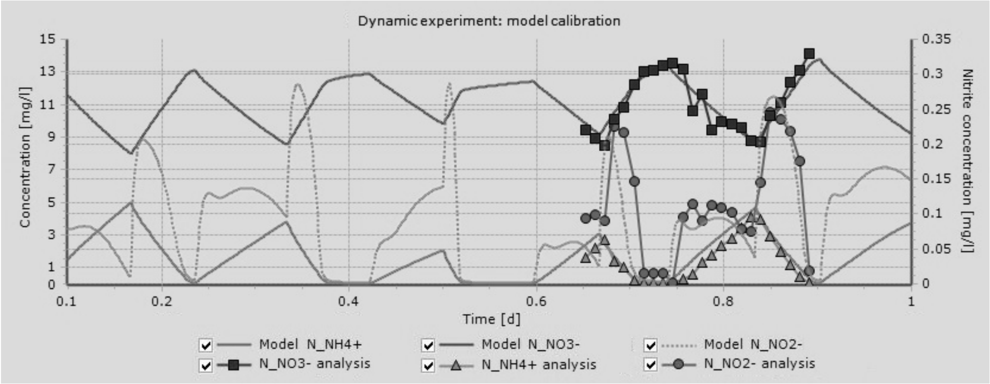

Figure 1. Results of the model calibration: ammonium, nitrite and nitrate.

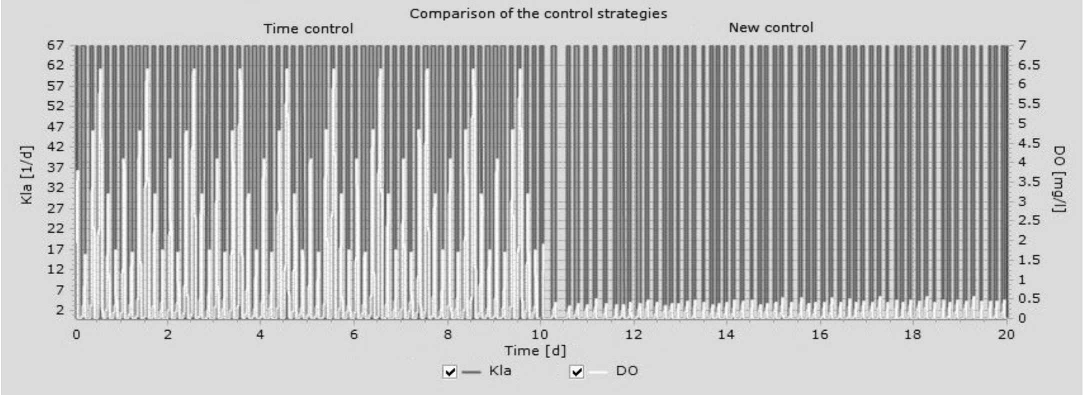

Figure 2. Simulation comparison between the timer and the new control: cycles and DO fluctuations.

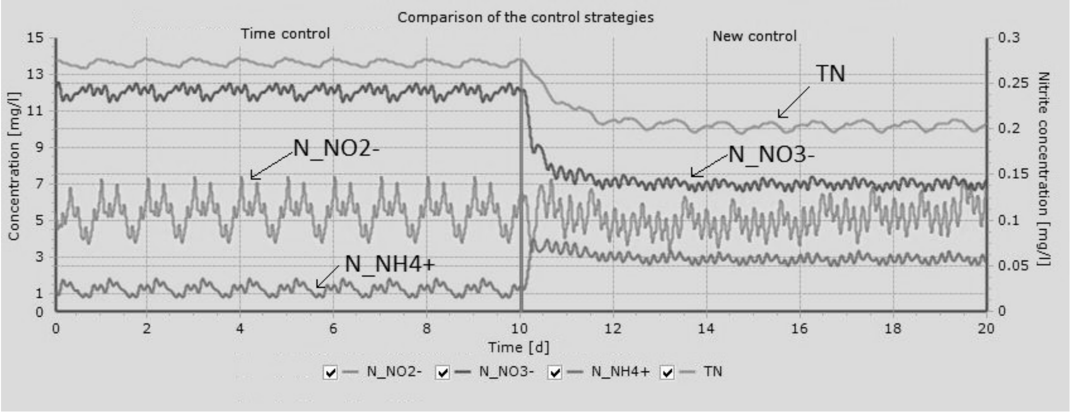

Figure 3. Simulation comparison between the timer and the new control strategy: nitrogen compounds trend in the effluent

Table 1. Comparison between the timer and new control strategy: average values of the TN removal efficiency and the cycle partition

	Timer	New control
	Jan. 2013 – Sep. 2013	Oct. 2013 – Jan. 2014
TN in the influent flow [mg/l]	31.1	31.5
TN in the effluent flow [mg/l]	14.5	12.3
TN removal efficiency [%]	53	61
Cycle partition	55% mixing-45% aeration	70% mixing-30% aeration

CONCLUSIONS

The modelling of the plant through the WEST software allowed to highlight the benefits due to the change of the time control with a control based on ammonium and nitrate sensors of the alternate cycle process in a municipal WWTP. The new control simplifies the WWTP management, allows to manage periodic inhibitions of the nitrification process and to increase nitrogen removal (8% in the first trial period). Moreover, it allowed to lower the DO in the oxidation tank and to change the average partition of the cycles from 55% mixing and 45% aeration to 70% mixing and 30% aeration, thus reducing the energy consumptions of the plant.

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Efficient Technologies - Novel technologies

(Wednesday, 25 June 2014, Aula T3 Polo Zanotto)

(K11) Towards Management of the Bacterial Resource for Nutrient Removal in Granular Sludge Biofilm Systems

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Abstract

The granular sludge biofilm sequencing batch reactor technology can become a next generation standard for high-rate biological nutrient removal from wastewater. This attractive process innovation based on mobile granular biofilms formed by self-aggregation of microorganisms is slowly penetrating the wastewater treatment market. Whereas full-scale plants are currently designed and installed, the design of operation strategies should rely on advanced understanding of mechanisms of microbial selection and granule formation. Based on five years of research conducted from process to biofilm and microbial scales, we provide an applied methodology towards efficient management of the bacterial resource in granular sludge.

Keywords
Bacterial resource management; biological wastewater treatment; granular sludge technology

INTRODUCTION

The aerobic granular sludge (AGS) biofilm technology can become a new and economically attractive standard for high-rate biological nutrient removal (BNR) from wastewater and secondary clarification in single sequencing batch reactors (SBR) (Giesen et al., 2012). Theoretical savings of up to 0.4 € m^{-3} and 5.2 mio€ y^{-1} were calculated for a Swiss wastewater treatment plant of 200’000 person-equivalents (Weissbrodt, 2012). The design of operation strategies should further rely on an advanced understanding of microbial selection mechanisms towards efficient granulation and stable BNR. Based on five years of investigation of the underlying trigger factors, we propose a methodology towards efficient management of the bacterial resource in AGS.

MECHANISMS OF BACTERIAL SELECTION IN GRANULAR SLUDGE

The combination of molecular microbial ecology and laser scanning microscopy methods revealed that granulation mechanisms rely on predominant populations involved (Weissbrodt et al., 2013a). The application of wash-out conditions to select for fast-settling biomasses was shown to exert selection pressures at both biofilm and microbial scales (Weissbrodt et al., 2012a). Ensuring full uptake of organic loads under anaerobic conditions by adaptation of loading rate, anaerobic contact time, and sludge retention time can efficiently select for nitrifiers, polyphosphate-accumulating organisms (PAO) and their glycogen-accumulating competitors (GAO) over unfavorable fast-growing heterotrophs such as *Zoogloea* spp. and filamentous *Burkholderiales* affiliates.

Multifactorial experiments conducted with mature AGS revealed that, in addition to a full anaerobic selector, slight alkaline conditions (pH>7.3), lower mesophilic temperatures (<20°C), adapted starvation phase lengths, and presence of the 3-carbon substrate propionate in the feed favorably trigger for enhanced biological phosphorus removal by preferential selection of PAO over GAO, and stable production of granular biomass (Weissbrodt et al., 2013b). Multivariate analyses informed that fluctuations in nutrient loads and dissolved oxygen set-points impact on bacterial community composition and BNR performance (Weissbrodt et al., *in revision*). Efficient nitrification (>99%), phosphorus- (>97%), and nitrogen- (>60%) removal was obtained with a mean granule diameter of

1.5±0.9 mm and a biofilm area to reactor volume ratio of 628 m_F^2 m_R^{-3}.

High-resolution analysis of bacterial communities with the molecular PyroTRF-ID workflow (Weissbrodt and Shani, et al. 2012b) revealed that AGS systems are composed of populations belonging to the core microbiome of activated sludge. Fundamentals gained on microbial selection from activated sludge systems should thus be integrated for AGS ones as well.

BACTERIAL RESOURCE MANAGEMENT METHODOLOGY

These findings were aggregated with previous knowledge gained from activated sludge, SBR, and biofilm systems in order to propose a methodology with the following milestones towards efficient management of the bacterial resource for efficient granulation and robust BNR in AGS systems:

1. Characterization of the local composition of the influent wastewater and of underlying temporal variations in nutrient concentrations and ratios, alkalinity, and temperature.
2. Model-assisted SBR design including (i) reactor and bed geometry, (ii) feeding conditions and bed loading, (iii) aggregate types, i.e. pure granular or hybrid granules-flocs system, (iv) alternating redox conditions, and adaptation of dissolved oxygen set-points to size distributions.
3. Use of the flexibility of the SBR technology for dynamic control of anaerobic contact time and starvation phase length. Control loops should be based on on-line sensing of soluble species.
4. Shaving of wastewater fluctuations by addition of ammonium from high-loaded side streams, of propionate from pre-fermented excess sludge, and of lime in the influent. Recovering heat from the wastewater upstream may help to reach a lower mesophilic temperature.
5. Controlled removal of biomass from these biofilm systems in order to promote a moderate and stable sludge retention time (e.g. 15 days), a balanced bacterial community, and effective phosphorus removal on the long term.

CONCLUSION AND OUTLOOK

Based on the bacterial selection mechanisms identified at fundamental level, the proposed applied methodology should lead to an optimal bacterial community continuum required for efficient granulation and BNR in the granular sludge ecosystem. This methodology should now be validated at pilot scale with high-complexity influents, and can serve as a base for optimization of the operation of full-scale systems. The “health” state of the biological system can be controlled periodically with molecular microbial ecology analyses. Overall, this study highlights that bacterial resource management is the seed for granular sludge wastewater treatment systems.

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(P55) Assessment of crude glycerol for Enhanced Biological Phosphorus Removal: stability and role of LCFA

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Abstract

Enhanced Biological Phosphorus Removal (EBPR) of urban wastewaters is usually limited by the available carbon source required by Polyphosphate Accumulating Organisms (PAO). External carbon sources as VFA or other pure organic compounds such as glucose, glycerol or methanol have been tested at lab scale demonstrating its ability to enhance PAO activity, but the application of this strategy at full-scale WWTP is usually limited by its cost. The utilization of industrial by-products with some of these organic compounds provides lower cost, but it has the possible drawback of having inhibitory or toxic compounds for PAO. This study is focused on the utilization of crude glycerol, the industrial by-product generated in the biodiesel production, as a possible carbon source to enhance EBPR in carbon-limited urban wastewaters. Crude glycerol has non-negligible content of other organic compounds as methanol, VFA and Long Chain Fatty Acids (LCFA). VFA and methanol have been demonstrated as carbon sources enhancing PAO activity, but there is no previous study about the effect of LCFA on PAO. This work presents the operation of an EBPR SBR system using crude glycerol as sole carbon source, studying its long-term stability. The effect of LCFA is also studied at short and long-term, demonstrating for the first time EBPR activity with LCFA as sole carbon source and its long-term failure due to the increased hydrophobicity of the sludge.

Keywords

Crude glycerol, EBPR, hydrophobicity, LCFA, PAO

INTRODUCTION

EBPR, based on the enrichment of activated sludge with PAO, is considered the most sustainable technology to meet the stricter discharge requirements of WWTP (Broughton et al., 2008). PAO can take up carbon sources under anaerobic conditions storing them as poly-β-hydroxyalkanoates (PHA) for its utilisation under the presence of an electron acceptor as oxygen, nitrate or nitrite. During this part of the process, PAO are able to accumulate phosphorus (P) in excess, which is then removed through the waste. The effectiveness of EBPR depends on the nature of the carbon source used, being the presence of volatile fatty acids (VFA) a key factor to obtain a high P removal capacity (Chu et al., 1994; Randall et al., 1997; Guerrero et al., 2011). To increase the VFA content of low organic carbon wastewaters the utilisation of waste materials that could be fermented to VFA is a very attractive alternative to overcome VFA deficiency.

Crude glycerol is a by-product of biodiesel fuel production; 1L of glycerol is produced for every 10L of biodiesel fuel (Johnson and Taconi, 2007). This by-product has many impurities that together with the increase of its production has transformed it in a waste material with associated disposal costs (Yazdani and Gonzales, 2007; Escapa et al., 2009). Pure glycerol has been reported for wastewater treatment as a proper external carbon source for denitrification in WWTP (Grabinska-Loniewska et al., 1985; Akunna et al., 1993; Bodík et al., 2009, Torà et al., 2011) and for EBPR (Guerrero et al., 2012). Although these uses of pure glycerol seem promising, the utilization of crude glycerol with impurities, mainly salts, methanol and long chain fatty acids (LCFA), faces new operational problems.

Regarding LCFA treatment, wastewaters with high LCFA content are not effectively treated by high-rate anaerobic technology. LCFA adsorption onto the sludge leading to sludge flotation and sludge washout has been widely reported in the literature (Alves et al., 2009). The observed sludge washout and process failure does not seem to be due to microbial activity inhibition, but to problems of fluid dynamics as reduced settleability of sludge.

The aim of this work was to study the feasibility of using crude glycerol as a sole carbon source on EBPR, evaluating its long-term stability and the problems associated to the presence of LCFA. Direct utilisation of crude glycerol by a propionic fed-PAO with a step-wise increase of concentration for its acclimation was used in an anaerobic/aerobic sequencing batch reactor (SBR) configuration. The aim was obtaining sludge able to ferment glycerol to propionic acid for PAO uptake to achieve stable operation. The effect of LCFA was studied in combination to VFA and also as a sole carbon source in the same SBR configuration.

MATERIAL AND METHODS

Two SBRs were used in this study. They were monitored for dissolved oxygen (Hamilton, Oxyferm 120 probe), pH (Hamilton, polilyte Pro120 probe), ORP and temperature. Both SBR (10L) contained a PAO-enriched sludge developed with propionic acid as sole carbon source and operated with 4 cycles per day with configuration of 2 h anaerobic phase, 3.5 h aerobic phase, 25 min of settling and 5 min to extract 5 L of the supernatant. Temperature was controlled at 25 ± 1°C. HCl (1M) and NaOH (1M) were added to control the pH at 7.50 ± 0.05. A constant nitrogen gas flow was sparged during the anaerobic phase to maintain strict anaerobic conditions. Dissolved oxygen (DO) was maintained from 2.5 to 3.5 mg·L^{-1} in the aerobic phase to avoid oxygen limitations. A volume of 5 L (synthetic wastewater + concentrated carbon solution) was added during the first 5 minutes of the cycle, resulting in a HRT of 12 h. The initial phosphorus concentration was 20 mg P-PO$_4^{3-}$·L^{-1}. The sludge residence time was kept at 15 days with periodic wastage at the end of the aerobic phase.

RESULTS AND DISCUSSION

After the initial EBPR sludge development with propionic acid, the feed was switched to crude glycerol as sole carbon source. A low amount of crude glycerol was used the first cycle and then it was increased progressively reaching a stable operation with 200 mg·L^{-1} at the beginning of the cycle. Figure 1 shows a representative cycle monitored during the steady state operation. COD uptake was linked to P-release and also PHB and PHV storage. Several cycles were monitored for this system during the 140 days period of operation (the system evolution in time will be detailed in the full paper). Figure 2-left summarizes the performance of the SBR during this period regarding the anaerobic P-release/C-uptake ratio and the P-uptake, P-release and net P-removal. The P/C ratio progressively increased from 0.16 to around 0.3 at days 90-100. This PAO activity was also reflected in the high P-release, P-uptake and net P-removal (Figure 2).

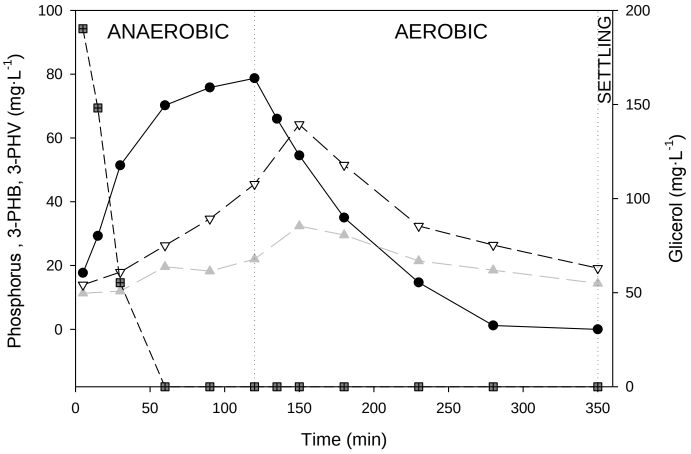

Figure 1. Example of a SBR cycle with crude glycerol as carbon source. (■) COD, (●) P-PO$_4^{3-}$, (▽) PHV, (▲) PHB.

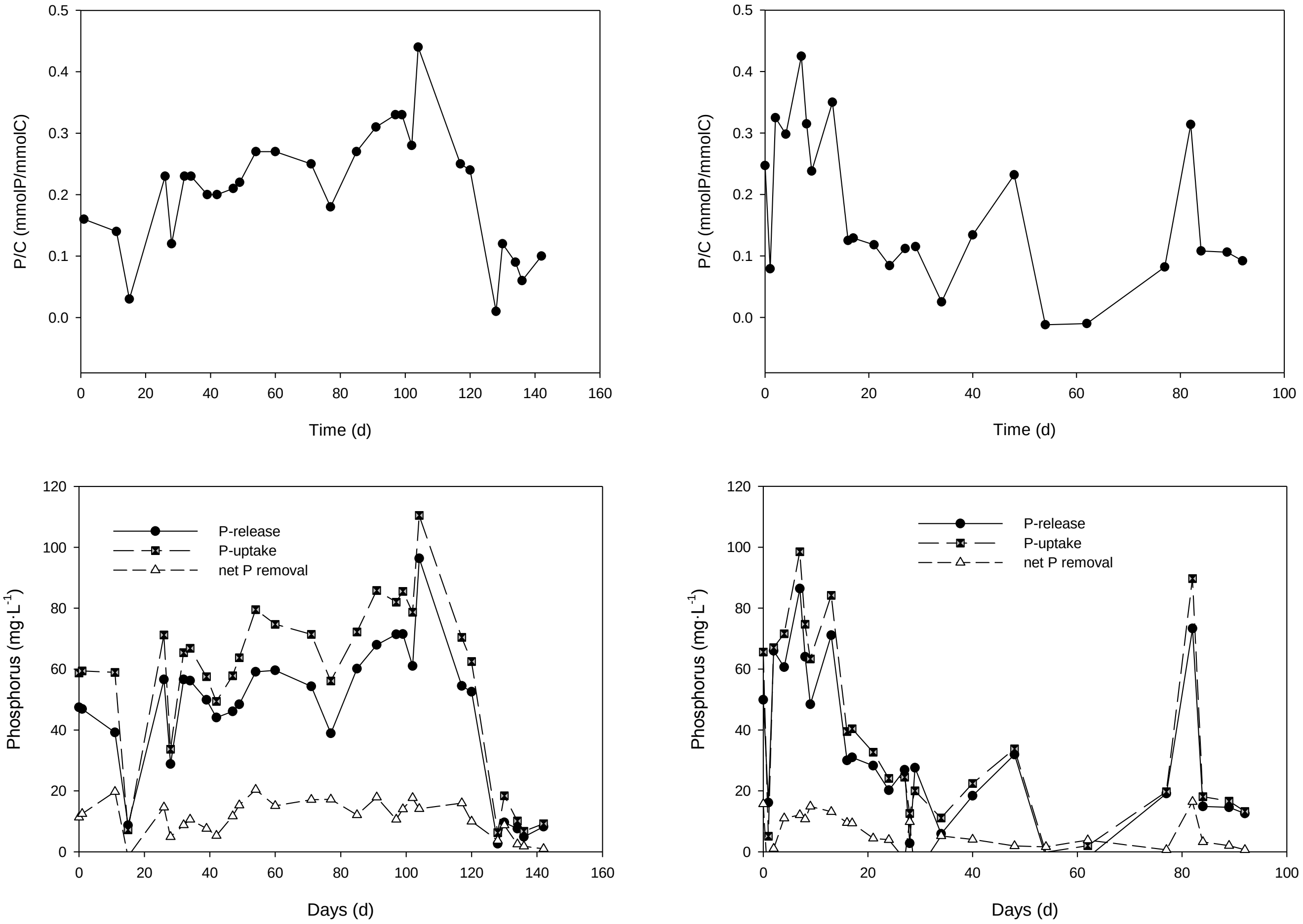

Figure 2. Evolution of the P/C ratio (Top) and the P release, P-uptake and net P-removal (Bottom) for the glycerol-fed sludge (Left) and for the LCFA-fed sludge (Right).

However, the system unexpectedly decreased its PAO activity from day 110 on. Net P-removal was never totally lost, but the decrease of P/C ratio, P-release and P-uptake was remarkable.

After analysing and discarding different hypothesis (to be discussed in the full paper), the effect of LCFA seemed to be important due to its known effect of performance decrease on anaerobic digestion (Alves et al., 2009). For this purpose, another SBR developed also with propionic acid was switched progressively to the use of LCFA as sole carbon source. The system was operated satisfactorily with LCFA leading to high PAO activity during the first 15 days of operation. Similar P/C ratio, P-release, P-uptake and net P-removal was observed when using LCFA or crude glycerol as carbon sources (Figure 2 right).

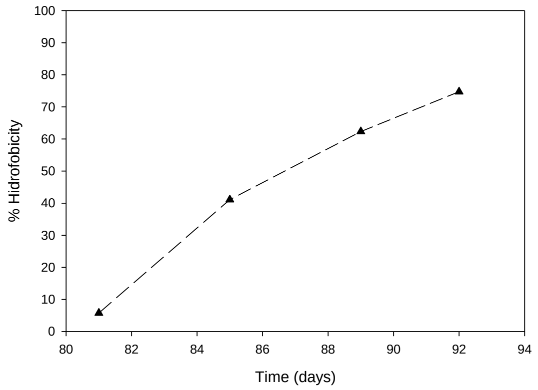

Figure 3. Evolution of the percentage of hydrophobicity for the LCFA after EBPR activity recovery.

However, PAO activity was highly reduced after day 15, producing an unstable operation with low net P-removal activity. After analysing different hypothesis, it was concluded that the loss of activity was related to the long-term effect of LCFA, which is adsorbed on the microorganism surface decreasing the diffusivity of the substrates (VFA) and products (phosphate). To corroborate this hypothesis, after 60 days of operation, the system was left under starvation conditions for some days to enhance the consumption of adsorbed LFCA and then the carbon source was switched back to propionic acid. A very high PAO activity was observed, indicating that PAO were still present in the system but its activity was hidden by LCFA. FISH quantification (to be shown in the full paper) also corroborated that the amount of PAO was maintained almost constant during the whole operational period. After observing PAO activity, the system was again fed with LCFA and hydrophobicity of the sludge was analysed. The increasing trend of hydrophobicity demonstrated the LCFA adsorption on the sludge surface which led to a decrease of PAO activity.

CONCLUSION

Crude glycerol is a suitable carbon source to enhance EBPR activity in urban wastewaters with low carbon source content. However, an excess of crude glycerol with high LCFA content could lead to a decrease of PAO activity due to the adsorption of LCFA on the microorganism surface. The long-term operation with crude glycerol seems feasible provided that is not used as the sole carbon source. LCFA is also demonstrated as a carbon source able to maintain PAO activity at short-term, but producing operational problems related to the biomass increased hydrophobicity when operating with an excess of LCFA in a longer period.

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(P56) Treatment performance of practical-scale DHS reactor employing third-generation sponge media

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Abstract
A practical-scale down-flow hanging sponge (DHS) reactor using the third generation sponge media (DHS-G3) was applied for treatment of the effluent from UASB reactor treating municipal sewage. The process performance of the DHS-G3 was evaluated by conducting on-site experiment in India over one year. The DHS reactor exhibited an excellent performance in removal of organic matter and ammonium-nitrogen at a relatively short HRT of only 0.66 hr. Distribution of heterotrophic and autotrophic bacteria along the DHS was clarified by determining oxygen utilization activity of retained sludge on various different substrates.

Keywords
Municipal sewage treatment; down-flow hanging sponge (DHS); oxygen utilization rate (OUR)

INTRODUCTION

The activated sludge process, currently the most popular method for sewage treatment, consumes enormous quantities of energy, 70% of which is used for aeration. In contrast, the up-flow anaerobic sludge blanket (UASB) system is an economical sewage treatment process that requires no power for aeration, and is becoming a core process in developing countries in warm regions. UASB reactors built in India are designed for a hydraulic retention time (HRT) of 8.5 hr and have ponds downstream for polishing the UASB effluent (called final polishing units (FPU), design HRT 24 hr). However, sewage treatment by the FPU-combined systems has been unable to satisfy current effluent quality standards. Our research group has been conducting basic research since the latter 1990s on the down-flow hanging sponge (DHS) process (Tandukar *et al.*, 2007) as an efficient post-treatment technology that does not detract from the economic superiority of UASB. A practical-scale DHS reactor using the DHS-G3 was constructed at a municipal sewage treatment plant in India that employs a practical-scale UASB reactor. In this study, a practical-scale DHS reactor was operated and continuously monitored under practical conditions. The reactor was operated for recirculation and at increased load, and its capabilities under these conditions were compared and evaluated.

MATERIAL AND METHODS

The DHS reactor consisted of a concrete cylinder 5.5 m in diameter and 5.31 m in height (Figure 1). The 4 levels of the reactor in the main axial direction contained 104 ventilation holes between sponge layers to provide air to the reactor interior. The UASB effluent was pumped to the top of the reactor and the wastewater was uniformly distributed onto the sponge carriers by a moving distributor, which rotated due to the water head differential. After distributing, the UASB effluent flowed downward through the sponge carriers under the force of gravity and flowed out as DHS effluent. The DHS-G3 are cylindrical, 32 mm in diameter and 32 mm long and are composed of polyurethane sponge supported inside a polyethylene plastic net to prevent them from being squashed. The total effective sponge volume was 27.7 m^3. Table 1 presents the operating conditions for the DHS reactor.

The samples provided for analysis during continuous operation were raw sewage, UASB effluent, FPU effluent, and DHS effluent. In addition, once a month, samples were taken from the ventilation holes and a profile measurement was taken along the main axis of the DHS reactor. The analysis items were BOD, SS, VSS, ammonium-nitrogen (NH_4^+-N) and faecal coliform (FC).

An oxygen utilization rate (OUR) test was performed using DHS retained sludge in Phase 1 and in Phase 3. The sludge was squeezed from the sponges, washed in 10 mM phosphate buffer solution (pH 7.0), concentrated in a centrifuge (6,000 rpm, 10 min), and finally the test slurry was adjusted to 4-6 gVSS/L. The substrates were placed in a 100-ml BOD incubator and agitated with a stirrer. A DO sensor (GU-Z, Iijima Electronics Corp.) was then immediately inserted and measurements were initiated. A nitrification inhibitor (allylthiourea, ATU) was added to give a concentration of 2 mg/L to the test slurries in all of the test conditions other than NH_4^+-N and nitrite-nitrogen (NO_2^--N).

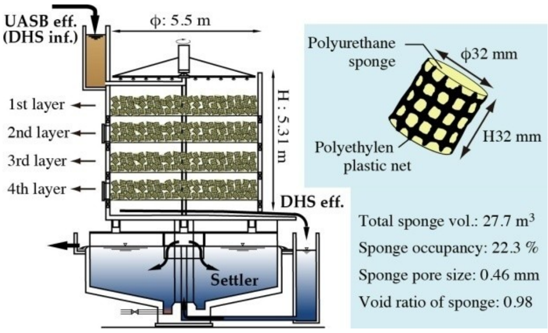
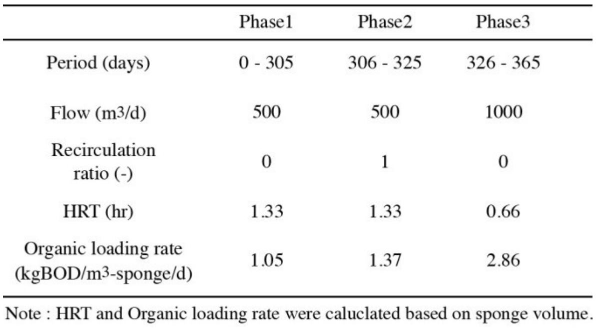


Figure 1. A schematic diagram of the DHS reactor

Table 1. Operating conditions of the DHS reactor



	Phase1	Phase2	Phase3
Period (days)	0 - 305	306 - 325	326 - 365
Flow (m3/d)	500	500	1000
Recirculation ratio (-)	0	1	0
HRT (hr)	1.33	1.33	0.66
Organic loading rate (kgBOD/m3-sponge/d)	1.05	1.37	2.86

Note : HRT and Organic loading rate were caluclated based on sponge volume.

RESULTS AND DISCUSSION

Performance during the whole experimental period

Table 2 provides an overview of the water quality results. From start of operation to the end of the test, the quality of the DHS effluent indicated high treatment performance, providing water that satisfied the Indian effluent quality standards on every parameter except for FC. The mean unfiltered BOD over the experimental period was 130 (SD ± 38) mg/L for the raw sewage, 62 (± 20) mg/L for the UASB effluent, and 42 (± 13) mg/L for the FPU effluent. The DHS effluent was 10 (±6) mg/L in Phase 1, 7 (± 2) mg/L (Phase 2), and 13 (± 6) mg/L (Phase 3). As for the BOD removal rates, about 50% of the total BOD in the water was removed in the UASB reactor, while at least 90% of it was removed in the UASB+DHS system combining a UASB reactor with a DHS reactor, under all operating conditions. The geometric means of FC were 1.1×10^7 MPN/100 ml in the raw sewage, 6.3×10^6 MPN/100 ml in the UASB effluent, and 5.7×10^5 MPN/100 ml in the FPU effluent. In the DHS effluent were 4.7×10^5 MPN/100 ml in Phase 1, 5.9×10^4 MPN/100 ml in Phase 2, and 1.3×10^6 MPN/100 ml in Phase 3. The log transformed reduction values associated with the UASB+DHS system were relatively high, at least 1.5 log in Phases 1 and 1.8 log in Phase 2. However, in Phase 3, possibly because the contact time between the wastewater and sludge was insufficient due to the reduced HRT, the log decrease was lower (0.7 log). The mean NH_4^+-N during the test period was 23 (± 6) mg/L in the raw sewage and 26 (± 6) mg/L in the UASB effluent. The levels in the DHS effluent were 10 (± 5) mg/L in Phase 1, 6 (± 3) mg/L in Phase 2, and 19 (± 4) mg/L in Phase 3. The recirculation operation in Phase 2 was an effective approach for removing NH_4^+-N (NH_4^+-N removal 80%). The concentration of DO in the DHS effluent was 5.6 – 6.7 mg/L, which demonstrated that the existing system was capable of taking up sufficient oxygen.

Start-up characteristics

Start-up characteristics of the DHS reactor were evaluated with respect to BOD and FC removal in Phase 1. The unfiltered BOD profiles along the DHS reactor were taken 24 hours after the start of operation and then at 66, 126 and 250 days (Figure 2(A)). Since the concentrations of the inflow to a DHS reactor vary with fluctuations in the composition of the incoming wastewater, we considered that we could fit the logarithm of the BOD reduction rate to the first order reaction equation for the region where it could be approximated as linear (Figure 2(B)). These results indicate that after 24 hours, most of the removal was occurring in the 1st layer, and that almost none occurred in the 2nd or lower layers. This was attributed to the solid components contained in the UASB effluent getting trapped in the sponge media. The reduction rate constants at 24 hours, 66 days, 126 days and 250 days were 1.33/h, 2.04/h, 2.45/h, and 2.52/h. No great difference in BOD concentration between the 3rd and 4th layers was found at day 126 and day 250, indicating that nearly all the biodegradable BOD components had broken down by the 3rd layer.

Figure 2(C) showed a first order reaction equation for the rate of FC removal. There was no clear difference between the slopes of the lines at 24 hours and at 66 days. The slope gradually increased from around day 87 and the removal rate constant was greater than 2.30/h on day 126 and on day 250. It has been reported that FC removal in the DHS reactor is achieved by adsorption into and inactivation by the retained sludge, or by protozoa which prey upon the FC (Tawfik *et al.*, 2006). Just after initiating operations, the sludge had not yet accumulated, which meant that FC in the wastewater were removed by becoming trapped in the sponge; as for BOD removal, they cannot be considered to have been biologically removed. The concentration of retained sludge on day 66 was about 3 gVSS/L-sponge, but since no increase in the gradient of the removal rate constant was observed, we surmise that the sludge concentration had not reached the value needed for removal of FC. The retained sludge concentration was 5.0 gVSS/L-sponge on day 87 when FC removal performance began to increase. This concentration increased to 11.4 gVSS/L-sponge on day 250. The gradient of the removal rate constants of both BOD and FC indicated that the sludge had grown enough for removing BOD and FC in 4 months. However, it should be noticed that, in the early stage of the start-up period, adsorption of BOD and FC into sponge media played an important role for removal of those components, guaranteeing the effluent water quality in some expand.

Table 2 Summary of water quality parameters

Parameter	Sewage	UASB eff.	DHS eff.			FPU eff.
			Phase 1	Phase 2	Phase 3	
Unfiltered BOD, mg/L	130 (38)	62 (20)	10 (6)	7 (2)	13 (6)	42 (13)
Filtered BOD, mg/L	57 (22)	38 (12)	6 (4)	4 (1)	7 (5)	15 (8)
FC, MPN/100mL	1.1 x 10^7	6.3 x 10^6	4.7 x 10^5	5.9 x 10^4	1.3 x 10^6	5.7 x 10^5
NH_4^+-N, mg/L	23 (6)	26 (6)	10 (5)	6 (3)	19 (4)	22 (7)
SS, mg/L	229 (98)	51 (15)	14 (6)	10 (4)	20 (4)	66 (25)
DO, mg/L	-	-	6.0 (1.0)	6.7 (0.6)	5.6 (0.7)	3.5 (5.6)
Removal		by UASB		by UASB+DHS		by UASB+FPU
Unfiltered BOD, %		51 (15)	91 (5)	94 (2)	91 (4)	65 (14)
FC, log		0.2 (0.4)	1.5 (0.7)	1.8 (0.8)	0.7 (0.6)	1.2 (0.7)
NH_4^+-N, %		-	63 (18)	80 (5)	46 (9)	15 (20)
SS, %		73 (13)	93 (4)	94 (3)	89 (6)	65 (21)

Figures in parentheses represent standard deviations.

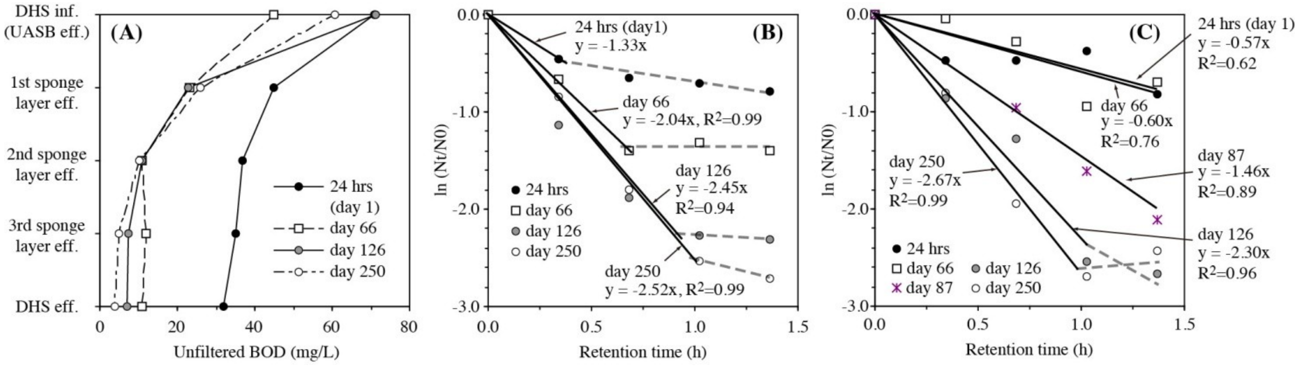


Figure 2. Unfiltered BOD profile along DHS height (A), and reduction rate constants of unfiltered BOD (B) and FC (C)

OUR of DHS-retained sludge

In order to clarify the distribution patterns of heterotrophic and nitrification bacteria along the height of the reactor with respect to organic loading rate, OUR tests on organic and inorganic substrates were conducted in Phases 1 and 3. Figure 3 shows the findings from the OUR for each substrate, performed in Phase 1 (organic loading rate: 1.05 kgBOD/m^3-sponge/d) and Phase 3 (organic loading rate: 2.86 kgBOD/m^3-sponge/d). OUR in Phase 1 was 1.65 - 2.49 mg O_2/gVSS/h in the glucose substrate. In contrast, values increased along the DHS reactor in Phase 3 (varying 1.03 - 6.53 mg O_2/gVSS/h in the glucose substrate). No variation in OUR was observed along the DHS reactor in the organic substrate in Phase 1. In Phase 3, however, the OUR increased in the downward direction in the DHS reactor, primarily because of the high OUR due to heterotrophic bacteria in the lower portion of the DHS reactor. The OUR of NH_4^+-N and NO_2^--N substrates in Phase 1 tended to increase in lower part of the DHS reactor, showing maximum values in the 3rd sponge layer (16.25 mg O_2/gVSS/h (NH_4^+-N substrate) and 6.98 mg O_2/gVSS/h (NO_2^--N substrate)). Notably, maxima also occurred in the 3rd sponge layer in Phase 3 (12.18 mg O_2/gVSS/h (NH_4^+-N substrate) and 7.42 mg O_2/gVSS/h (NO_2^--N substrate)), but the OUR was 25% lower in the NH_4^+-N substrate in Phase 3 than during Phase 1. Thus, these results suggest that nitrifying bacteria tend to increase along with the reactor height, and to decrease with increase of organic loading because of the competition on oxygen with heterotrophic bacteria.

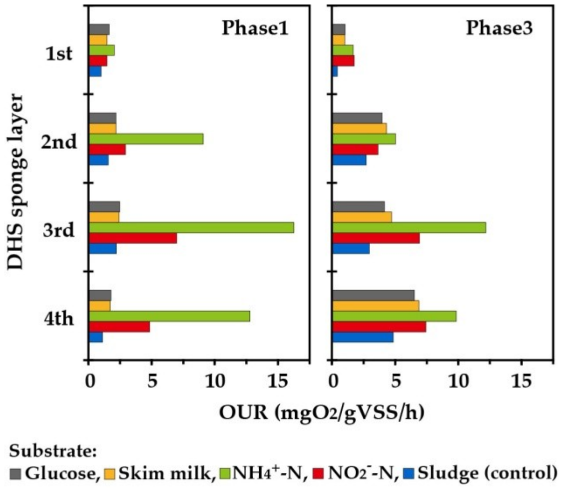


Figure 3. Measured OUR values in Phase 1 and Phase 3

CONCLUSION

In this study, a DHS reactor filled with the third generation sponge media was operated under practical conditions downstream of a UASB reactor in India. The quality of the DHS effluent indicated high treatment performance, providing water that satisfied the Indian effluent quality standards on every parameter except for FC. We therefore believe that application of the DHS-G3 should be promoted in efforts to expand the use of DHS reactors at this time.

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(P57) Reducing the energy consumption of aerobic sewage treatment by removing the bubbles

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Abstract

Bubble aeration has been the cornerstone of aerobic biological wastewater treatment for the past 100 years and while it is effective, it is also inherently inefficient with maximum oxygen transfer efficiencies of 40%. Bubbleless-aeration technology has evolved to the point where it is now ready to effectively and efficiently meet the requirements of a wastewater treatment plant. To demonstrate this, a 1000 litre OxyMem Membrane Aerated Biofilm Reactor (MABR), was installed at a full scale municipal wastewater treatment plant, downstream of the primary treatment tanks. The reactor was operated in parallel to the full scale Activated Sludge (AS) plant. After a 3 month start up, the MABR achieved COD and ammonia removal rates of greater than 75% and 80% respectively with a remarkably low aeration energy requirement. Aeration energy was estimated at 8kg O_2/kWhr for the MABR compared to 2.2kg O_2/kWhr for the fine bubble diffusers installed in the AS. This is the first time a MABR of this scale has been successfully deployed at a wastewater treatment plant.

Keywords

Biofilm, Membrane, Aeration

Introduction

Currently the energy requirement for the water industry in industrialised nations accounts for 2% of the entire electricity demand. While pumping is the major energy demand on the water treatment side in conventional sewage treatment plant the aeration of the aerobic processes accounts for 60% of the operational spend. While major advances have been made in aeration technology there is still only 35% of the oxygen supplied available for the polluting degrading bacteria. The Membrane Aerated Biofilm Reactor (MABR) has shown great promise through-out the past twenty years as a viable alternative option for the biological treatment of wastewaters. This has been demonstrated numerous times at lab and small pilot scale. (Downing, 2008; Stricker, 2009). The main process advantage of the MABR is the counter diffusion of oxygen and pollutants into the biofilm allowing for aerobic bacterial processes in an anoxic tank. While the major economic advantage is the dramatic reduction in the energy required to supply the oxygen for the aerobic processes (Casey et al,2008). The MABR concept has been trialled treating various different wastewaters and at various scales (Syron, 2007) but has yet to be installed at a full scale as a standalone treatment system.

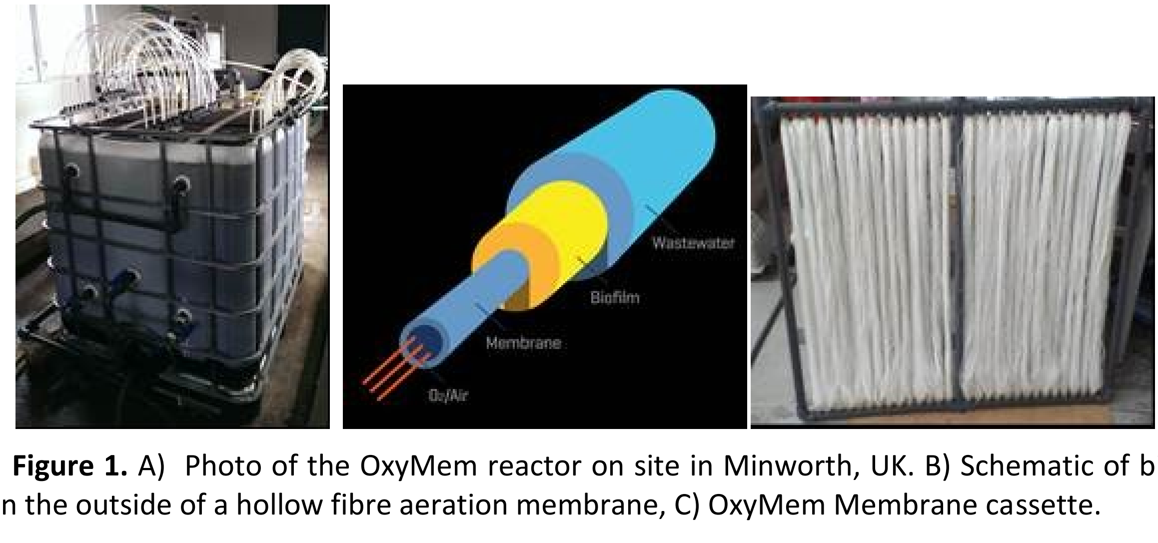

Figure 1. A) Photo of the OxyMem reactor on site in Minworth, UK. B) Schematic of biofilm growing on the outside of a hollow fibre aeration membrane, C) OxyMem Membrane cassette.

Material and Methods

Oxymem's gas transferring membranes are made from a non-porous diffusive PDMS, manufactured to be both the biofilm carrier and aeration membrane, a 1000 litre OxyMem MABR with a total surface area of 239m^2 was installed in Severn Trent's, Minworth Sewage Treatment Works in Birmingham, UK. The unit treated primary effluent taken directly from the distribution chamber to the AS basins. Biofilm control was carried out through an intensive air scour which varied in duration from 5-15mins and in frequency from 1-4 times a day. Through-out the course of the site trial (still underway) the energy consumption of the reactor was monitored, along with COD and Nitrogen removal and solids production.

Results and Conclusions

The energy requirement for aeration in the OxyMem reactor was less than 30% that of the recently upgraded fine bubble diffusers installed on site. This was due to the reduction in air supply pressure and the superior oxygen transfer efficiency of membrane diffusion over a rising bubble. Due to the unique oxygen profile in the membrane attached biofilm, the bulk liquid remained anoxic through-out the operation of the reactor, this resulted in almost complete de-nitrification of the oxidised ammonia >90%. The initial simultaneous rates of reaction were 2 gCOD/m^2 day and 0.3gN/m^2 day. As was highlighted in previous studies of MABRs, biofilm control proved to be critical to the continuing stable performance of the MABR. Trials were carried out to evaluate the effects of inadequate biofilm control on the reactor performance; these resulted in an increase in effluent suspended solids and a decrease in reactor performance. Stable operation was regained when the Biofilm control was recommenced. It was also observed that proposed Oxymem reactor provided a very effective at solids separation. After the biofilm control event the detached biomass settled very quickly to the bottom of the reactor. When excessive solids built up in the reactor this led to a reduced performance. As the reactor was not designed for automatic sludge removal a regime was put in place to manually desludge every week. This resulted in a stable pollutant removal. The rapid settling in the OxyMem reactor also resulted in some TSS removal which was not intended. This occurred during stable operation when desludging was occurring everyweek.

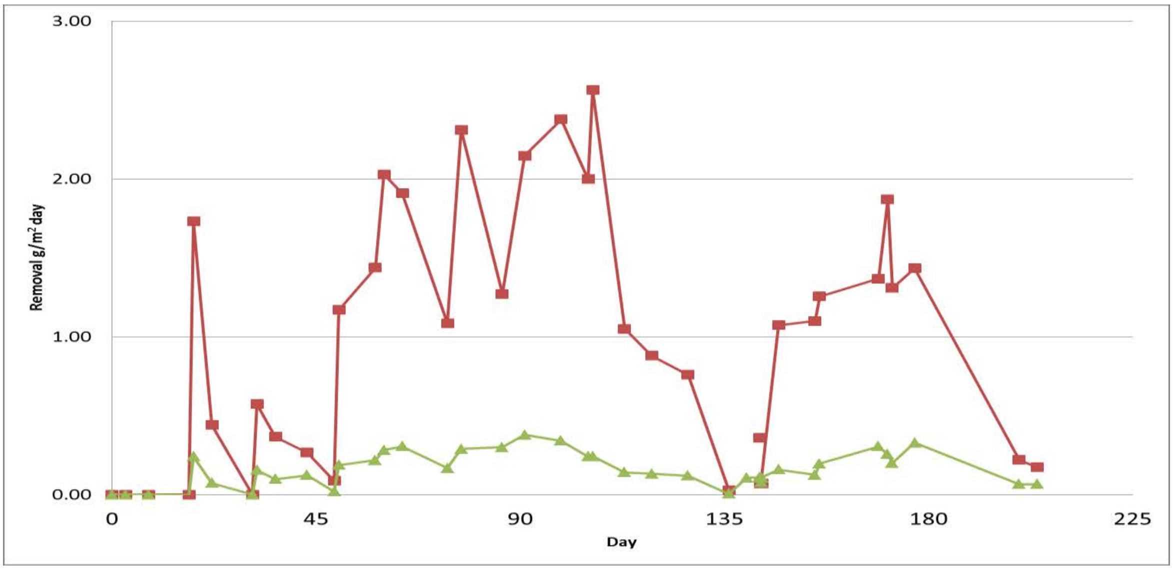

Figure 2 Areal based removal rate for -🟥- dissolved COD and -▲- N-NH4 over the course of the reactor Operation

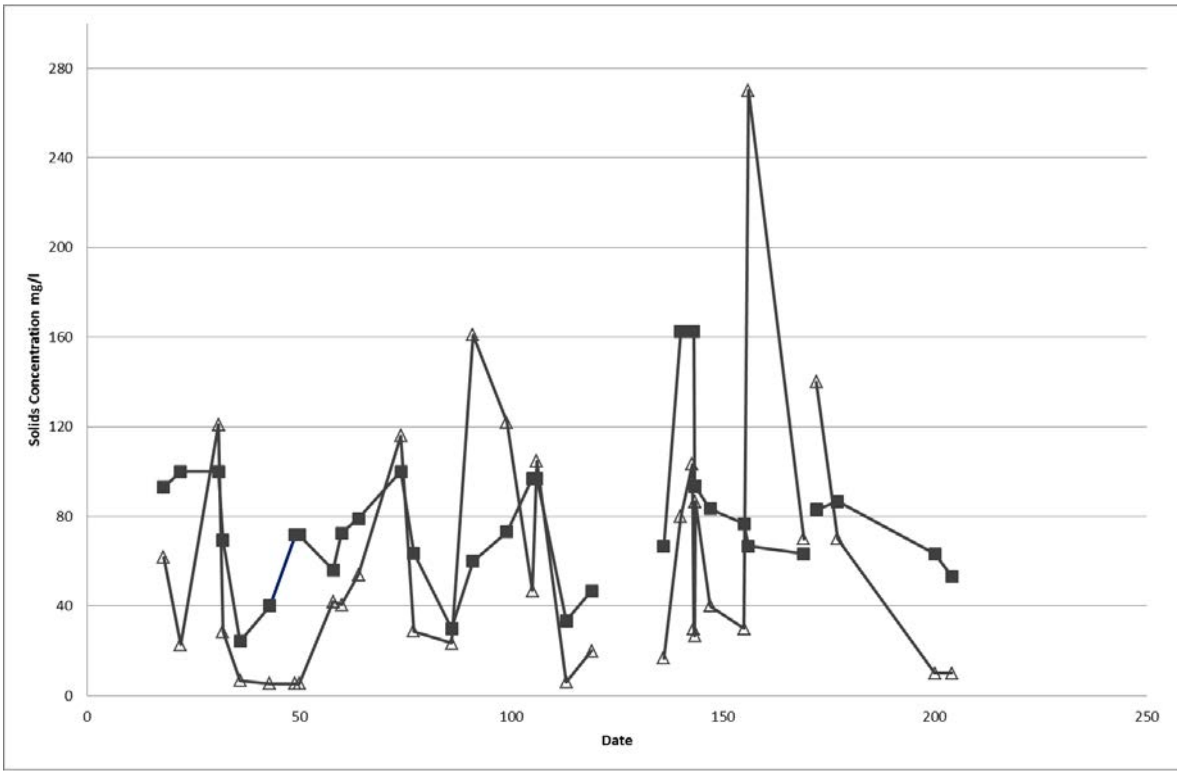

Figure 3 TSS Concentration -■- Influent and -Δ- Effluent during reactor operation

Conclusions

The OxyMem MABR reactor has proven successful at 1000 litres to date and with the an upgraded reactor designed for sludge removal due shortly. Future trials will be at ever increasing scales.

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(P58) Challenges in the Design of a Community-based Vermifiltration System for Wastewater Treatment

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Abstract

A pilot-scale, three layered, vermifiltration unit was set up and investigated with different operating conditions for municipal wastewater treatment. In such a system, earthworms are expected to play significant role in the removal of key contaminants. Hence, it is essential to maintain the worms in the healthiest condition possible throughout the process. This study aims to identify the factors that impede worm health and activity in the system. Environmental conditions such as pH, temperature, moisture, aerobic conditions, hydraulic retention time, hydraulic loading rate and worm density are some of the factors to consider. Similarly, system design and operation in terms of such parameters as maintaining an appropriate influent feeding rate through the top soil layer, as well as soil porosity, are important considerations - since flooding/pooling in the system can result in the worms drowning. To date, the unit has been shown to efficiently remove up to 94%, 70%, 93% and 97% of COD, TOC, TSS and turbidity respectively.

Keywords

Vermifiltration; municipal wastewater treatment; developing countries; *Eisenia foetida*; *Eisenia andrei*

INTRODUCTION

In developing countries, approximately 90 per cent of wastewater generated is discharged directly into waterways without any kind of treatment and almost half of the population of developing world does not have access to sufficient sanitation (Corcoran 2010; Rammont and Amin 2010). This leads to contaminated freshwater and reduces access to safe drinking water, posing a threat to environmental and human health. Considering the threat to freshwater availability, and the fact that more than 1.8 million children under 5 years die globally due to waterborne diseases every year, it is essential to develop and implement appropriate technologies to treat wastewater before discharging it to waterways. Many developing countries are not able to build or maintain wastewater treatment plants based on advanced technologies and therefore need to consider economical, small-scale, and less technical, treatment systems. Vermifiltration is one such technology that uses earthworms and microorganisms to treat wastewater. This kind of treatment system provides opportunities to recognize wastewater as a resource and encourages its reuse for different applications or for return to waterways. This will ultimately reduce the stress on freshwater availability and improve environmental and public health (Massoud et al. 2009; Kivaisi 2001).

Vermifiltration uses versatile 'waste-eating' earthworm species such as the Indian Tiger Worm (*Eisenia foetida*), the Red Tiger Worm (*Eisenia andrei*) and the Indian Blue Worm (*Perionyx excavates*), as the major filter media (Wang et al. 2013; Li et al. 2012; Sinha et al. 2008). Such species have the capability to survive in harsh environments (Hughes et al. 2007) and to multiply rapidly. In a vermifiltration system, the first layer usually traps suspended solids by an adsorption process, which is synchronously fed by worms and microbes present in soil. Organic and inorganic suspended solids are then stabilized through a complex biodegradation process involving worm and microbe activity which also results in soil aeration, enhancing the effectiveness of filtration (Tomar and Suthar 2011). This research investigates the challenges associated with designing and operating a vermifiltration system in the context of municipal wastewater treatment at the community level, whilst at the same time being economic, technologically simple and easily operated and maintained. This presentation focuses on the overall efficiency of the unit in removing pollutants from sewage wastewater.

MATERIALS AND METHODS

Vermifiltration unit set up

A pilot-scale vermifiltration unit was constructed which consisted of distinct layers of soil, sand and gravel as shown in **Figure 1**. Sample collection pipes were fitted at the bottom of each layer in order to allow systematic analysis of the effluent.

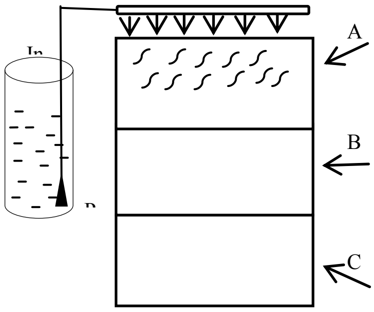

Figure 1: Schematic diagram of vermifiltration unit A) Soil with earthworm B) Sand C) Gravel.

Experimental design

Raw sewage was fed into the unit and left for 50 days to culture biofilm in the filter materials (Xing et al. 2010). The unit was then operated for ten months under different operating conditions – 1.43 m/hr, 0.91 m/hr, 0.6 m/hr and 0.0084 m/hr hydraulic loading rate (HLR) and 4.32 hrs, 12.96 hrs, 19.52 hrs and 182.02 hrs hydraulic retention time (HRT), respectively. Initially, approximately 1.5 kg (~6,000) of earthworms (*Eisenia foetida, Eisenia andrei* and *Perionyx excavatus*) was introduced into the soil layer (1 m^2). After ten days of acclimatization, influent was fed into the unit. The system was then operated in steady state mode for approximately four months. When worms died due to pooling in the upper layer, the system was started again with almost 3 kg (~12,000) of worms.

Table 1: Influent characteristics over time

Influent	**Range**	**Mean ± SE**
Temperature (°C)	**11.6 - 24.0**	**18.6 ± 0.8**
pH	**5.56 - 8.47**	**7.77 ± 0.12**
Conductivity (mS/cm)	**0.52 - 1.41**	**1.00 ± 0.05**
Turbidity (NTU)	**34 - 685**	**272 ± 37**
TSS (mg/L)	**59 - 566**	**242 ± 25**
DO (mg/L)	**0.02 - 8.16**	**1.65 ± 0.59**
COD (mg/L)	**34 - 594**	**328 ± 28**
NH_3-N (mg/L)	**5.0 - 122.0**	**66.8 ± 5.8**
NO_2-N (mg/L)	**0.3 - 20.0**	**7.5 ± 1.0**
NO_3-N (mg/L)	**2.7 - 28.6**	**9.9 ± 1.6**
TN (mg/L)	**12.0 - 136.6**	**83.3 ± 6.5**
TOC (mg/L)	**34 - 228**	**91± 9**
TP (mg/L)	**23.4 - 46.2**	**34.9 ± 1.7**

Sample analysis

Influent and effluent samples (from the three layers) were collected and analysed (in triplicate) for the standard physico-chemical parameters shown in **Table 1 -** using standard methods (American Public Health Association, 1998). Heavy metals such as cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (MN), nickel (Ni) and zinc Zn) were tested in influent and effluent using Inductively Coupled Plasma (ICP) Spectrophotometry.

Biofilm analysis

Filter material from each of the three different layers (soil, sand and gravel) were collected and freeze-dried. Then humic acid like (HAL) fraction was isolated using the method described in Li et al. 2011. Scanning electron microscopy (SEM) was used to determine the microstructures of extracted HAL fractions, soil, fibre and vermicast.

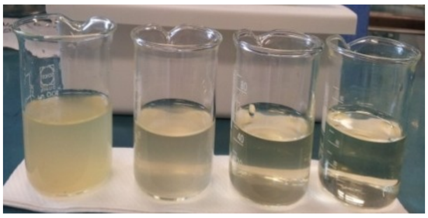

Figure 20: Influent, Effluent from soil layer, sand layer and final effluent (from left to right).

RESULTS AND DISCUSSION

Performance of the unit

Some general observations are as follows. **Figure 3** depicts the COD and TOC removals over the course of the experiments. For COD, the highest percentage change of 94% was achieved when the vermifiltration unit (with worms) was operated with a HLR of 0.6 m/hr and a HRT of 19.52 hours. For TOC, the highest percentage change was 70% at 0.91 m/hr HLR and 12.96 hrs HRT. During the overall run, TSS and turbidity were removed by 75.3% and 78.3% respectively. Moreover, NO_2-N and NO_3-N decreased by 39.1% and 91.4% respectively, however NH_3-N increased by 45.9%. **Figure 2** depicts the appearance of the wastewater as it moves through the unit. The unit with worms present produced effluent with higher TN and TP at 0.6 m/hr HLR and 19.52 hours HRT, increasing up to 43.6% and 31.0% respectively. In contrast, TN and TP decreased in the control (system without worms) by factors of up to 86% and 82% respectively at HLR 0.0084 m/hr and HRT 182 hrs. During the overall run, temperature and pH increased by 4.7% and 5.8% respectively and conductivity decreased by 37.0%. The heavy metal concentration in the influent was not significant.

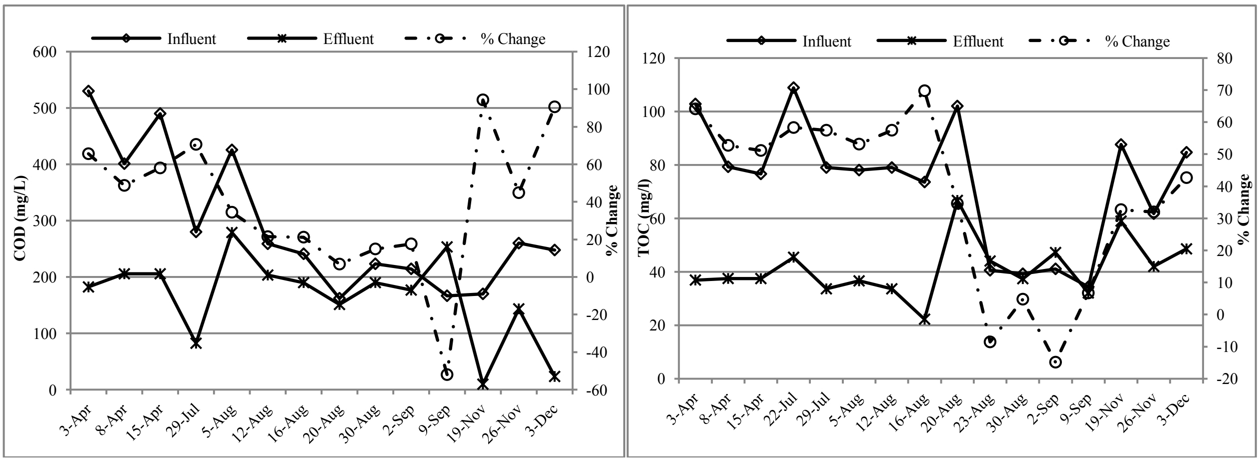

Figure 3: COD and TOC removal after the introduction of worms in the system.

Environmental Conditions

In a vermifiltration unit, earthworms are used as a major filter media. They usually live on the top soil layer and it has been observed that influent water quality has direct impact on them. Therefore, it is important to maintain optimum environmental conditions to keep the worms healthy and active in the system (Baumgartner 2013). In this study we have placed a focus on the influent water quality (IN) and the effluent water quality from the soil layer (EF1) as they are determinative/indicative of the environmental condition of the soil layer.

Temperature: The optimal temperature range for worms to remain active in the system is considered to be 15°C to 25°C (Klein 2008). During our study period, the IN and EF1 temperatures ranged 11.6°C – 24.0°C and 10.4°C – 22.6°C respectively.

pH: The best pH to keep worms active is neutral (7). However, they can survive in the pH range of 4.5 to 9. During the study period, the IN and EF1 pH ranged 6.8 – 8.5 and 6.9 – 7.4 respectively.

Aerobic environment: Keeping the system aerobic is a major challenge. Dissolved oxygen in the influent was negligible, and the study did not observe any significant change in EF1.

Population and density of worms: The unit started with a large population and density of worms (~12,000 /m^2) since this provides a better removal rate for organic contaminants (Klein 2008).

Hydraulic Retention Time and Hydraulic Loading Rate: Higher HRT and low HLR is found to be favorable for the worms to remove pollutants most effectively. **Figure 4** depicts what can happen when these parameters are not regulated properly.

Figure 4: Dead worms on the top soil layer due to pooling of influent.

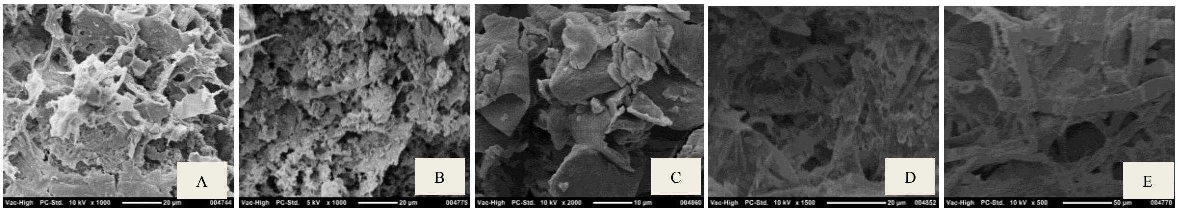

Figure 5: Scanning electron microscopy of A. Vermicast; B. Soil; C. HAL fraction isolated from sand; D. HAL fraction from gravel; E. Fiber on the top soil layer.

Scanning Electron Microscopy

SEM micrographs of vermicast, soil, HAL fraction isolated from sand and gravel and biofilm and fiber (which impeded flow through the top layer) are presented in **Figure 5**. Li et al. 2011 reported that a compacted lumpy structure provides better permeability of water.

System design

During the set up of the filter unit and operation period, we experienced the following problems in terms of system design:

Wastewater application method: To minimize the impact of water pressure on worms and evenly distribute influent in the system a frame with 2 mm diameter holes was developed, which became blocked due to the presence of fiber in the influent. Hence, the diameter of holes was increased up to 8 mm to promote a good flow. Regular cleaning of the holes in the frame is found to be required. This component could benefit from even further development.

Clogging: The study observed fiber in the influent (even though the influent was passed through a 2 mm screen) and soil compaction are the two major reasons for the clogging the system. The fiber created a thin firm layer on the top of soil, as shown in **Figure 5E**, blocking the passage of water through the soil. A parallel laboratory scale study on the water percolation rate through the soil is being conducted to enable us to optimize the soil mix and improve its porosity.

CONCLUSIONS

The vermifiltration unit set up to treat municipal wastewater was operated for almost a year. Different challenges emerged over time in order to ensure a healthy worm population. Environmental conditions such as temperature, pH, moisture, aerobic environment, hydraulic retention time and hydraulic loading rate were identified as major challenges in order to optimize the system. Moreover, for this influent, system clogging was observed due to fiber in the influent resulting in a decreased water percolation rate through the top soil layer. However, under certain conditions the unit was observed to perform very well for the removal of TSS, turbidity, COD and TOC.

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(P59) Biodegradation of naphthalene sulfonate polymers by Pleurotus ostreatus in packed-bed bioreactor

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Abstract

The ability of white rot fungus *Pleurotus ostreatus* to biodegrade 2-naphtalene sulfonic acid polymers (NSAP) contained in petrochemical wastewater was evaluated. The biodegradation experiment was conducted in a packed-bed bioreactor with a bed made of straw, which acted as both support and co-substrate for the fungi. The reactor worked at a Hydraulic Retention Time (HRT) of 3d and showed a stable NSAP degradation (35 ± 5%). Respirometric tests conducted on the effluent from the packed-bed bioreactor showed that the fungal treatment was also able to significantly increase the bCOD/COD ratio, which rose from 9% (raw wastewater) to 40% (treated wastewater). It was observed that the fungal degradation of the straw in the bed releases non-biodegradable by-products. Taking into account this contribution, the combined treatment of fungi and activated sludge was able to reduce the initial COD by up to 73%.

Keywords
Biodegradation; HPLC; naphthalene sulfonate polymers; packed-bed bioreactor; respirometric test; white-rot fungi

INTRODUCTION

White-rot fungi (WRF) are organisms capable of extensively degrading lignin within lignocellulosic substrates. The ligninolytic enzymes of white-rot fungi, known as Lignin-Modifying-Enzymes (LMEs) are Laccase (Lac), Lignin Peroxidase (LiP) and Manganese Peroxidase (MnP) (Pointing, 2001). These enzymes have a broad substrate specificity and have been implicated in the transformation and mineralization of organopollutants with structural similarities to lignin (Pointing, 2001). It has been demonstrated that WRF can be involved in the degradation and/or mineralization of xenobiotic compounds such as dyes (Borchet and Libra, 2001), insecticides (Bumpus and Aust, 1987), PAH (Bezalel et al., 1996) and other compounds.

In most cases degradation of recalcitrant compounds by WRF requires the presence of another carbon source; glucose is the most used, although variable concentrations in the range 100mg/L ÷ 10g/L have been reported in literature (Leidig et al., 1999; Blánquez et al., 2008). Glucose is a rapidly biodegradable carbon source and therefore, when used in non-sterile conditions, it may foster bacterial growth, which often compromises fungal biodegradation (Borchet and Libra, 2001). To date few studies have focused on the research of an alternative to glucose as an additional carbon source to enhance the growth of fungi with ligninolytic extracellular enzymes and biodegradation of xenobiotics (Libra et al., 2003; Ehlers and Rose, 2005), while avoiding or limiting bacterial growth.

Previous studies focusing on the use of fungi for biodegradation of recalcitrant compounds showed that attached biomass seems to be preferable to suspended biomass because it has been shown that degradation capacity and tolerance to toxic pollutant concentrations can be increased when fungal biomass is immobilized (Pallerla and Chambers, 1998, Ramsay et al.,2005); furthermore, attached biomass appears to be more effective in suppressing bacterial growth (Gao et al., 2008).

This study focuses on the degradation of 2-naphtalene sulfonic acid polymers (NSAP) by the fungus *Pleurotus ostreatus.* These compounds are commonly employed in several industrial sectors covering a wide range of activities from textile mills and leather tanning operations to the production of pharmaceuticals, azo dyes, pesticides, cosmetics, polymers and construction materials (Germirli Babuna,

2009) and exhibit only limited biodegradability in conventional wastewater treatment plants (WWTPs) (Shiyun et al., 2002).

In this study we propose the use of a packed bed bioreactor (PBR) with a bed made of straw, which acts as both physical support and co-substrate for fungi.

MATERIALS AND METHODS

Wastewater

The wastewater was collected from a petrochemical industry located in Italy and contains a mixture of NSAP as the largest fraction of organic pollutants (Briganti et al., 2012). The wastewater has a slightly basic pH (about 7.9), high COD concentration (3500mg/L) and a very low bCOD/COD ratio (<10%), which confirm the recalcitrant nature of NSAP. Other wastewater characteristics include absence of phosphate and low nitrogen content (5.5 mgN_NO_3^-/L; 0.187mgN_NH_4^+/L and absence of nitrite).

Bioreactor

Pleurotus ostreatus was grown on autoclaved straw and subsequently put in a 500ml PBR for treating wastewater. The PBR, which worked at a Hydraulic Retention Time (HRT) of 3d, was initially fed with a mineral medium (6g/L $NaNO_3$, 0.52 g/L KCl, 0.52 $MgSO_4 \cdot 7H_2O$, 1.52 g/L KH_2PO_4, 10 mg/L $FeSO_4$, 3 mg/l $CuSO_4$, 2mg/L $ZnSO_4$), with the purpose of evaluating the contribution of straw degradation metabolites to the final COD, and then fed with the wastewater, the pH of which was adjusted to 7 using HCl 0.2M, in order to make the wastewater more suitable for fungal treatment (Deacon, 2006).

Untreated and treated wastewater were analyzed by High Performance Liquid Chromatography (HPLC) coupled with UV-Vis diode array detection and the separation method was adapted from the protocol described by Song et al. 2003. Fungal enzymatic activities (Lignin Peroxidase, Manganese Peroxidase, Laccase) were controlled daily following previously reported methods (Tien and Kirk, 1983; Vyas et al., 1994; Niku-Paavola et al.,1988).

Raw wastewater and reactor effluent were also analyzed in terms of COD and bCOD. These latter analyses were conducted through respirometric tests, carried out using samples of activated sludge (AS) taken from the oxidation tank of the WWTP managed by Consorzio Cuoiodepur Spa (Pisa, Italy), which treats tannery wastewater and the biomass of which is acclimated to natural and synthetic tannins, including sulfonated naphthalene-formaldehyde condensates (Munz et al., 2009).

RESULTS AND DISCUSSION

The bioreactor worked continuously for three months, showing a stable Lac activity, varying in the range 0.1÷0.5 U/ml. Neither MnP nor LiP were detected.

Figure 1 shows a comparison between chromatograms of raw wastewater and treated effluent: in untreated wastewater at least ten fractions referable to NSAP are evident, while the effluent chromatogram shows flatter fractions from 3 to 10 (corresponding to high molecular weight compounds). On the contrary, in the first 6-7 minutes (corresponding to fractions 1 and 2) new peaks appeared in the effluent chromatogram, probably associated with the formation of new compounds with lower molecular weight, suggesting that the mechanism in place is a biodegradation/depolymerization of NSAP.

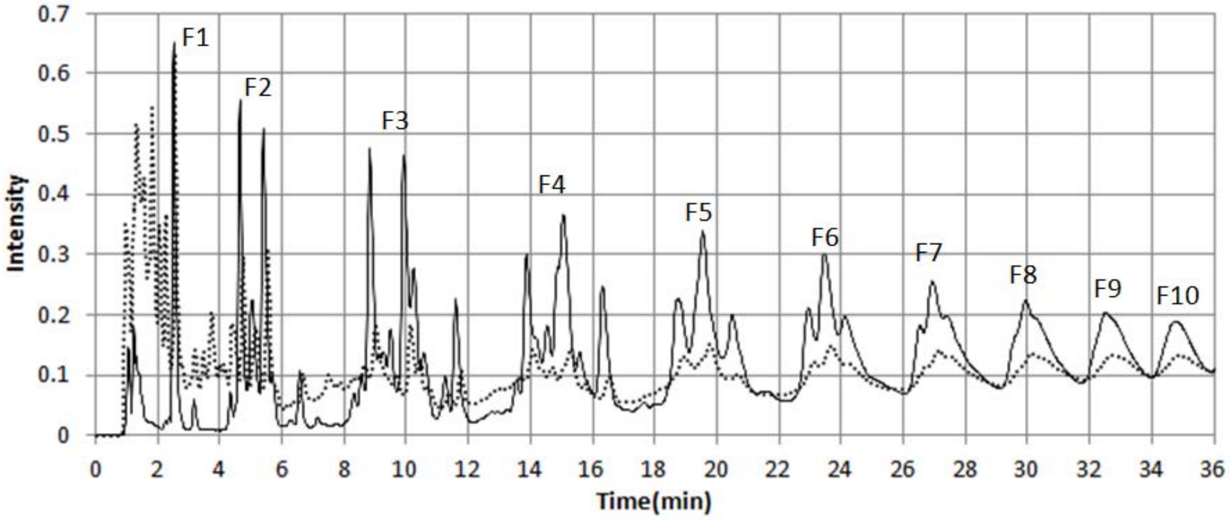

Figure 1. Wastewater chromatogram before fungal treatment (continuous line) and after (dotted line).

Biodegradation (about 35 ± 5% in terms of reduction of area related to fractions from 3 to 10) was stable in the course of the experiment.

As regards COD and bCOD values, even though the COD value was not reduced after PBR, the results of respirometric tests showed a clear increase in the bCOD/COD ratio from 9% (raw wastewater) to 40% (table 1).

Results suggest the idea of using fungi as a pre-treatment for the activated sludge (AS) process since, according to the respirometric tests, the combined treatment would enable the removal of up to 40% of the original COD.

The contribution of metabolites from the straw degradation significantly affected the results of the bioreactor. Indeed, the by-products released by the PBR when fed with mineral medium significantly contribute to the COD but not to the bCOD. Taking this contribution into account, the combined treatment of PBR and AS could theoretically be able to reduce the COD by up to 73%.

Table 1. COD and bCOD of raw wastewater and PBR effluent (mean values).

	COD (mg/L)	bCOD (mg/L)	bCOD/COD
Influent	3480	315	0.091
Effluent of PBR fed with wastewater	3560	1413	0.397
Effluent of PBR fed with mineral medium	1200	0	0

CONCLUSIONS

An effective NSAP depolymerization was obtained through a biological process with *P. ostreatus* in a PBR fed with petrochemical wastewater: the fungal treatment made it possible to reduce the concentration of high molecular weight polymers, which are refractory to biodegradation. The potential of a two-phase process was evaluated: the combination of fungal treatment in a PBR and AS process was able to remove up to 40% of the initial COD.

In the tested conditions (attached biomass, slowly biodegradable co-substrate) *P. ostreatus* showed stable enzymatic activity and degradation capacity in non-sterile environment; nevertheless the use of straw as co-substrate caused the release of by-products which contribute to non-biodegradable COD. For this reason, the research of a completely biodegradable support for fungi is one of the main goals for future investigations.

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(S42) Organic matter characterization by prep-HPLC for reclaimed water quality in constructed wetland

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Abstract

Constructed wetland is one of the alternative water treatment processes to reuse water because it operates with low energy consumption and shows high contaminant removal rate. However, conventional water quality criteria cannot guarantee availability of reclaimed water in this situation where thousands of organic chemical compounds are released into wastewater from households. To improve the water quality criteria, organic matters in water were characterized preparative HPLC. Preparative HPLC fractionates organic matters and enables the isolated organic matters to further analyses. In this study, availability of reclaimed water from a constructed wetland treatment and organic matter characterization in the water were investigated. The influent and effluent water qualities of a constructed wetland were measured in an autonomous decentralized community in Korea. DOC removal rate by constructed wetland was shown 80 %. Most of ammonium nitrogen in influent was changed into nitrate nitrogen in effluent. Organic matters in influent and effluent were fractionated. Each fractionated sample showed different SUVA values. These results suggest that constructed wetland can be applied to water reuse process and preparative HPLC can be used effective organic characterization method for evaluating the availability of reclaimed water.

Keywords
water reuse; greywater; constructed wetland; prep-HPLC; NOM characterization

INTRODUCTION

Water reuse is become one of the spotlighted topics in water treatment field as the available water is decreasing by environmental pollution or surging water demand. Several processes for water reuse are operating in many areas (Ogoshi *et al*., 2001; Greenway, 2003). However, water reuse processes require energy to reclaim wastewater.

Constructed wetland is one of the alternative water treatment processes to reuse wastewater because it requires low maintain cost and energy consumption. This system is operated by ecological treatment processes such as the uptake by plants, sedimentation, precipitation, adsorption, microbial activity, physico-chemical reaction. Several studies about removal of contaminants from wastewater showed high level of treatment efficiency. i.e. 80 % removal of phosphorus, 58~68 % removal of nitrogen, and 67~90 % removal of BOD_5 (Arias *et al*., 2003; Juwarkar *et al*., 1995).

In the situation that the amount of reclaimed water usage is increasing, reclaimed water quality can be a more important factor than drinking water quality because reclaimed water source is wastewater. However, as the numerous organic chemical compounds are released into natural water system from households in everyday, it is difficult that BOD and COD measurement represent for water quality sufficiently. Thus, organic matters in water are an essentially considerable factor to use safe and appropriate reclaimed water. Various methods are used to characterize organic matters, but some methods have limitation. Despite various organic matters are contained in water sample, the methods only can measure whole organic matters parameters not each organic matter parameter specifically. To solve this problem, preparative HPLC (prep-HPLC) was used in this study. This instrument isolated large masses of organic matters by separations based on chromatography theory. The isolated samples can be fractionated and be used for further analyses. The objective of this study is to evaluate the contaminant removal efficiency of constructed wetland and to investigate changing of organic matters during the treatment process. Constructed wetland treatment efficiency was evaluated in terms of dissolved organic matter (DOC) concentration, salt ion concentration and nutrient concentration. Organic matters in influent and effluent were characterized using prep-HPLC. The fractionated organic matter samples were further characterized using TOC analyser and ultraviolet-visible spectrometer to calculated SUVA value.

MATERIALS AND METHODS

Sampling

The wastewater sample was taken from a constructed wetland in a small autonomous decentralized community, Namwon city, Jeollana-do, Korea(35°.43´S,127°.64´E). In there, every household uses a dry-composting ecological toilet and only greywater from kitchen and bathroom flow in the constructed wetland. The capacity is 15 m^3/d. As vertical subsurface flow is connected to horizontal subsurface flow in series, the greywater is treated by combination of aerobic and anaerobic system. The greywater treatment efficiency for water reuse was measured through influent and effluent of the constructed wetland. Sampling was performed once a month from July, 2012 to October, 2013. Samples were filtrated with 0.45 micro-filters (Mixed cellulose acetate, Advantech, Japan) and were stored at 4 ℃ for further analyses.

Analytical methods

Preparative HPLC (LC-9201, JAI, Japan) with UV detector (UV detector 3702, JAI, Japan) was used for the fractionation of the organic matter in samples. Sample (5 ml) was injected into Toyopearl column (250×40 mm, Grom, Germany). Eluent was made up with 2.4 mM sodium phosphate, 1.6 mM disodium hydrogen phosphate, and 96.0 mM sodium chloride. The flow rate of the eluent was 2ml min^{-1}. Rotary evaporator (EYELA, Japan) was used to concentrate samples because samples, which DOC concentration is low (1 mgC/L ~5 mgC/L), easily were diluted with eluent in the column during analysis. DOC was measured using a total organic carbon analyser (TOC-V CPH, Shimadzu, Japan). Ultraviolet-visible spectrometer (UV-1601, Shimadzu, Japan) was used to measure UV absorbance at 254 nm of samples. Specific UV absorbance (SUVA) value was calculated from UVA_{254} and DOC value. Ion concentration was measured using ion chromatography (ICS-90, Dionex, CA, USA). AS14 column (250 × 4 mm, Dionex, CA, USA) and CS12A column (250 × 4 mm, Dionex, CA, USA) were equipped for anion and cation measurement, respectively.

RESULTS AND DISCUSSION

Water characteristic of influent and effluent samples was summarized in Figure 1. Because measured samples were taken from the wastewater released from households, there were some variations depending on season and personal event in the village. However, compared to influent, the variation of effluent measured values was small. It means that the constructed wetland treated well the greywater with constant performance despite of influent variation. This constructed wetland removed 80 % of DOC. The average of measured DOC in effluent was 2.5 mgC/L. This value is lower than average DOC value (3 mgC/L) in Koren rivers. Chloride and sodium ion concentration were measured to verify reclaimed water availability about salinity, but there is no significant different. While ammonium nitrogen in influent changed into nitrate nitrogen through the constructed wetland. These results might relate to microbial activity depending on the matters in the constructed wetland

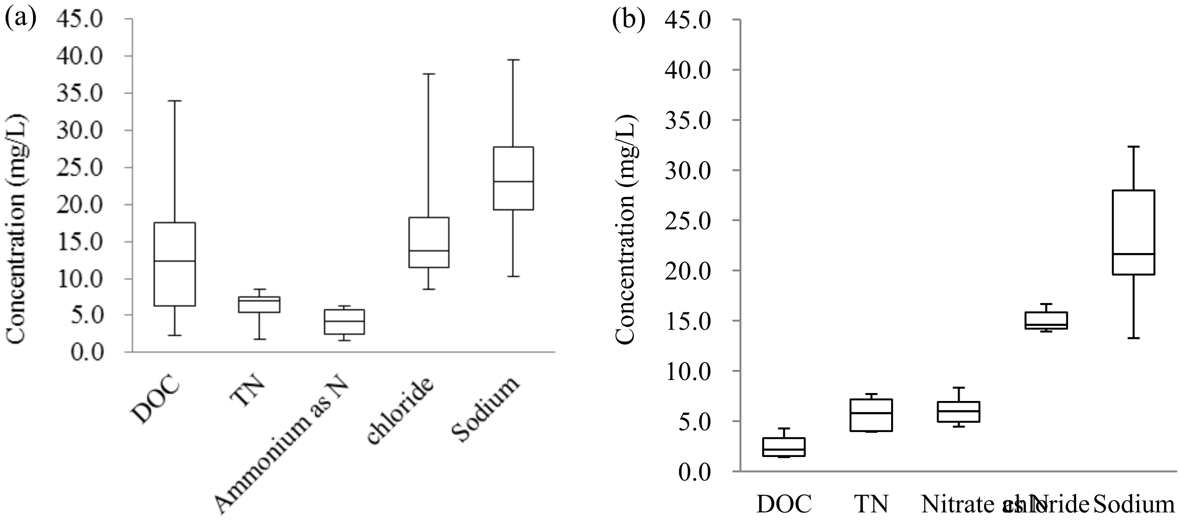

Figure 1. Water characteristic of (a) influent and (b) effluent samples

Concentrated sample (sampling date : Oct.21.2013) was injected into prep-HPLC for fractionation. The chromatogram of samples is shown in Figure 2. Effluent sample was separated into two peaks (E1, E2) and influent was separated into six peaks (I1, I2, I3, I4, I5, I6). Separation principle of Toyopearl GROM column is size exclusion, so the molecular weight of each peak is different. From the chromatogram, peaks in similar time have similar organic size. Therefore, it could be realized that some parts (I4, I5, I6) of organic matters in influent were removed by the constructed wetland compared to effluent.

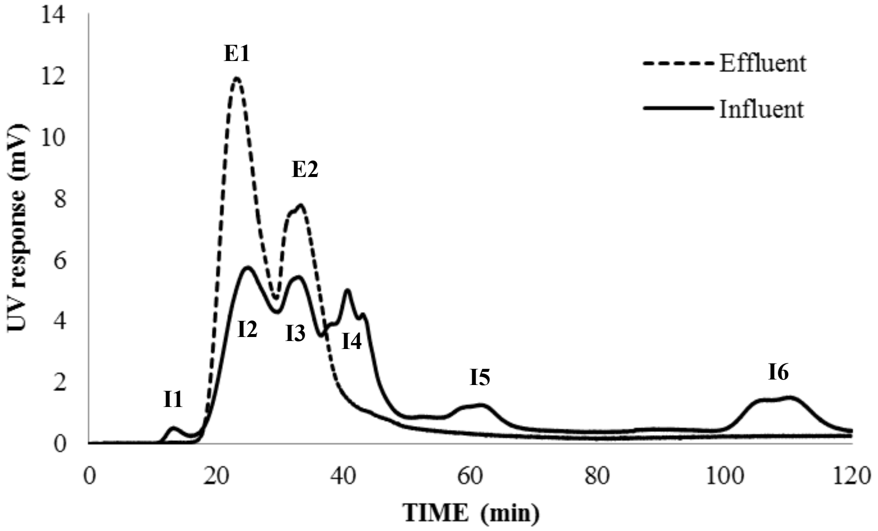

Figure 2. Prep-HPLC chromatogram from influent and effluent of constructed wetland

SUVA values were calculated from the fractionated samples to characterize each peak (Table 1). E1 and E2 peaks have similar molecular size with I2 and I3 but their SUVA values were higher than I2 and I3. Because SUVA values can explain hydrophobicity, this result explains that organic matters in E1 and E2 might be changed into humic substance by humicification. In the case of I5 and I6, they show high SUVA values but these values could be overestimated by low DOC concentration. However, it is obvious that organic matters existed in I5 and I6 because UV detector was responded.

Table 1.SUVA values of fractionated samples

Sample		DOC (mgC/L)	UV (254nm)	SUVA
Effluent	E1	5.3	0.1310	2.5
	E2	2.1	0.0602	2.8
Influent	I1	4.0	0.0150	0.4
	I2	7.4	0.0729	1.0
	I3	8.7	0.0948	1.1
	I4	1.8	0.0458	2.6
	I5	0.5	0.0206	4.5
	I6	0.2	0.0172	7.1

CONCLUSTIONS

Water reuse is indispensable to make sustainable water management. Sustainable water management should include the two concepts which are low energy consumption and stable good water quality. From these points, constructed wetland is a good alternative treatment system. High removal efficiency of contaminants was also investigated in this study. Therefore, obtaining reclaimed water from constructed wetland can be an efficient and economic water reuse process. Organic matter characterization using prep-HPLC can be an effective method to understand contaminant removal processes and to improve water treatments. Only SUVA values were used to characterize fractionated organic samples in this study, but pyrolysis or reactivity with oxidants also will be further researches.

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(S43) Sunlight Penetration in Arctic Wastewater Stabilization Ponds

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Abstract
Wastewater treatment in the Arctic is affected by unique arctic environmental conditions: extended photoperiod, low temperatures and short summers. The small azimuth angle of the sun and the characteristics of wastewater are expected to impact sunlight penetration in arctic wastewater stabilization ponds (WSPs). It is crucial to understand the behavior of sunlight penetration in arctic WSPs because disinfection performance relies strongly on solar radiation. An irradiance profile was measured in Pond Inlet and Clyde River, Nunavut, Canada. The systems had a maximum euphotic depth (1% light level) of 0.15, 0.78 and 0.51 metres in Clyde River primary and secondary ponds and Pond Inlet single-celled WSP, respectively. Reduction efficiencies of total coliforms and *Escherichia coli* demonstrate that the two-celled system in Clyde River performs better in terms of disinfection than the single-celled system in Pond Inlet. The high volume that sunlight penetrates in the Clyde River secondary pond (46% of the total pond volume) is anticipated to be the source of the better performance.

Keywords
Arctic, disinfection, sunlight, wastewater stabilization pond,

INTRODUCTION

Arctic, isolated communities are faced with many challenges to provide basic water services due to extreme climate, geographical location and socioeconomic factors. Wastewater stabilization ponds (WSPs) are a promising technology to provide adequate treatment in the North due to their cost effective nature and ability to operate with minimal interference. WSPs attenuate organic and nutrient loads and can achieve excellent indicator-microorganism removal efficiencies (Davies-Colley et al., 2000) through biological, passive mechanisms. Arctic environmental conditions such as short summers (2-4 months) and lower temperatures can greatly affect biological activity (Tilsworth and Smith, 1984), which drives the performance of WSPs. Extended solar radiation and subsequently sunlight penetration are a unique environmental factors that influences pond environments in the North. The sun has a small azimuth angle and extended photoperiod. Nunavut (Canada) residents are more conservative in their water use because piped collection and distribution systems are rare (Tilsworth and Smith, 1984); this leads to concentrated wastewater, which can affect arctic sunlight penetration.

Understanding sunlight penetration is essential to predicting disinfection performance in northern wastewater treatment systems. Previous studies found have that solar radiation was the most potent factor in terms of disinfection (Curtis et al. 1992; Davies-Colley et al. 2005, Maı¨ga et al. 2009). Sunlight provides energy for algal growth via photosynthesis, which drives aerobic treatment (Davies-Colley et al., 2005). Algae growth increases pH and dissolved oxygen, and these physiochemical properties also affect pathogen removal (Curtis et al., 1992, Oualia et al., 2013). This paper presents sunlight penetration analyses for two case study locations in Nunavut. Two configurations are investigated, single-celled and two-celled WSPs, to characterize these systems in terms of disinfection performance in the Arctic.

METHODOLOGY

Sunlight penetration was studied at two sites located on Baffin Island in the Nunavut Territory of Canada: Pond Inlet (72°41’57” N, 077°57’33” W) and Clyde River (70°28’26” N, 068°35’10” W). The Pond Inlet WSP consists of a single celled wastewater stabilization pond, whereas the Clyde River WSP uses a two-celled system in series. Table 1 presents the details of each system. The summer treatment season is generally from the middle of June to early September, and the WSPs are discharged at the end of the season before freezing. During the sampling season of 2013 the water temperatures for both systems ranged from 18-4°C with an average of 10°C.

Table 1. Specifications of Clyde River and Pond Inlet wastewater treatment systems

	Clyde River		Pond Inlet
	Primary	Secondary	
Depth of water column (m)	1.5	3.0	1.5
Volume (m^3)	10,000	23,000	38,000
Surface Area (m^2)	6,700	13,700	25,000
Daily inflow (m^3/d)	92	-	104
Population	900	-	1500

A downwelling irradiance profile was measured using a JAZ-COMBO spectrometer manufactured by Ocean Optics (Florida, USA) in July 2013. All measurements were recorded during minimal cloud cover and low wind conditions (reduced ripples on the WSPs). Choppy wave conditions can make it difficult to measure accurate depths, and wavelets can act as lenses and cause a “flicker” in irradiance measurements. The irradiance profile was used to calculate the euphotic depth, the depth at which irradiance is decreased to 1% of the surface magnitude. The total volume of sunlight penetrated was calculated using the maximum euphotic depth and surface area of each WSP.

Total coliforms and *Escherichia coli* (*E. coli)* were measured in June and September 2013 to examine the performance of the two systems at the beginning and end of the summer treatment season. Samples were collected at five locations in the Pond Inlet WSP and at three locations in each Clyde River cell. The samples were then shipped by plane to Iqaluit for analysis using Colilert solution from IDEXX laboratories.

RESULTS AND DISSCUSION

Sunlight penetration at different wavelengths is shown in Figure 1. Euphotic depth is used as an indicator of the portion of the water column impacted by sunlight; hence the portion affect by sunlight induced disinfection.

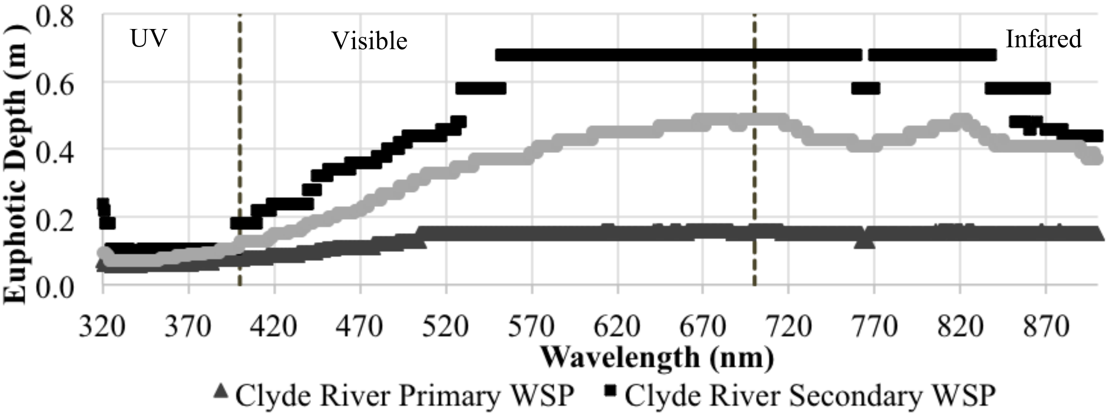

Figure 1. Euphotic depth in arctic WSPs varying with wavelength

Although UV is more damaging to pathogenic bacteria, the UV portion of the light spectrum is much more rapidly attenuated. Table 2 presents the maximum euphotic depth in the UV region at 400 nm. The more abundant and longer wavelengths damage pathogens through reactions with exogenous and endogenous sensitizers. Craggs et al. (2004) found that longer wavelengths cause substantial pathogenic inactivation due to their ability to penetrate a greater portion of the water column. Due to the relatively shallow penetration of the UV spectrum it is expected that the finding reported by Craggs et al. will be applicable in arctic wastewater treatment.

Table 2. Sunlight penetration of a two-celled system, Clyde River, and a single-celled system in Pond Inlet

	Clyde River		Pond Inlet
	Primary	Secondary	
Maximum euphotic depth (m)	0.15	0.78	0.51
Euphotic depth at 400 nm (UV) (m)	0.18	0.08	0.12
Volume sunlight penetrated (m^3)	1,005	10,686	12,750
Portion affected by sunlight (%)	10	46	34
	35		

A much larger volume of the water column was contacted by sunlight in the Clyde River secondary (46%) cell than the primary cell (10%). Despite the lower sunlight penetration, the primary pond removed 87.2% of total coliforms and 85.5% of *E. coli,* as shown in Table 3. This could be due to other factors such as sedimentation or predation. Overall, the two-celled system performed better than the single-celled system in terms of disinfection with a greater percent removal at the end of the treatment season in September, which is indicated in bold in Table 3. Since the total portion of the two-celled system contacted by sunlight (35%) was approximately the same as the Pond Inlet single-celled (34%) system, it is anticipated that the deeper sunlight penetration in the secondary cell enhanced the disinfection performance of the overall Clyde River system.

Table 3. Average (μ) and standard deviation (σ) of bacterial most probable number (MPN), and percent reduction of raw wastewater. PI denotes Pond Inlet single-celled system, CR-P Clyde River primary cell and CR-S denotes Clyde River secondary cell.

	Total Coliforms (MPN/100ml)			*E. coli* (MPN/100ml)		
	(μ)	(σ)	(%)	(μ)	(σ)	(%)
Raw PI	7.38E+08	8.34E+08	-	2.83E+07	2.35E+07	-
Raw CR	3.85E+08	5.79E+08	-	2.61E+07	3.41E+07	-
June PI	5.47E+06	5.30E+06	99.3	6.01E+05	3.22E+05	97.9
Sept. PI	9.35E+06	7.46E+06	**98.7**	1.06E+06	3.21E+05	**96.3**
June CR-P	6.48E+06	4.37E+06	98.3	3.37E+05	2.27E+05	98.7
Sept. CR-P	4.95E+07	5.18E+07	87.2	3.78E+06	1.46E+06	85.5
June CR-S	1.11E+07	1.03E+07	97.1	4.27E+05	1.64E+05	98.4
Sept. CR-S	6.05E+05	4.27E+05	**99.8**	2.89E+04	4.81E+04	**99.9**

Note: the high standard deviation is likely due to poor mixing after the daily inflow.

CONCLUSION

Passive wastewater treatment, specifically WSP treatment, in the arctic is highly susceptible to environmental conditions of the North. The ability of sunlight to penetrate these ponds appears to be linked to indicator microorganisms' removal efficiencies. It was found that a two-celled system in series provides a greater disinfection performance with a 99.8% reduction in total coliforms (98.7% for the single-celled) and 99.9% reduction in *E. coli* (96.3% in the single-celled).

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(S44) Sequential Anaerobic Aerobic Treatment for the Biodegradation of Pulp and paper Mill Wastewater

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Abstract

Laboratory scale studies were performed for the sequential anaerobic treatment of pulp and paper mill wastewater with special emphasis on the removal of Adsorbable Organic Halides (AOX). Anaerobic hybrid reactor consisting of a UASB at the bottom and an anaerobic filter on the upper side. The effluent form anaerobic hybrid reactor was passed through a column type sequencing batch reactor (SBR) operated in a continuously automatic mode under aerobic conditions using timers and solenoid valves. The anaerobic reactor was seeded with digester sludge obtained from a sewage treatment plant while SBR was seeded with activated sludge. The influent from Naini Tissue Mill, Kashipur, India was fed to the anaerobic hybrid reactor. The anaerobic hybrid reactor was operated at HRT of 24 hours and SBR was operated with a 24 hour cycle which was reduced to 18 hours. The overall BOD and COD removal efficiency from the reactor systems was found to be 90% and 85% respectively. The overall AOX removal efficiency was found to be 80%. The study revealed that the reactor systems employed in the present investigation was found effective for removing AOX and organics from the pulp and paper Mill wastewater.

Keywords

AOX; Anaerobic treatment; Aerobic Treatment; pulp and paper industry; hybrid reactor

INTRODUCTION

The pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulosic materials and water during the manufacturing process, and releases chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbons in the effluent. About 500 different chlorinated organic compounds have been identified including chloroform, chlorate, resin acids, chlorinated hydrocarbons, phenols, catechols, guaiacols, furans, dioxins, syringols, vanillins, etc. These compounds are formed as a result of reaction between residual lignin from wood fibres and chlorine/chlorine compounds used for bleaching. Colored compounds and Adsorbable Organic Halogens (AOX) released from pulp and paper mills into the environment poses numerous problems. Physical, chemical and biological treatments systems have been used in the past for the treatment of pulp and paper mill wastewater. Biological treatment is generally preferred owing to complete mineralization of organics. However, sometimes intermediate products of biological treatment are more toxic than the parent compounds and needs to be handled carefully. In order to treat the intermediate compounds sequential anaerobic aerobic treatment has been proposed in the present investigation. The products of anaerobic decomposition shall be degraded aerobically in a SBR which may result in complete mineralization of toxic compounds. A number of reactors configuration have been used as biological treatment systems. In the last decade. Sequencing batch reactor (SBR) has gained importance over other reactors for the treatment of wastewaters**.** The SBR process is characterized by a series of five process phases. The five phases of a SBR system are the Fill, React, and Settle, Decant and Idle Phases. Sequential batch reactors have advantages of low operating costs, no sludge settler required, no recycling pumps required, good control over filamentous bulking, tolerance to shock loads and peak flow denitrification during anoxic fill and settle stage.

Granulation has been studied widely and successfully industrialized for the last two decades, e.g., anaerobic granulation. To overcome the drawbacks of a long startup period, high operation temperature, operation stability and effluent with low dissolved oxygen (DO), aerobic granulation technology has been developed. The biomass is retained as granules formed by the naturally self immobilization of the bacteria under aerobic condition. The advantages of aerobic granules are the clear-out shape, compact and strong microbial structure, fast start-up, good settling ability, high biomass retention and ability to withstand a high organic loading rate. Aerobic granulation has been successfully achieved for the biodegradation of a number of phenolic compounds. The objective of the study was to assess the performance of sequential anaerobic aerobic reactor systems for the treatment of pulp and paper Mill wastewater emphasis shall on the removal of AOX compounds.

MATERIALS AND METHODS

The anaerobic hybrid reactor used in this study, was fabricated with Perspex material and has an internal diameter 5 mm. the total height of the reactor was 1450mm and the filter media used was a cutting of PVC pipe in the reactor. The effective volume of the reactor was 2.50 liters.

The anaerobic hybrid reactor consisted of a UASB at the bottom and an anaerobic filter at the top. Anaerobic filter provided effective gas liquid solid separation. The height of the UASB rector was 450mm and that of anaerobic filter was 780mm. This was due to provision of equal HRT in both the reactors. Freeboard of 220mm was also provided. The media used for anaerobic filter was PVC pipe of inner diameter 25mm which has been cut into pieces nearly of length 1 inch. The schematic diagram of the Experimental Setup is shown in Fig. 1

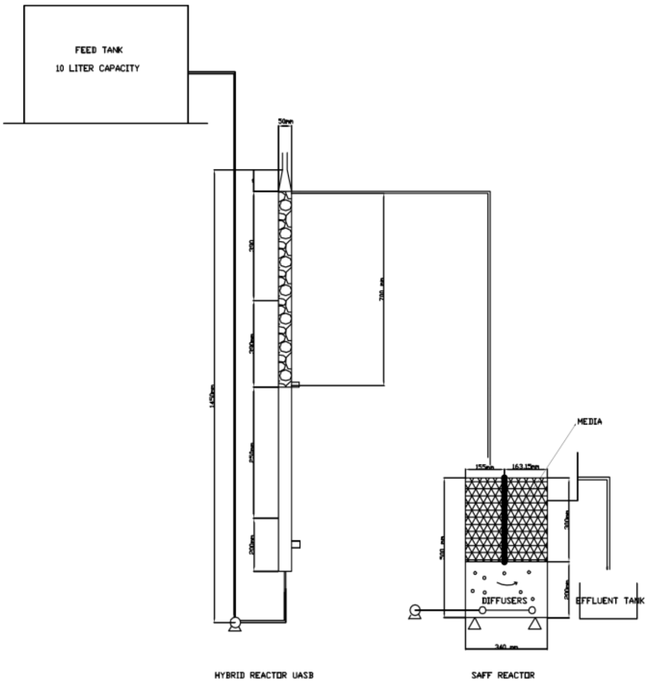

Fig.1 Schematic Diagram of Anaerobic Hybrid Reactor

The effluent of the anaerobic hybrid reactor was treated in a column type sequencing batch reactor (SBR). Laboratory scale Sequencing Batch Reactor System (SBR) was fabricated with Perspex material and had a total volume of 3.46-liter. The dimensions of the reactor were 7 cm in diameter and 90 cm in height. One air pump system, model EK- 8000, 6.0 W, was used for supplying diffused air to the reactor. The entire experimental setup was automated with Solenoid valves, Gate valves followed by automatic on-off timers with different time-dependent cycles. A tank of 12 liter capacity was provided for the influent to the SBR . The experimental set up in shown in Figure 2.

The anaerobic hybrid reactor was seeded with the digested sewage sludge obtained from Okhla Sewage treatment plant, New Delhi, India. The sequencing batch reactor was seeded with the aerobic sludge obtained from the aeration tank of the pulp and paper wastewater treatment plant of Naini Tissue Mill, Kashipur, India. All analysis was carried out as per Standard Methods. The wastewater from Naini Pulp and paper industry was used as an influent to the anaerobic hybrid reactor. Initially HRT of 24 hours was used which was subsequently reduced to 18 hours after achieving significant COD and AOX removal. In SBR initially a 24 hour cycle was used with 10 minutes of fill, 22 hours react time, 60 minutes settling time, 20 minutes withdrawal and 30 minutes idle time. The cycle was reduced to 18 hours with reduction in the react time from 22 hours to 16 hours.

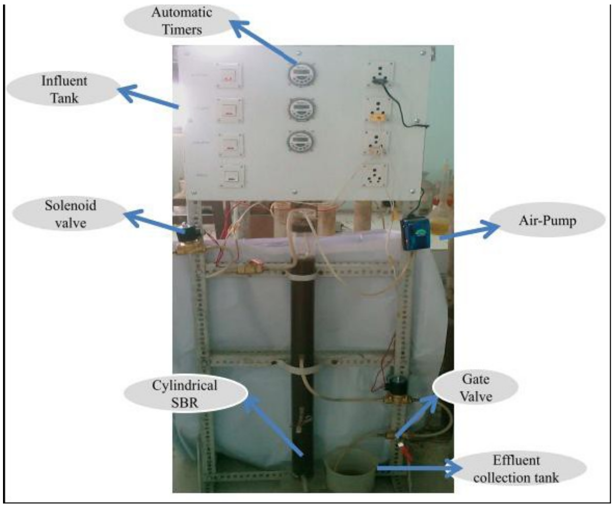

Fig.2. Reactor Set up for Sequencing Batch Reactor

RESULT AND DISCUSSIONS

The present investigation has been done to assess the biodegradability potential of sequential anaerobic - aerobic process for the treatment of pulp and paper Mill wastewater, emphasis being made for the removal of adsorbable organic halides (AOX). The anaerobic hybrid reactor was operated with 24 hours cycle for 180 days with diluted wastewater of COD of 500 mg/L. The COD was increased to 750mg/L, 1000 mg/L and finally the raw wastewater was fed without dilution with an average COD of 1400 mg/L. the COD was increased after achieving a constant COD and AOX removal efficiencies. Once an appreciable biodegradation of pulp and paper Mill was achieved (COD removal ~ 85% and AOX removal ~80%) the HRT was reduced to 18 hours and the cycle of operation of SBR was reduced to 18 hours with raw wastewater as an influent feed to the anaerobic hybrid reactor. After reducing the HRT there was a decrease in the COD removal efficiency. It took around 30 days to recover the COD and AOX removal efficiencies. The reactors were operated for another 90 days for obtaining complete mineralization of pulp and paper Mill wastewater. The effluents form anaerobic hybrid reactor and SBR were analysed for pH, alkalinity, BOD, COD and chlorides. pH was monitored daily and the influent and effluent pH were within the permissible range. Sufficient Alkalinity (~1200 mg/L) was maintained in the anaerobic hybrid reactor. BOD was analysed on weekly basis while COD was anlaysed on alternate days. AOX was analysed weekly using AOX Analyser (Analytic Jena Germany). The AOX of raw wastewater was in the range of 12-15 mg/L while under steady state conditions the AOX in the effluent of SBR was ~ 3mg/L.

The effluents from anaerobic hybrid reactor as well as SBR was also analysed for intermediate and toxic products of biodegradation using GC MS (Clarus 600, Perken Elmer, USA). The results of GC MS were obtained in the forms of peaks and the relevant compounds were obtained using the dictionary of the equipment. It was observed that the compounds present in the effluent of the anaerobic hybrid reactor were absent in the effluent of SBR thus indicating the complete mineralization of pulp and paper mill wastewater. The overall BOD and COD removal efficiencies of the sequential anaerobic - aerobic reactor system were found to be 90% and 85%. While AOX removal efficiency of 80% was achieved through the reactor system employed in the present investigation.

CONCLUSIONS

The results of the sequential anaerobic aerobic biological treatment of pulp and paper mill wastewater showed complete mineralization of pulp and paper mill wastewater. It took around 210 days to achieve 90% BOD removal, 85% COD removal and 80% AOX removal. The pH and alkalinity values were within the permissible ranges. The treated effluent was analysed through GC MS. The results showed the absence of intermediate products of biodegradation.

ACKNOWLEDGMENT

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(S45) Cultivation of aerobic granular sludge for the treatment of petrochemical wastewater

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Abstract
In this study, aerobic granular sludge was cultivated in a Granular sludge Sequencing Batch Reactor (GSBR) to evaluate the possibility of treating petrochemical wastewater produced by the Integrated Gasification Combined Cycle (IGCC) and characterized by high concentrations of organic matter (up to 260-380 mg_{TOC}/L), ammonium (400-550 mg_{NH4-N}/L) and toxic substances (e.g. cyanides, phenols and formates). Small granular aggregates appeared soon and progressively increased in size (granule diameter raised from 0.2 up to 2.1 mm) and density (up to 61 g_{TSS}/L_{gran}). Total organic carbon (TOC) removal was high (up to 89.4±6%), while N and P removal efficiencies strongly fluctuated during the start-up, indicating unsteady conditions. Preliminary results observed during GSBR start-up showed that aerobic granular sludge can be a viable solution for the treatment of petrochemical wastewater, which is worthy of being further investigated.

Keywords
aerobic granular sludge; GSBR; petrochemical wastewater; wastewater treatment.

INTRODUCTION

Petrochemical wastewater contains high concentrations of organic and inorganic pollutants, generally removed by the combination of biological and physical-chemical treatments (Lotito et al., 2012). Since this kind of wastewater requires considerable investments to obtain an effective removal of pollutants before the discharge into receiving water bodies, the implementation of the novel aerobic granular sludge technology could represent a promising solution and a good alternative to conventional systems. Actually, the aerobic granular sludge technology was already shown to require less area (-80%) and energy (-30%) in comparison to conventional biological treatment systems, therefore its possible implementation as the sole treatment step in place of a chemical-physical-biological treatment is worthy of being investigated.

The peculiar structure of stable granular aggregates allows the simultaneous presence of anaerobic/anoxic conditions in the inner part (where heterotrophic bacteria can develop), while in the surface and intermediate layers, due to diffusion of oxygen and organic matter into the granules, both heterotrophic and autotrophic bacteria coexist: this leads to the possibility of obtaining a simultaneous and successful removal of various contaminants in a single reactor. Moreover, diffusive phenomena involved in granule shaped biomass constitute a barrier against toxic and inhibitory substances (Carucci et al., 2010), thus making aerobic granular sludge potentially suitable to treat heavily polluted industrial wastewater.

In this study, aerobic granular sludge was cultivated in a Granular sludge Sequencing Batch Reactor (GSBR) to treat a petrochemical wastewater obtained from the Integrated Gasification Combined Cycle (IGCC). Process performance in terms of organic matter and nutrient removal was analysed during the early start-up of the GSBR, together with the physical and morphological properties of the granules, in order to preliminarily assess the feasibility of the aerobic granular sludge technology in treating petrochemical wastewater containing toxic substances.

MATERIALS AND METHODS

Reactor set-up and operation

A glass GSBR with a working volume of 4.2 litres, an internal diameter of 10.4 cm and a working height of 50 cm was used to carry out the experiments. The reactor was operated at room temperature (20 – 25°C) and controlled pH (6.8 – 7.2) in 4-h cycles, each cycle consisting of 60 min feeding (anaerobic, from the bottom of the reactor and without mixing), 165-175.5 min aeration, 8-1.5 min settling and 5 min effluent withdrawal. Settling time was initially set to 8 min, in order to avoid sludge washout, and was gradually decreased to 1.5 min as granulation occurred. A membrane pump was used to provide air, which was introduced via a fine bubble aerator at the bottom of the reactor. Dissolved oxygen (DO) concentration was monitored, but not controlled throughout the cycle. Since the effluent was drawn at 25 cm from reactor bottom, the corresponding volumetric exchange ratio (effluent volume/total working volume) was 0.5 and the resulting Hydraulic Retention Time (HRT) was 8 hours. Activated sludge drawn from a municipal wastewater treatment plant was used as inoculum.

Wastewater characteristics

Raw petrochemical wastewater was obtained from the Integrated Gasification Combined Cycle, part of the SARAS SpA facilities operating in Sarroch, Italy. The wastewater was characterised by high pH (10-10.8) and high concentrations of TOC (260-380 mg/L), ammonia (400-550 mg_{NH4-N}/L) and formates (1000-1500 mg/L), as well as by the presence of toxic cyanides (up to 15 mg/L) and phenols (up to 2.5 mg/L). Real wastewater is currently treated at full scale by a combination of chemical-physical (i.e. steam stripping) and biological treatments (i.e. trickling filter). A mixture of synthetic and real wastewater (1-10%) was used in the early start-up (approximately 100 days): in order to facilitate granule formation, a readily biodegradable organic substrate (sodium acetate, NaAc) was added to the synthetic medium and the amount of real wastewater was increased gradually. Influent composition was as follows: TOC 270-517 mg/L, PO_4-P 20-25 mg/L, NH_4-N 35-60 mg/L.

Analytical Methods

Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), NH_4-N and PO_4-P were determined according to Standard Methods (APHA, 2005). The TOC concentration was measured with a TOC analyser (SHIMADZU TOC-V CSN). Samples were taken from the influent, effluent, at the end of the anaerobic feeding (t60) and during the reaction phase at fixed intervals. All samples were filtered (0.45 μm) and properly diluted with de-ionized water before analysis. Granule density was determined according to Beun et al. (1999). Image Analysis was performed on representative granule samples taken at the end of the anaerobic feeding, soon after completely mixed conditions were established: granules were put into a Petri dish on a dark background and photographs were taken in b/w mode using a high resolution camera placed onto a horizontal holder. ImagePro Plus (v.6) was used to calculate granule diameter. Content of extracellular polymeric substances (EPS) in granules was monitored during the start-up: 50 ml samples were taken at t60 to extract and analyse EPS, according to Park et al. (2008).

RESULTS AND DISCUSSION

The progressive formation of aerobic granules took place in three different Phases, as reported in Table 1.

Table 1. Different experimental Phases, according to GSBR operating conditions.

Phase	Duration (days)	% real w.w.	Settling time (min)	Minimum settling velocity (m/h)
1	1-14	0-2	8-5	1.9-3.0
2	15-62	2-3	5-3	3.0-5.0

3	63-112	3-10	3-1.5	5.0-10.0

Small granular aggregates with an average diameter of 0.2 mm (Figure 1a) appeared within the first 10 days of operation (Phase 1), with a poor selective pressure in terms of minimum settling velocity and amount of real wastewater in the influent. During Phase 2, the amount of aerobic granules in the GSBR progressively increased together with the observed average diameter (0.8 mm), even though granule surface was covered with filaments and finger-typed structures (Figure 1b). De Kreuk et al. (2010) related such surface morphology to hydrolysis reactions, mainly occurring at the surface of the granules: substrate is consumed locally, enhancing substrate gradients inside the granules and stimulating the outgrowth of filamentous structures, which likely will break off due to shear stress during reactor operation. During Phase 3, granules became dominant in the system and were characterized by bigger size (average diameter was 2.1 mm) compared to previous Phases, but filaments still covered granule surface, as shown in Figures 1c and 1d.

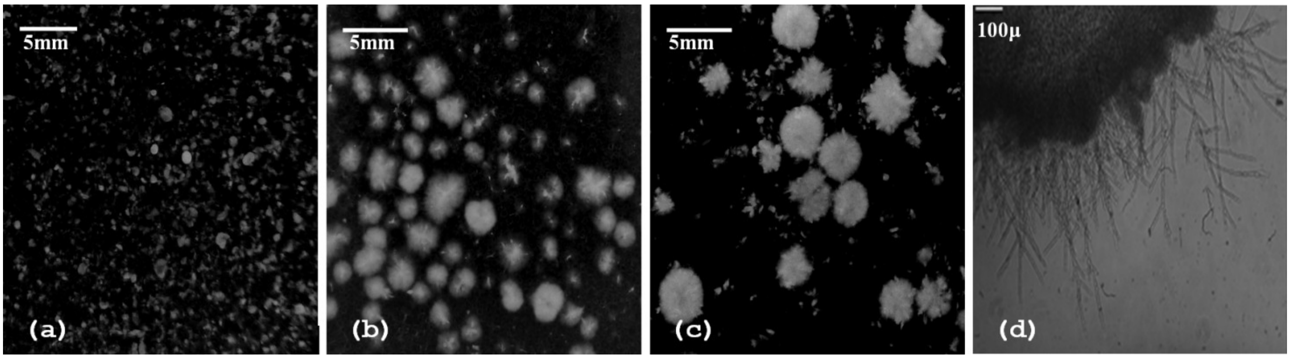

Figure 1. Aerobic granules observed at the end of Phase 1 (a), Phase 2 (b) and Phase 3 (c,d).

The progressive shift towards bigger size fractions is shown in Figure 2: aerobic granules with a mean diameter below 0.5 mm represented 81.4% of total granules at the end of Phase 1 and completely disappeared at the end of Phase 3.

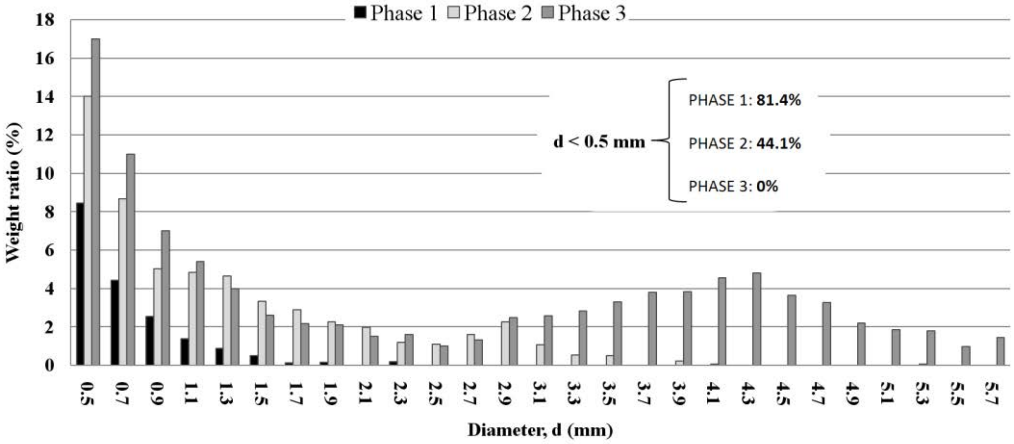

Figure 2. Particle size distributions at Phase 1 (days 1-14), Phase 2 (days 15-62) and Phase 3 (days 63-112).

Correspondingly, the percentage of aerobic granules belonging to the biggest size fractions (d ≥ 2.5 mm) increased from 0% (Phase 1) to 45.7% (Phase 3), respectively.

The increasing amount of real w.w. in the influent seemed to boost granulation, since the harsher environment probably forced granule self-aggregation as a defensive strategy against toxic and inhibiting substances: granule density increased from 8 g_{TSS}/L_{gran} (Phase 1) to 61 g_{TSS}/L_{gran} (Phase 3) and a positive correlation between EPS content and the amount of real w.w. dosed in the influent was observed (in particular, proteins peaked at 24.8 mg/g_{VSS} at the end of Phase 3). Extracellular polymeric substances (especially carbohydrates and proteins as the major components) play an important role in granule formation and, as reported by Sheng et al. (2010), EPS production increases when biomass is exposed to stressful conditions.

Aerobic granules showed good performance in terms of TOC removal during the early start-up procedure (average value of TOC removal efficiency was 89.4±6%); on the contrary, both PO_4-P and NH_4-N removal by aerobic granular sludge were unstable and removal efficiencies varied between 52-89% and 33-77%, respectively.

CONCLUSION

The possibility to achieve granule formation in a GSBR treating petrochemical wastewater was investigated in this study. The following conclusions can be drawn:

- aerobic granular sludge could successfully develop into the GSBR and completely overcame floc-shaped biomass: the increasing selective pressure (in terms of minimum settling velocity and amount of real wastewater in the influent) strongly influenced both physical and morphological characteristics of aerobic granules, as well as EPS production;
- GSBR performance was good in terms of TOC removal, while N and P removal strongly fluctuated during the early start-up phase.

Given such promising results, the experimental activity is currently proceeding with the gradual increase of real petrochemical wastewater in the influent and with the corresponding evaluation of process performance and granule characteristics at different synthetic/real w.w. influent ratios.

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(S46) Biodegradation by fungi: an effective tool for the implementation of landfill leachate treatment

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Abstract

Landfill leachate and textile wastewaters have many features in common: both show dark colour, high concentrations of recalcitrant pollutants and COD, and are very toxic. *Porostereum spadiceum* MUT 1585, a fungus able to decolourise textile wastewaters, was tested for the treatment of both a row landfill leachate and an effluent coming from a landfill leachate treatment plant. The experiment was performed with free and immobilised biomasses. The decolourisation, the chemical oxygen demand and the toxicity were monitored. The raw leachate was too toxic to allow the fungal growth, whereas the effluent colour was halved in one week. Peroxidases were the main enzymes involved in the process. The fungal treatment caused the increase of toxicity towards two target organisms.

Keywords

Biodegradation; decolourisation; ecotoxicity*;* fungi; leachate; *Porostereum spadiceum*.

INTRODUCTION

Landfill leachates are mainly constituted by recalcitrant and toxic xenobiotics, indicated by their low BOD/COD ratio (<0.5 mg/L), which is a limit for the growth and the metabolic activity of heterotrophic bacteria in activated sludge. The ineffectiveness of traditional treatments is particularly evident in the persistence of the dark colour in effluents coming out from leachate treatment plants (Primo et al., 2012).

The same problem related to the ineffectiveness of activated sludge has been observed in the treatment of textile wastewaters, which are characterised by the high concentration of recalcitrant compounds and COD, dark colour and high toxicity. Towards textile wastewaters, the fungal biodegradation has been demonstrated to be a useful implementation of traditional oxidation treatment by activated sludge. Indeed, extracellular oxidative enzymes with non-selective catalytical activity, produced by white rot fungi, can be active towards recalcitrant compounds with high redox potential, which are hard to handle by bacteria (Wesemberg et al., 2003). Recently, the complementarity of fungi with respect to bacteria was demonstrated in the treatment of textile wastewaters. Actually, these organisms were active towards different aspects of textile wastewaters: fungi were effective in the removal of colour but increased COD, whereas bacteria decreased COD and were ineffective towards colour. Consequently, the authors hypothesised that the best point for the implementation of fungal treatment in wastewater treatment plant is before the activated sludge (Anastasi et al., 2012). In this way, the crucial problem of the fungi-bacteria association treatment (i.e. the competition between the two organisms, which generally turns in the of dominance of bacteria) is overcome.

The same approach could be useful also in the treatment of landfill leachate. Thus, in the present work *Porostereum spadiceum* (MUT 1585), kindly provided by the *Mycotheca Universitatis Taurinensis,* was studied to assess its potential in the decolourisation of a landfill leachate sampled before and after the activated sludge in conventional wastewater treatment plant. The exploitation of a support for the immobilisation of the biomass and its effect on decolourisation yields were evaluated.

MATERIALS AND METHODS

Wastewaters

The two samples came from a wastewater treatment plant located in the central part of Italy. One was a crude leachate coming from municipal landfill in the methanogenic phase and the other one was a leachate previously treated by biological oxidation with activated sludge and nitrification/denitrification process. Both samples were dark colour, they had high content of ammonium and salts, and 8.5 pH. Immediately before use, pH was adjusted to 5 and 0.1 g/L of glucose was added to both samples, in order to enhance fungal growth.

Biodegradation experiment

The fungus was precultured in 9 cm Petri dishes containing agarised malt extract medium (MEA: 20 g glucose, 20 g malt extract, 20 g agar, 2 g peptone, 1 L deionized water). Twenty disks (5 mm diameter) taken from the margin of the fungal colony were used as inoculum in 500 mL flasks containing 200 mL of a high nitrogen content medium, GHY (10 g/L glucose and 3.8 g/L yeast extract) both in absence (free biomass) and in presence (supported biomass) of polyurethane foam cubes (PUF) for biomass immobilization, as previously described (Anastasi et al., 2012).

After 7 days, the culture broth was replaced with 100 mL of the effluents and the cultures were incubated for 7 days, at 25 °C and 120 rpm. Daily, a sample was collected, and colour and enzymatic activities were measured. The decolourisation percentage (DP) was calculated as the decrease of the spectrum (360-790 nm) area with respect to the untreated effluent. At the end of the experiment, COD and toxicity were also evaluated. Abiotic controls (without fungal inoculum) were set up and each culture condition was assayed in three biological replicates.

Enzymatic analyses

Laccase activity was assayed at 25 °C, monitoring the oxidation at 420 nm of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), in 0.1 M sodium citrate buffer, pH 3.

Manganese-independent (MiP) and manganese-dependent (MnP) peroxidases activities were measured at 25 °C, monitoring the oxidation at 590 nm of 3-dimethylaminobenzoic acid/3-methyl-2-benzothiazolinone hydrazone hydrochloride (DMAB/MBTH), in 0.1 M succinate lactate buffer pH 4.5. For MnP, 25 µM $MnSO_4$ was added to the reaction mixture.

Ecotoxicological tests

An algae test was performed according to the standard UNI EN ISO 8692: 2005 using a monospecies culture of *Pseudokirchneriella subcapitata* (Korshikov) Hindak. A cell suspension (2.5 10^4 cell) was inoculated in 2.5 mL of different effluent dilutions (100 %, 50 %, 25 %, 12.5 %, 6.5 %, 3.2 %, 1.6 % and 8 %). The trial was performed in triplicate. Moreover, an abiotic control (effluent without the algal inoculum) and 6-replicated biotic control (algal inoculum in water without effluent) were performed, as prescribed by the method. After 48 h incubation at 23 °C in the light (8000 lux), the cells concentration was spectrophotometrically measured by means of the conversion from the absorbance to cell concentration thanks to a linear correspondence of this parameter previously assessed. The inhibition of the algal growth was expressed as a percentage with respect to the average algal growth observed in the 6 biotic controls.

A dicotyledonous plant *Lepidium sativum* L. was used for phytotoxicity tests, according to the standard method UNICHIM 1651: 2003. The seeds (90% germination warranty) were put in 9 cm Petri dishes containing 5 mL of diluted effluent (100 %, 50 %, 25 %, 12.5 %, 6.5 %, 3.2 %, 1.6 % and 8 %) and a paper filter (Whatman No.1) to overcome the effect due to the surface tension of the water. The controls were carried out using distilled water instead of diluted effluent. All the trials were performed in 4 replicates. The seeds were incubated for 72 h in the dark at 25 °C. At the end of the test, the inhibition of the germination index (GI) was calculated as a percentage with respect to the average observed in the 4 controls.

RESULTS AND DISCUSSION

The raw leachate was too toxic to be treated with the fungus. Actually, the fungal biomass did not grow in the presence of the raw leachate, and no enzymatic activity was recorded (data not shown).

The partially treated leachate still displayed a high toxicity (10% inhibition at 12% dose for *P. subcapitata* and 58% inhibition at 100% dose for *L. sativum*) but *P. spadiceum* MUT 1585 was able to grow and remain active under these harsh conditions. The fungus strongly decolourised the effluent (40-50%), with no significant differences between free (F) and supported biomass (S). These results are not in accordance with Saetang and Babel (2010), who found consistent enhancements of the *T. versicolor* activity, when it was immobilized on PUF.

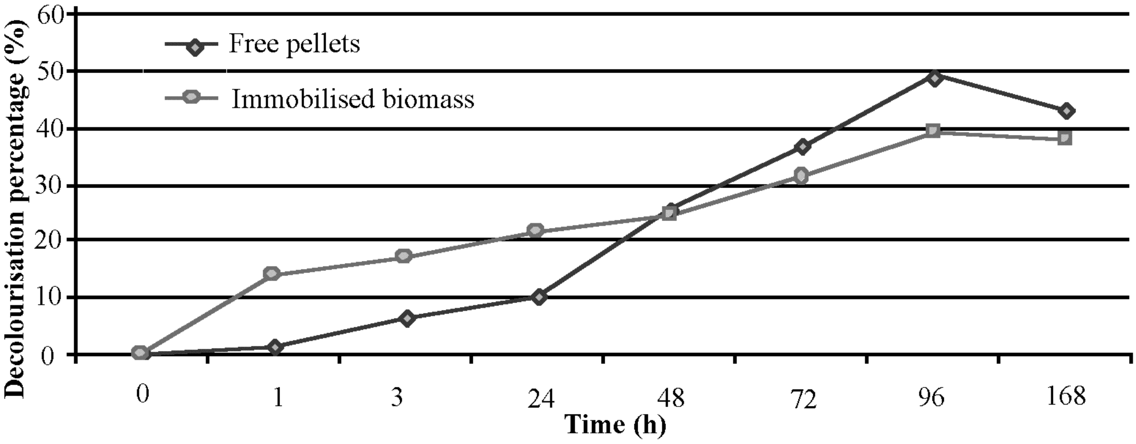

Figure 1. Decolourisation percentage (DP) of landfill leachate by *P. spadiceum* MUT 1585 as free (F) or immobilized biomass on PUF (S).

P. spadiceum MUT 1585 was able to constantly maintain the effluent at acidic pH (5.0-5.2), which is an optimal value for oxidative enzymes activity. A complex enzymatic pattern was monitored. During the first 3-6 h, laccases were mainly produced (about 80 U/L), whereas peroxidases were constantly secreted during the experiment (Figure 2).

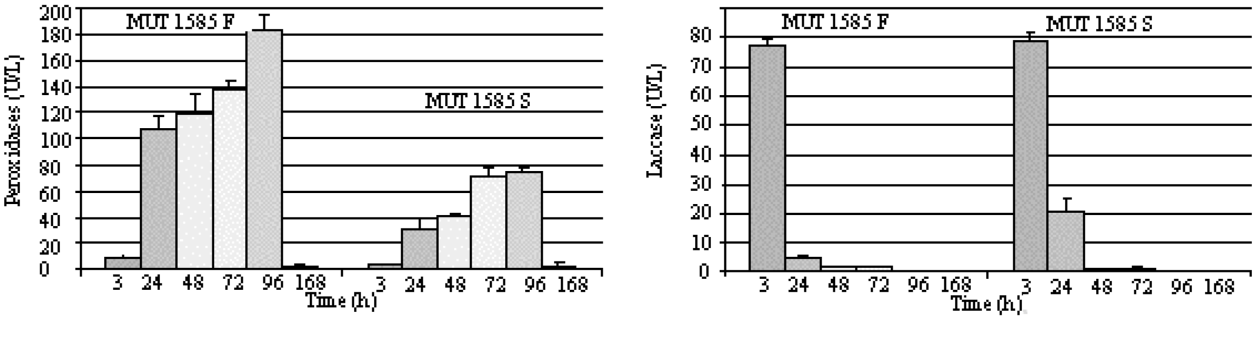

Figure 2. Peroxidases and laccases (U/L) by *P. spadiceum* MUT 1585 as free (F) or immobilized (S) biomasses.

A good correlation among DP, pH and enzymatic production could be drawn. Hence, the decolourisation achieved by *P. spadiceum* MUT 1585 was clearly ascribable to the effective degradation of the colored compounds of landfill effluent. However, the process turned into a general increase of the toxicity recorded by both the ecotoxicity tests (Table 1). This datum is in accordance with Anastasi et al. (2012), which recorded an increase of toxicity after fugal treatment of textile wastewaters. However, in this case the removal of toxicity and COD was achieved by means of the treatment with activated sludge after fungal biodegradation (Anastasi et al., 2012).

Table 1. Toxicity variation of GI% and I% of the treated samples with respect to the control.

	L. sativum	*P. subcapitata*
	(Δ GI%)	(Δ I%)
MUT 1585 F	-24.3	+180.7
MUT 1585 S	-44.0	+72.5

CONCLUSION

Landfill effluents confirmed to be very harsh to treat. Their extreme chemico-physical conditions highly limit a proper fungal development and activity. *P. spadiceum* MUT 1585 is a powerful agent of bioremediation for the treatment of landfill leachate. The fungus showed to be able to grow and remain active in restrictive environmental conditions (presence of toxic molecules, few easily degradable carbon sources, competition with bacteria) and degrade recalcitrant coloured molecules through the production of laccases and peroxidases. These last enzymes seem to be the main catalysts involved in the degradation of coloured components. Eventually, the colour degradation resulted in the compliance with Italian law on wastewaters colour (not visible at the dilution 20:1).

Further experiments will be carried out to optimize the fungal treatment, in order to increase the effectiveness of the process in terms of decolourisation and detoxification. This goal could be achieved by the cooperation between fungi and bacteria by means of a re-circulating treatment. A FIRB project is now in progress.

ACKNOWLEDGEMENT AND FUNDING

University of Turin. Uniproject Srl. Project FIRB (Fondo per gli Investimenti della Ricerca di Base, Italian Ministry of University and Research) 2013 (2014-2016) "In situ bioaugmentation to exploit the combination of fungi and bacteria for recalcitrant compounds removal". National Coord. Dr. Munz G. (Univ. of Florence). Local Coord. Dr. Tigini V.

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Benchmarking and Decision Support tools

(Wednesday, 25 June 2014, Aula T3, Polo Zanotto)

(K12) A knowledge-based decision support tool for selecting Eco wastewater treatment technologies in today's global complexities

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7. Water 2020 Cost Network

Abstract

There is a clear need for a decision support tool that can address the complexity of selecting wastewater treatment technologies and account for the technical, environmental, economic, and social challenges the water sector is faced with today. The Novedar_EDSS, an environmental decision support system software tool, is now being commercialized for this purpose and is undergoing a rigorous and systematic validation process. Presented herein are results for one validation case study from the U.S. highlighting the comparison of the Novedar_EDSS with the state-of-the-art. In a matter of hours, the Novedar_EDSS produced comparable results to that of the state-of-the-art approach. Also presented are two case studies from Italy and France to demonstrate the application of the tool for different relevant problems in Europe. The results highlight the significant advantage the Novedar_EDSS offers over the state-of-the-art and its high market potential for sustainable / Eco wastewater treatment technology selection.

Keywords

Eco, Environmental decision support systems, technology selection

Introduction

Given the rapid pace of urban development across many parts of the world, specifically China, India, and countries in the Middle East, Africa, and Latin America (City Mayors Foundation, 2013), new wastewater treatment plants are needed to meet the public health and ecological standards that are increasingly being enforced. Where growth is not as fast, like in the U.S. and Europe, new WWTPs are in less demand; however, there is still need to retrofit existing WWTPs to meet more stringent water quality regulations. Moreover, in developed countries, reclaimed wastewater effluent is increasingly accepted as a water resource alternative for several end-uses, e.g. agricultural, industrial and indirect potable use (NRC, 2012). As water scarcity, the growing number of leading edge alternatives to conventional wastewater treatment, and growing pressure on balancing technical, environmental, economic, and social criteria in water projects, add complexity to the fundamental drivers for installing new/retrofitted treatment facilities, decision making inherently becomes highly complex. There is a clear need for a decision support tool that can address the complexity of selecting wastewater treatment technologies and effectively account for all of the technical, environmental, economic, and social challenges the water sector is faced with today. At the moment, one can only use separate tools for each technical, environmental, and economic evaluations, then integrate the various outputs, and then restart the process for each technology being evaluated for making comparisons, which is highly labour-intensive, especially as the number of technologies being evaluated increases. Recognizing this limitation in the industry, the Novedar_EDSS (Molinos-Senante et al., 2012; Garrido-Baserba et al., 2012a; Garrido-Baserba et al., 2012b), an environmental decision support system software tool was developed through the Novedar_Consolider Project (a research consortium of nine Spanish universities, and two Dutch universities), with technical, environmental, economic, and social capabilities all in one platform. As part of the tool's commercialization, which is currently underway, a rigorous validation process is being conducted. Presented herein, is a validation case study from the U.S. comparing the technology selection results through the state-of-the-art approach versus that of the Novedar_EDSS. Also presented are two case studies from Italy and France to also demonstrate the application of the tool for different relevant problems in Europe.

Methods

The architecture of the EDSS is based on a rule-based hierarchical decision approach and uses quantitative and qualitative information, heuristics and the use of reasoning processes (expert judgment) to produce suitable process flow diagrams for any specific scenario and then ranks them based upon the specific criteria priorities established by the user (Garrido-Baserba et al., 2012a). To test the Novedar_EDSS capabilities in producing results that are comparable to the state-of-the-art, the case study of Steichen et al. (2009) was used as it included a sustainability assessment using the state-of-the-art tools of various wastewater treatment technology alternatives for a planned new wastewater treatment plant. The same influent wastewater characteristics and effluent requirements were input into the Novedar_EDSS, and similar non-economic critieria, such as operational reliability, operational flexibility, aesthetics, and environmental were established for the technology rankings. A similar case study was conducted for a retrofitted wastewater treatment plant in France (results to be included in full paper). For the Italian case study, the tool was used to compare the sustainability of upgrading/retrofitting three decentralized wastewater treatment plants versus the construction of one large centralized plant and decommissioning the existing plants. Each existing plant was evaluated individually using the Novedar_EDSS tool and selecting the configuration best matching the actual planned retrofit. The technical, environmental, and economic results were then aggregated for the three plants and compared to that of the scenario for the one large plant.

Results and Conclusions

Table 1 summarizes a comparison of results for the technology ranking based upon the non-economic factors established for the project. The Novedar_EDSS included the same technologies included in the shortlist of technologies developed by Steichen et al. (2009), and ranked them essentially in the same order as they were scored through the state-of-the-art approach. The economic evaluation also produced similar costs, although reasonable differences are expected as costs will vary from one place to the next, especially in different parts of the world. However, the tool will have the capability of specifying cost indices that appropriate for the location of the project. Table 2 provides a summary of the Italian case study comparing the retrofitting scenario versus the construction of one large centralized plant. When looking at the whole plant level, retrofitting the existing plants is more economical as seen in Table 2, economic and cost benefit results. However, when looking at the secondary treatment line, which is what the EDSS tool scores, the new centralized plant has significant advantages in terms technical, environmental and economic criteria because there is the freedom to select the best theoretical technology, whereas, for the existing plants, you are limited to selecting the configuration that it is the best practical retrofit.

These results demonstrate the significant advantage that Novedar_EDSS offers over the state-of-the-art, as the results were produced in a matter of hours, whereas comparable results were produced in a matter of weeks through the state-of-the-art approach. Therefore, the Novedar_EDSS will fill a significant gap, in sustainable/Eco wastewater treatment technology selection as urban development and more stringent effluent requirements are met across the globe, once the technology is fully transferred from research to industry.

Table 7 - Summary of U.S. Case Study Results: Comparison of State-of-the Art versus Novedar_EDSS

Technology	SOA Score	Novedar_EDSS Score
MBR	0.81	3.93
MBBR*	0.80	4.25
MLE	0.72	3.81

*MBBR was technology actually selected as best using state-of-the-art approach.

Table 8 – Summary of Italy Case Study Results

		Scenario			
Criteria		Retrofit WWTPs 1 - 3		New Centralized WWTP	
		All Lines	Secondary	All Lines	Secondary
Costs	O&M (M€/yr)	2,96	0,66	5,15	0,47
	investiment (M€)	28,69	17,99	58,59	13,39
	total equivalent costs (M€)	**81,19**	**29,41**	**152,88**	**22,01**
	reactants (M€/yr)	4,93	0	2,79	0
Scores	total		**4,45**		**6,74**
	economic		1,43		1,53
	environmental		1,27		2,58
	operational		1,75		2,62
Cost Benefit Analyis	total equivalent costs (M€)	**81,19**		**152,88**	
	Accumulate benefit (M€)	**0,97**		**22,70**	
	net profit value (M€)	**-83,27**		**-130,18**	

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(P60) WATERLILY®, water footprint calculation tool: application to urban water cycle

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Abstract

Water use impact assessment, also named water footprint, has an increasing interest and methodologies are quickly evolving, within the frame of life cycle assessment. In this work, we proposed to apply an adaptation of Ridoutt and Pfister (2013) methodology to address both consumptive and degradative use of water for several options of urban water cycle management. We implemented several new endpoints such as ecotoxicity and toxicity to human from USEtox, and aquatic acidification from IMPACT2002+. The assessment encompassed the life cycle of three urban water cycle scenarios. The functional unit was the distribution of one cubic meter of water to users.

Keywords
Water footprint, urban water cycle, micropollutants, tertiary treatment

INTRODUCTION

The concept of water footprint has been introduced in 2002 by Hoekstra. It has been defined as the total volume of freshwater used to produce the foods and services consumed by the individual or community or produced by the business. To go further and better characterize the consumed volumes, researchers introduced the impact dimension on ecosystems, human health and natural resources. Hence, since the water footprint concept has been launched, several calculation methodologies have been developed and promoted by different initiatives, among them the water footprint network (Hoekstra *et al*. 2011), the United Nations Environment Programme (UNEP)/Society of Environmental Toxicology and Chemistry (SETAC) Life Cycle Initiative's working group on the assessment of freshwater use and consumption in life cycle assessment (LCA) called "WULCA" (Kounina *et al*. 2012) and the International Organization for Standardization (ISO) water footprint working group (ISO/TC207/SC5/WG8, ISO 14046 draft). From these initiatives, a general consensus for water footprint calculation, based on the LCA approach, has emerged that will be formalised thanks to the publication of the international standard ISO 14046: Water footprint- Principles, Requirements and Guidelines.

The WATERLILY® tool was developed to calculate water footprint of the whole urban water cycle management including the drinking water and wastewater treatment plants as well as the drinking water distribution networks and sewer, based on the LCA approach. This assessment permits to integrate the environmental aspect along with technical and economic aspects in the definition of urban water cycle management strategy or the monitoring of the environmental performance along years.

This study aims at assessing and comparing comprehensive water footprints of several scenarios for urban water cycle, including advanced tertiary treatment of wastewater before discharge in the environment and reuse.

MATERIAL AND METHODS

Goal, scope and case definition

The perimeter of this water footprint assessment goes from surface water withdrawal (#1, Figure 1) from river for drinking water production, to treated wastewater discharge (# 5 or #7, depending on the scenario). Functional unit of this study is the distribution of one cubic meter of water to users. This study includes direct water consumption generated by the drinking water uses (Users step) and also indirect water consumption due to the consumption of energy and the use of reagents at drinking water plant (DWP) and wastewater treatment plant (WWTP). It also takes into account direct water quality degradation through discharge from the WWTP as well as indirect water quality degradation due to energy and use of reagents. The three scenarios studied are detailed hereafter (Figure 1):

Scenario 1: a conventional WWTP and no reuse of the treated wastewater

Scenario 2: additional advanced treatment (AT) to the WWTP for quality improvement of the discharged wastewater, without reuse of the treated wastewater.

Scenario 3: additional advanced treatment (AT) to the WWTP as implemented in scenario 2. In addition, 50% of the treated wastewater is sent back to users for reuse (#3). As a consequence, in this scenario, surface water withdrawal (#1) is reduced.

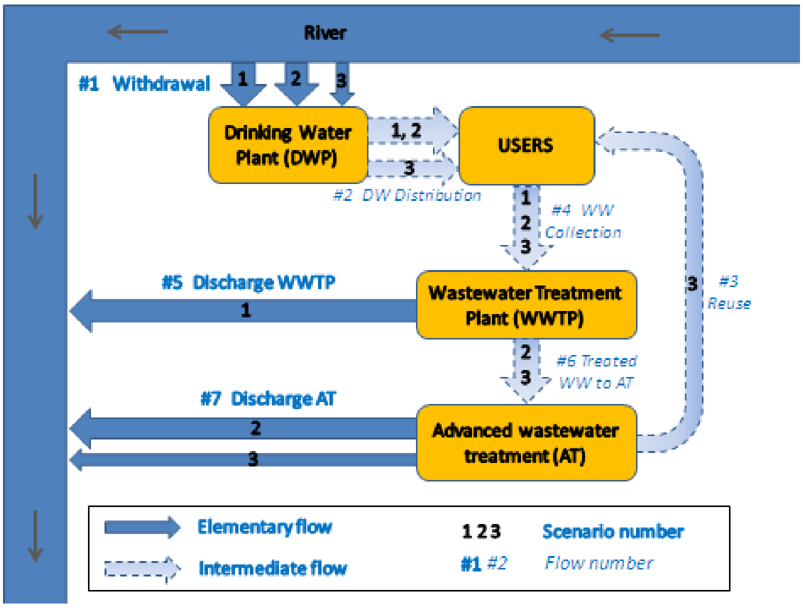

Figure 21. Framework of the three urban water cycle scenarios for water footprint assessment

Impact assessment methodology

The comprehensive water footprint profile is composed of several category indicators that may be evaluated at both midpoint and endpoint levels and further aggregated in a unique water footprint. Category indicators (midpoints) and their associated characterization models are summarized in Table 1. Based on these indicators, the water footprint is calculated according to an adaptation of the Ridoutt and Pfister (2013) method which permits to integrate both consumptive and degradative water use (CWU and DWU) into a single stand-alone indicator after weighting using the ReCiPe endpoint modelling system. The final result is expressed in litre of water consumption equivalent (L H_2O eq), units more meaningful for public communication.

Table 9 Midpoint indicators and associated characterization models

Type of indicators	Midpoint indicator	Characterisation model
Water consumption	Water scarcity	Water stress index (Pfister *et al.*, 2009)
Water degradation	Aquatic eutrophication	ReCiPe (Goedkoop *et al.*, 2009)
	Aquatic acidification	IMPACT 2002+ (Jolliet *et al.*. 2003)
	Ecotoxicity	USEtox (Hauschild *et al.*, 2008)
	Toxicity to Human	USEtox (Hauschild *et al.*, 2008)

Water footprint Inventory assessment

This inventory aims to collect information on the elementary flows within the perimeter of the study for each scenario. It includes quantity and quality aspects of water and wastewater (Table 2 and 3). To be as comprehensive as possible during water footprint inventory assessment, reagents and energy consumption at each treatment steps (DWP, WWTP and AT) were taken into account as well as equipments. The collected information permits to quantify indirect impacts on both water consumption and water degradation, based on updated LCA database.

Table 10 Water flow inventory Midpoint indicators and associated characterization models

Type of flow	Flow number	Volume (x 10^5 m3/year) Scenario 1	Scenario 2	Scenario 3
Withdrawal	#1	100	100	55
DW Distribution	#2	100	100	55
Reuse	#3			45
Water distributed to Users	#2 + #3	100	100	100
User's consumption	USERS	10	10	10
WW collection	#4	90	90	90
Discharge WWTP	#5	90		
Treated WW to AT	#6		90	90
Discharge AT	#7		90	45

Table 11 Quality of water discharge from WWTP (#5) and AT (#7), including nitrogen, phosphorus and micropollutants

Category	Parameters	Concentration of pollutants unit	WWTP Discharge (#5)	AT Discharge (#7)
Nitrogen	Ammonia	mgN/L	2	0,5
Nitrogen	Nitrates	mgN/L	12	2
Phosphorous	Phosphorous	mgP/L	2	0,5
Hormones	Estradiol	ng/L	10	n.d.
Hormones	Ethinyl estradiol	ng/L	10	n.d.
Pesticides	Chloropyrifos	ng/L	50	n.d.
Pesticides	Diuron	ng/L	220	n.d.
PAHs	Anthracene	ng/L	220	n.d.
PAHS	Fluoranthene	ng/L	90	n.d.
Pharmaceuticals	Erythromycin	ng/L	100	n.d.
Pharmaceuticals	Ibuprofen	ng/L	300	n.d.

PAHs: Polycyclic Aromatic Hydrocarbon ; n.d.: not detected

RESULTS AND CONCLUSIONS

Midpoint impact assessment

The water scarcity midpoint characterization model is based on regionalized water stress index (WSI). In this example, only one WSI is applied (0.18 for France, Pfister et al. 2009) assuming that water consumption along life cycle of reagents 1 and 2 is done on the same territory. Midpoints characterization factors are issued from the characterization models summarized in Table 1. Water footprint profiles at midpoint are presented in Figure 2.

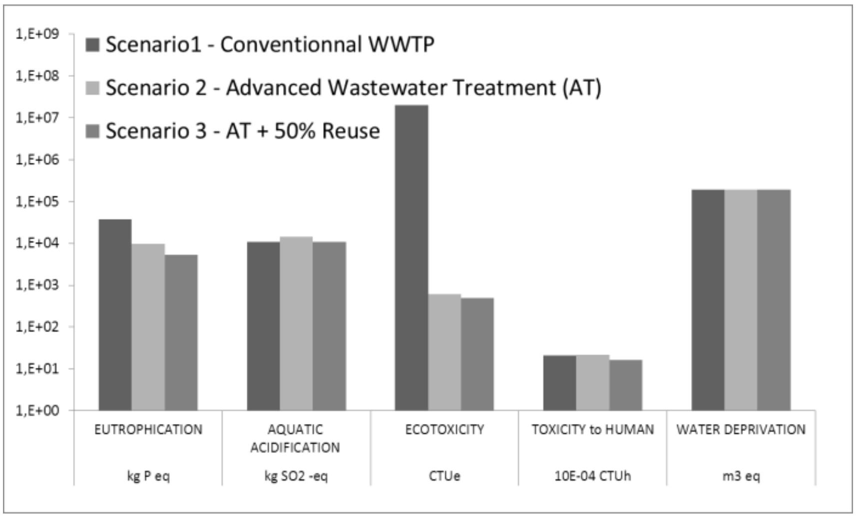

Figure 22. Midpoint impact value for each scenario

Comprehensive Water footprint and scenario comparison

Following the Ridoutt and Pfister method (2013), both consumptive and degradative water use (CWU and DWU) water footprints were calculated and added up to give a single stand-alone indicator (Comprehensive Water Footprint, Table 4). In this example, water footprints are expressed in function of the functional unit, i.e. 1 m3 of water distributed to users.

Table 12 Weighed water footprint and degradative and consumptive water use water footprint (in L H_2O eq / m^3 water distributed to users) for the three scenarios.

Scenario		Comprehensive Water Footprint	Degradative Water Footprint	Consumptive Water Footprint
1	WWTP	262	230	32
2	WWTP +AT	93	61	32
3	WWTP + AT + 50% Reuse	67	35	32

The water footprints obtained are clearly different depending on the scenarios (table 4). Water footprint of scenario 1 (conventional WWTP) is three times higher than the ones for scenario 2 and 3. This difference is mainly due to the DWU water footprint reduction promoted by the additional advanced treatment of nitrogen, phosphorous and micropollutants (scenario 2 and 3). In addition, the partial reuse of treated wastewater (scenario 3) reduces the pollutant load discharged into the environment, and so permits to reach the lowest water footprint.

In this study, CWU water footprint is the same for each scenario due to the fact that direct water consumption only occurs at user's step (10% of the distributed volume in each case). If treated wastewater was discharged in seawater, direct water consumption would be equal to the water volume, withdrawn from the environment. In this configuration, CWU WF would be 302, 302 and 166 L H_2O eq / m^3 water distributed to users, for scenario 1, 2 and 3 respectively. These new values highlight the interest of treated wastewater reuse to reduce the CWU water footprint and so the global water footprint.

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(P61) Energy benchmarking of wastewater treatment plants

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Abstract

The optimisation of wastewater treatment plants (WWTPs) in order to reduce costs and greenhouse gas (GHG) emissions is a significant priority for the water utilities. Identification of the most energy-consuming treatment process can be done by benchmarking the total energy consumption, this includes recording and analysing electrical, manual, chemical and mechanical energy consumptions that can be expressed in kWh/m^3 to allow comparison between different sites. Through energy benchmarking the highest energy consumption assets can be identified followed by an investigation and implementation of strategies to improve operational efficiency of the WWTP.

Two full-scale WWTP were benchmarked during this study. Both incorporated preliminary, secondary, and tertiary treatment processes, whereas Site 1 also had an additional primary treatment step. The results indicated that Site 1 required 2.32 kWh/m^3 against 0.98 kWh/m^3 for Site 2. Aeration presented the highest energy consumption for both sites with 2.08 kWh/m^3 for Site 1 and 0.91 kWh/m^3 in Site 2. Site 2 presented a lower effluent quality than Site 1 that was linked with insufficient aeration on the oxidation ditch.

This study demonstrated the effectiveness of the energy benchmarking exercise to identify the most energy consuming assets, nevertheless it points out the need to develop a holistic overview of the WWTP and when comparing sites, the need to include parameters such as effluent quality to allow an adequate benchmarking.

Keywords
Electrical energy, manual energy, mechanical energy, chemical energy, oxidation ditch

INTRODUCTION

The Water Industry is the fourth most electricity intensive sector in the UK (POST, 2007): the CO_2 emissions account for 5 million tons per year, almost 1% of UK's greenhouse gas (GHG) (Environment Agency, 2009). With this in mind, the UK Environment Agency (EA) developed strategies to help the water utilities mitigate their carbon impact. The report "Transforming wastewater treatment to reduce carbon emissions" outlines five key strategies, including "Improving Operational Efficiencies"(Environment Agency, 2009). This final strategy is the focus of this paper, which aims at breaking down the power requirement of wastewater treatment, ultimately leading to the improvedenergy management of the plant. In order to tackle this, the EA recommends beginning to benchmark the electricity used to assess precisely the existing consumption on site. From this a detailed breakdown of the electricity used in each process can be established to detect the most electricity-consuming assets. This result can be then used to decide how to optimise the wastewater treatment as more efficient processes will consume less electricity and thus will generate less GHG. Nevertheless, due to high diversity and sizes of technologies used for wastewater treatment, it is difficult to draw correlation between type of technology and energy use. As it has been previously demonstrated, the electricity consumption decreases as the size of the plant increased, for example, a plant treating 3,600 m^3/day consumes 0.5 kWh/m^3; whereas a plant treating 323,000 m^3/day only consumes 0.22 kWh/m^3 (Tao & Chengwen, 2009). This scaling effect makes the analysis of the data complex. Methodologies to benchmark the energy consumption in WWTPs have been developed and applied in particular in studies in Japan (Mizuta & Shimada, 2010) and in China (Tao & Chengwen, 2009) that mainly looked into different scale of the plants and operating loads. Singh et al. (2012), proposed a different methodological framework that included analysing electrical, manual, mechanical and chemical energy consumption on WWTPs. Singh, et al. (2012) concluded that the electrical energy had the biggest share (52%) followed by the manual energy (32%), the mechanical energy (9%) and the chemical energy (7%).

The energy consumption of two full-scale sites was benchmarked during this study. The benchmarking was done in kWh/m^3, to allow for comparison between sites that do not have the same inlet flow and also between the data from the different source of energies.

MATERIALS and METHODS

Description of full-scale wastewater treatment plants investigated

Two full-scale sites were investigated in this study, both feed mainly with domestic wastewater and located in East Sussex, England. Site 1 treated 1570 m^3/d and was composed of screening, degriting and ferric chloride dosing before the primary settling tanks (PST). The secondary treatment was an oxidation ditch (OD) aerated by three aqua-rotors and 6 surface aerators. The tertiary treatment was disc filters. The sludge was exported to another plant where it anaerobically digested and spread to land. The second plant (Site 2) treated 5300 m^3/d and was composed of screening and ferric chloride dosing before the OD. The OD had two lanes, each of them aerated by 4 aqua-rotors. After the biological treatment, the wastewater was treated in lagoons. The sludge was thickened in a picket fence tank and stored in a storage tank before being sent to Site 1 for centrifugation and further treatment.

Calculation of energy consumption

Data on electricity consumption was collected by implementation of power loggers (Fluke 1735 and Fluke 435 II) that monitored the energy consumption (kW) every 15 minutes over 4 weeks. Four power loggers were implemented, each one of them recording data for a group of assets. For Site 1, Cluster 1 recorded the power consumption on the preliminary treatment, Cluster 2 the primary and secondary treatments, Cluster 3 the secondary (surface aerators) and tertiary treatments and Cluster 4 the sludge handling. For Site 2, Cluster 1 recorded the power consumption on the preliminary treatment, Cluster 2 the secondary treatment (anoxic tank, half of the aerators and 2 pumps), Cluster 3 the secondary treatment (the other half of the aerators, 4 pumps and FSTs scrapers)and Cluster 4 the sludge handling.

The manual energy was calculated as the amount of energy spent by the operators on a site, according to the number of working hours and the type of activities they carry out. For this calculation, the relationship between the intensity of an activity and its power equivalent was used (WHO, 1985). For chemical energy calculation, it was taken in consideration the heat that is either released or absorbed during the reaction (enthalpy), and converting the amount of chemical used on site in kWh/m^3 using the standard enthalpy of the reaction for a given chemical. The mechanical, or fuel, energy represented the amount of diesel used on site every day for the oiling and repairing of the machines, heating the office and running the generator, which is used to produce electricity when it is cut. The carbon emissions were calculated by converting the kWh of electricity used into kg $CO_{2\ \mathrm{equivalent}}$, using a conversion factor, according to the methods described by DEFRA(2013).

RESULTS and DISCUSSION

The data collected indicated that the total energy required for the Site 1 was 2.32 kWh/m^3 and 0.98 kWh/m^3 for Site 2, which generated 1623 and 2290 kg of $CO_{2\ \mathrm{equivalent}}$ respectively (Figure 1). For both Site 1 and Site 2 the electrical input had the biggest share compared to the other types of energies with 90% and 93% of the total consumption respectively. The mechanical energy represented the second biggest share for Site 1 (9% of the total consumption with 0.212 kWh/m^3) whereas it is the third one for Site 2 (2.7% of the total consumption with 0.026 kWh/m^3). Contrary to Site 1, which used diesel to heat the office and run the generator, Site 2 only needed to run the generator. As a result, Site 1 used 1000 L/month of diesel against 416 L/month for Site 2, which explained the difference in the results. The chemical input represented the third share for Site 1 and the second one for Site 2 (0.86% and 4.1 %

respectively). Ferric chloride was dosed prior to the primary treatment to help remove the phosphate from the wastewater. The two following reactions take place: $Fe^{3+} + PO_4 \Rightarrow FePO_4$ and $Fe^{3+} + 3OH- \Rightarrow Fe(OH)_3$. Hence, only a fraction of the ferric chloride dosed is used to form a precipitate with the phosphate. At Site 1, 138.3 kg/day of ferric chloride were dosed and 11% of it was used to form $FePO_4$, the 89% remaining being used to form $Fe(OH)_3$, whereas 265.3 kg/day were dosed at Site 2 and 21% of the ferric chloride were used to form $FePO_4$, the 79% remaining being used to form $Fe(OH)_3$. And finally, the manual input has the last share for both sites and represents 0.14% and 0.03% of the total consumption respectively. At Site 1 the sludge treatment is the treatment step that requires the most energy and represents nearly 50% of the manual work on site, which correlates with the conclusions from other studies.

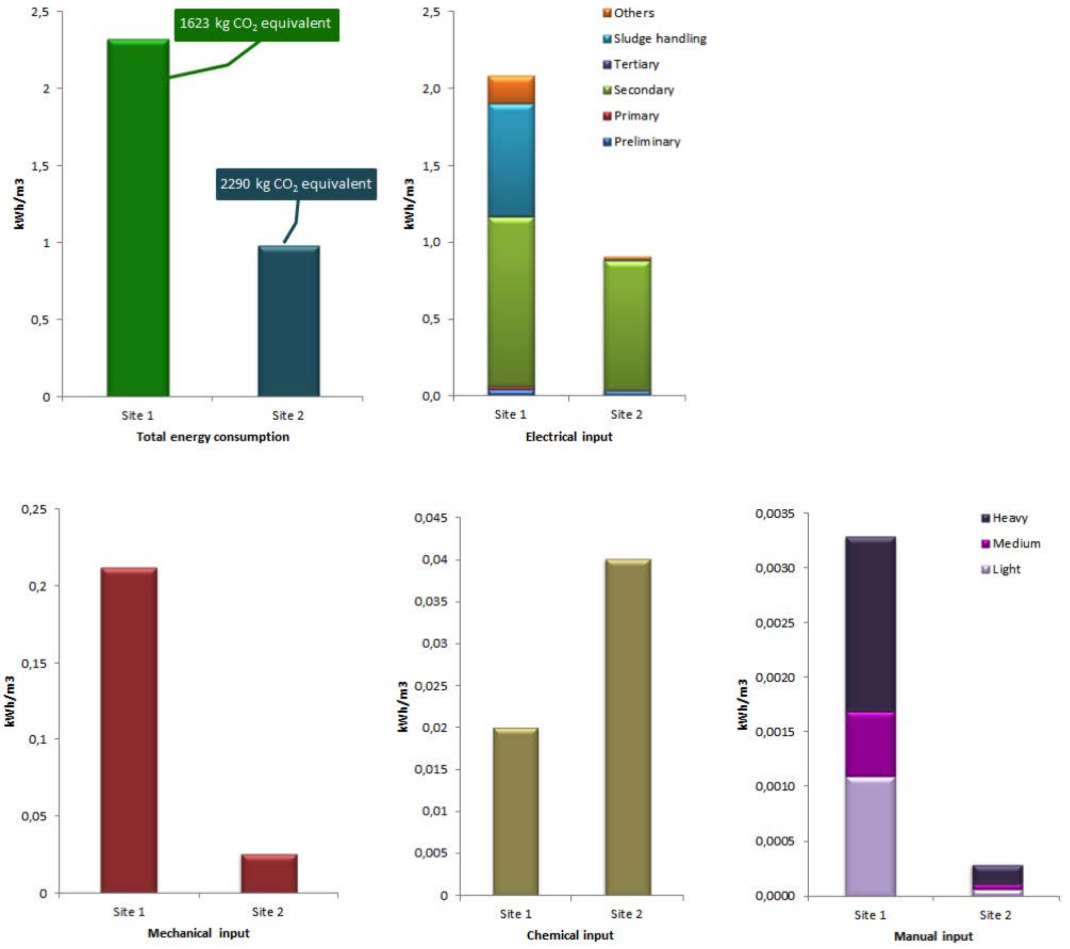

Figure 1. Electrical energy, manual energy, mechanical energy, chemical energy calculated for site 1 and site 2.

The energy benchmarking exercise identified the aeration as being the most electricity- consumer process. Nevertheless, although Site 2 did not included primary treatment, it was supervising to find that this site presented lower electricity consumption per cubic meter, when compared with Site 1 (Figure 1). The aeration capacities in both sites were investigated demonstrating that Site 1 had a maximum aeration capacity of 186 kW (4464 kWh/day) against 240 kW (5760 kWh/day) for Site 2. Consequently, this lack of aeration impacted the effluent quality, as the effluent COD and ammonia concentrationsfor Site 2 were 50.3 mg/L and f 1.3 mg/L, respectively and for Site 1 were 31.4 mg/L (COD) and 0.5 mg/L (ammonia). This led to the conclusion that Site 2 would need more aeration to reach a similar effluent quality than Site 1. Mass and energy balances completed on Site 2 demonstrated that the oxidation ditch would require 5218 kg O2/day and 3422 kWh/day to reach the same effluent quality than Site 1.

This study demonstrated the effectiveness of the energy benchmarking exercise to identify the most energy consuming assets, nevertheless it points out the need to develop a holistic overview of the WWTP and when comparing sites, the need to include parameters such as effluent quality to allow an adequate benchmarking.

CONCLUSIONS

- Total energy consumption on Site 1 and Site 2 was 2.32 kWh/m3 and 0.98 kWh/m3, respectively, including electrical, manual, chemical and mechanical energy consumptions
- Aeration in the oxidation ditch represented the largest energy-consuming in both sited with 0.942 kWh/m3 in Site 1 and 0.640 kWh/m3 in Site 2.
- Energy benchmarking of Site 1 and Site 2 were useful to identify the most energy consuming assets, nevertheless there was a need to include parameters such as effluent quality to allow an adequate comparison between sites.

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(P62) Benchmarking large municipal WWTPs using official questionnaires: The case study of Italy

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Abstract

This paper describes the implementation of a benchmarking method applied to large municipal wastewater treatment plants (WWTPs) providing (i) the identification of plants with low environmental performances and technological critical issues, (ii) the definition of appropriate improvement actions and (iii) the simulation of their suitability according to the continuous improvement approach. Moreover, WWTPs quality evaluation for each reference area (the district) was performed. In order to reach these goals the following issues have been addressed: large number of plants to be compared, incomplete data and different sources of information. The use of official questionnaires as those provided by the National Institute of Statistics (ISTAT) was considered the most suitable solution. The process outputs related to the Italian case study highlight the gap between Northern and Southern Italy.

Keywords

Benchmarking; Improvement actions; Multicriteria decision analysis; Municipal wastewater treatment plant; Questionnaire; Simulation

INTRODUCTION

In the past 20 years, several benchmarking projects have been undertaken within water industry all over the world. In many occasions the drive to benchmark was initiated outside the utility as in the cases of public debate about liberalisation/privatisation of public services or else requirements for large investments to improve the service in terms of coverage and quality (Cabrera et al., 2011). Regards this last aspect, a recent study conducted in Italy on a sample of 112 water utility companies, highlights that the total required investment in the Integrated Water Service (IWS) amounts to almost 29 billion euro corresponding to 715 euro per inhabitant (Co.N.Vi.R.I., 2011). The evaluation of the IWS investment requirement is an issue of great importance worldwide (OFWAT, 2009) which makes a benchmarking method an essential tool to be implemented. With reference to a large spatial area such as a country, the evaluation of plants quality level is generally hampered by the large number of plants to be compared, the incompleteness of the available data and the different sources to be considered (De Gisi et al., 2013). In order to achieve a good compromise, the use of official questionnaires such as those provided by the Italian National Institute of Statistics (ISTAT) can be considered a suitable solution. In this context, the main aim of the work was to define and apply a benchmarking method for large municipal wastewater treatment plants (WWTPs) with population equivalent (PE) not less than 50,000 inhabitants using official questionnaires for data acquisition. Considering the single WWTP, the developed method allowed (i) the identification of plants with low environmental performance and technological critical issues, (ii) the definition of appropriate improvement actions and (iii) the simulation of their suitability according to the continuous improvement approach. Moreover, plants quality evaluation for each geographical area (the Italian districts) was performed. With this purpose, a case study assessing Italian large WWTPs was developed.

METHODOLOGY

The framework of the proposed methodology is shown in Figure 1c. The first phase (Preparation) consists in the project planning and orientation and involved different stakeholders including the contractor (the Italian Ministry of Economic Development). The second phase (Performance assessment) was developed in two main parts: (1) data acquisition, (2) data analysis and assessment. Part 1 consists in the acquisition and validation of data related to the two groups of WWTPs according the Italian Law (sensitive and non-sensitive indicated with S-WWTPs and NS-WWTPs, respectively). Part 2 is aimed at assessing the single WWTPs quality by using appropriate evaluation criteria (14 and 15 for S-WWTPs and NS-WWTPs, respectively) related to three main aspects (technological equipment, legal requirements compliance and plant treatment capacity). To each aspect corresponds its own index as in the following: technological equipment index (ITE), environmental performance index (IEP), treatment capacity index (ITC). Furthermore, in order to reduce the amount of information related to any single plant, an aggregate parameter (called preference index, IP) was introduced. The third phase (Performance improvement) includes the identification of critical facilities and the definition of improvement actions. In this regard, three types of actions were considered: (1) basic actions, (2) structural actions, and (3) new connections for users. Finally, in order to evaluate the general quality level of the addressed areas (the Italian Districts) where plants are located, the ITE, IEP, ITC and IP indices were then extended to a district scale ($ITE_{DISTRICT}$, $IEP_{DISTRICT}$, $ITC_{DISTRICT}$ and $IP_{DISTRICT}$).

RESULTS AND CONCLUSIONS

Two types of results concerning WWTPs quality assessment, one related to single plant level and the other one related to the district level, were obtained. Regarding the single plant level, Table 1 shows the alternative matrix for S-WWTPs and NS-WWTPs related to Campania district case study. The combined analysis of the alternative matrix (see Table 1) and the evaluation criteria allows identifying the WWTPs affected by critical issues from technological and/or environmental point of views. The first type of plants are those inadequate in terms of technological equipment thus falling in a class different from class 1 (the best one, to which corresponds a value equal to 0.875 in the Table 1) according to C_{11}-C_{14} criteria. The second type of WWTPs is represented by those showing, on yearly basis, a number of non-compliant samples higher than 25% according to C_{211}-C_{225} criteria (see Table 1). Table 2 and Table 3 show the improvement actions and the expected results after their implementation, respectively. Considering the second type of results, Figure 2 shows the WWTPs quality assessment at district scale for all the Italian districts. A sensitive gap between the North and the Centre/South of Italy was observed mainly for S-WWTPs, which is mainly related to the effectiveness of the actions implemented by local authorities aimed at complying with the most recent legal constraints (EU Directive 91/271).

Finally, the following outcomes based on the achieved results can be pointed out:

- data without uncertainty are required as those provided by ISTAT;
- official questionnaires allows to evaluate WWTPs status quality identifying plants and critical processes although they also require a site-specific investigation;
- the use of appropriate indices allows to compare the WWTPs quality of different districts highlighting the most virtuous areas, and;
- more reliable results (and, consequently, a more accurate correlation quality/investments) may be obtained also taking into account small wastewater treatment plants.

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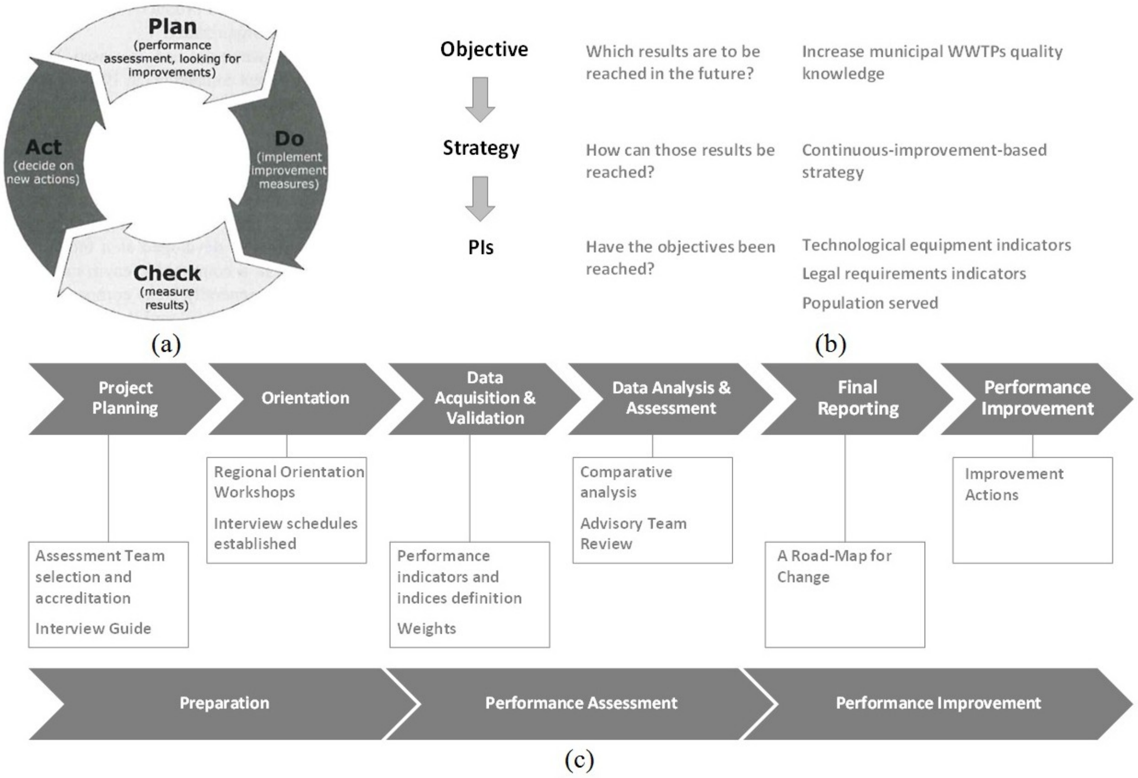

Figure 1. Methodology: (a) Plan-do-check-act cycle; (b) Objective, strategy and performance indicators (PI); (c) the adopted benchmarking process.

Table 1. Assessment and identification of critical plants for Campania District case study.

N.	**$PE_{eff,tot}$**	**Sub-Criteria**																
		C_{11}	**C_{12}**	**C_{13}**	**C_{14}**	**C_{211}**	**C_{212}**	**C_{213}**	**C_{214}**	**C_{215}**	**C_{221}**	**C_{222}**	**C_{223}**	**C_{224}**	**C_{225}**	**C_{31}**	**C_{32}**	**C_{33}**
S65	458,725	0.833	0.125(a)	0.125(a)	0.375(a)	0.875	0.875	0.875	0.125(a)	0.375(a)	0.125(a)	0.125(a)	-	-	-	0.683	0.370	0.750
S66	1,600,000	0.500(a)	0.125(a)	0.125(a)	0.375(a)	0.875	0.875	0.875	0.125(a)	0.875	0.125(a)	0.875	-	-	-	0.794	0.992	0.750
NS 6	96,250	0.833	0.625(a)	0.125(a)	0.375(a)	0.875	0.875	0.875	0.875	0.875	-	-	0.875	0.875	0.875	1.000	1.000	0.750
NS 13	100,000	0.833	0.125(a)	0.125(a)	0.875	0.875	0.875	0.875	0.125(a)	0.875	-	-	0.875	0.875	0.125(a)	0.721	0.482	0.750
NS 14	455,000	0.833	0.125(a)	0.125(a)	0.375(a)	0.875	0.875	0.875	0.125(a)	0.125(a)	-	-	0.875	0.875	0.875	0.999	0.210	0.750
NS 17	828,000	0.833	0.125(a)	0.125(a)	0.375(a)	0.625	0.875	0.875	0.875	0.875	-	-	0.875	0.125(a)	0.375(a)	1.000	1.000	0.250(a)

(a): plant performance with reference to the criteria potentially concerned by improvement interventions.

Table 2. Improvement actions for the Campania District municipal WWTPs case study.

Type	N. WWTP	$PE_{eff,tot}$	Actions						
			Baseline actions		Structural actions				New users to the sewerage system$^{(c)}$
			Disinfection	Treatment of booties	Secondary treatment	Phosphorous removal	Nitrogen removal	Filtration	
S$^{(a)}$	65	458,725	*			*	*	*	*
S$^{(a)}$	66	1,600,000	*		*	*	*	*	
NS$^{(b)}$	6	96,250	*			*		*	
NS$^{(b)}$	13	100,000				*	*	*	*
NS$^{(b)}$	14	455,000	*			*	*	*	*
NS$^{(b)}$	17	828,000	*	*		*	*	*	

$^{(a)}$: S = sensitive municipal wastewater treatment plants (S-WWTPs);

$^{(b)}$: NS = non-sensitive municipal wastewater treatment plants (NS-WWTPs);

$^{(c)}$: actions to be performed in cases where C_{31} and C_{32} are less than 1.

Table 3. Simulation results after improvement actions implementation with reference to Campania district municipal WWTPs case study.

Action	$IP_{DISTRICT}$ for S-WWTPs		$IP_{DISTRICT}$ for NS-WWTPs	
	Value	Class	Value	Class
A_0	0.417	3	0.668	2
A_1	0.484	3	0.699	2
A_2	0.802	1	0.840	1
A_3	0.812	1	0.803	1
A_4	0.869	1	0.871	1
A_5	0.867	1	0.857	1
Action	**$ITE_{DISTRICT}$ for S-WWTPs**		**$ITE_{DISTRICT}$ for NS-WWTPs**	
	Value	**Class**	**Value**	**Class**
A_0	0.103	4	0.182	3
A_1	0.170	3	0.208	2
A_2	0.267	1	0.297	1
A_3	0.276	1	0.286	1
A_4	0.333	1	0.324	1
A_5	0.333	1	0.324	1
Action	**$IEP_{DISTRICT}$ for S-WWTPs**		**$IEP_{DISTRICT}$ for NS-WWTPs**	
	Value	**Class**	**Value**	**Class**
A_0	0.279	3	0.410	1
A_1	0.279	3	0.410	1
A_2	0.500	1	0.467	1

A_3	0.500	1	0.437	1
A_4	0.500	1	0.467	1
A_5	0.500	1	0.467	1

A_0: current plant situation (status quo);

A_1: provides basic interventions as upgrading action regarding disinfection and in-situ treatment of tanker wastewater;

A_2: provides structural operations;

A_3: is the combination of basic actions and structural interventions without filtration;

A_4: is the combination of basic actions and structural interventions with filtration;

A_5: is the combination of basic actions, structural interventions (with filtration) and new connections for users (urban and industrial).

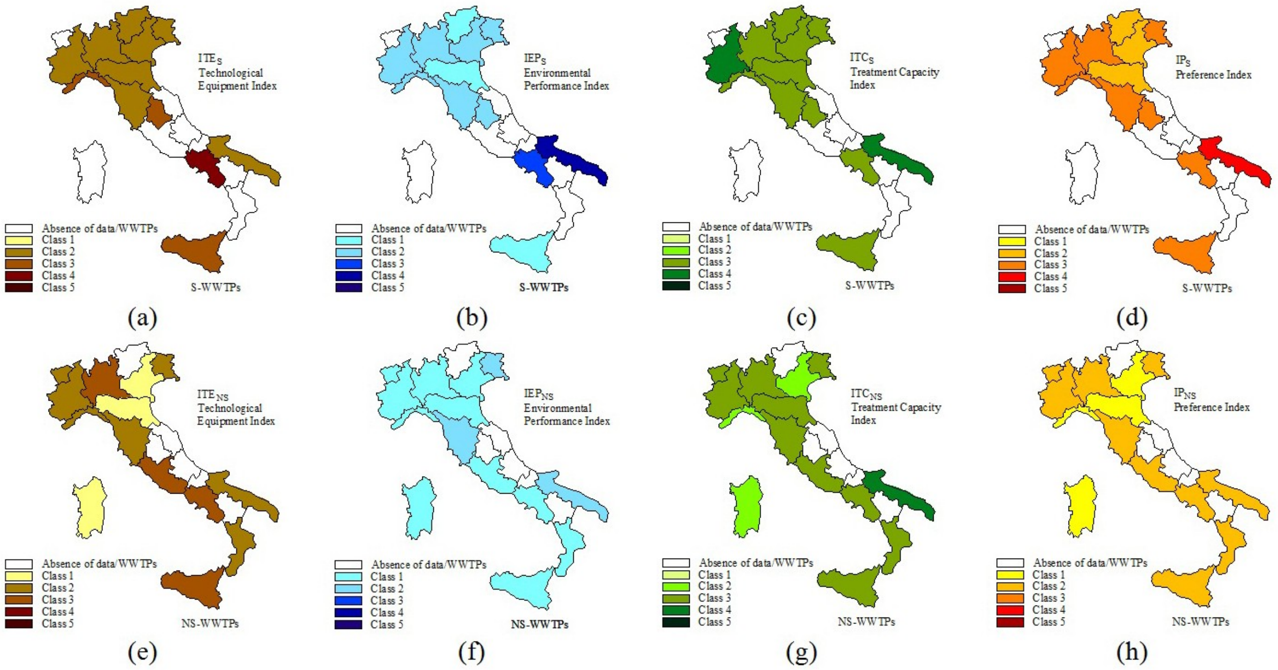

Figure 2. Assessment results for Italian districts (class 1 is the best): (a) $ITE_{DISTRICT}$ for S-WWTPs; (b) $IEP_{DISTRICT}$ for S-WWTPs; (c) $ITC_{DISTRICT}$ for S-WWTPs; (d) $IP_{DISTRICT}$ for S-WWTPs; (e) $ITE_{DISTRICT}$ for NS-WWTPs; (f) $IEP_{DISTRICT}$ for NS-WWTPs; (g) $ITC_{DISTRICT}$ for NS-WWTPs; (h) $IP_{DISTRICT}$ for NS-WWTPs.

Efficient Technologies - Non-conventional and emerging contaminants

(Wednesday, 25 June 2014, Aula T3, Polo Zanotto)

(P63) Oxidative degradation of yeast residue employed as biosorbent for organic compounds by Fenton reaction

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Abstract

The final disposal of waste biosorbents after using for contaminants sorption has been a limitation for their effective application in large scale as a material for water and wastewaters treatment. Converting biosorbent materials and organic contaminants adsorbed in environmental friendly compounds could be an alternative for this situation. In the present study, we performed a experimental design to evaluate the Fenton reaction in degrading yeast residue from alcohol industry, used as biosorbent for textile dyes. The degradation efficiency was monitored by solid residue (SR) reduction and total organic carbon (TOC) remaining in solution. The ANOVA shows an error of 9.6% for the effects and the interaction media for the employed model (SR reduction, which is the factor of greatest interest at this moment). After predicting the best conditions by the experimental design to obtain a higher SR reduction (60 min., 25 g of SR, pH = 3, H_2O_2 = 2500 mgL^{-1} and Fe^{2+} = 250 mgL^{-1}), SR reduction reached 62.2% and TOC reached 35.2%, which suggests that the oxidative advanced process can be an alternative to be explored to reduce or to completely degrade the biosorbent after sorption.

Keywords

Oxidative process; solid biosorbent degradation; chemometric approach.

INTRODUCTION

Biosorption is a viable alternative to remove organic and inorganic contaminants from aqueous medium, transferring these contaminants to a solid support. However, the disposal of biosorbent after sorption remains an issue to be solved, considering that deposition in landfills, incineration or calcination of the solid residues are not completely environmental friendly. Advanced oxidation processes (AOP) emerge as an alternative to partial or complete simultaneous degradation of the biosorbent residue and the organic contaminants. The AOP involves the formation of hydroxyl radical (OH•), which has high oxidation potential (E^o = 2.730 V). The basic principle featuring a AOP is the formation of OH•, either by chemical, physical, electrochemical, or photochemical process (Solozhenko et al, 1995). The OH• reacts with the organic matter, converting it to CO_2, H_2O and mineral acids such as HCl. In general, the organic matter dissolved in water is oxidized by straight chain reactions (usually involving free radicals) initiated, for example, by abstraction of a atomic hydrogen of the pollutant compound by OH• (Solozhenko et al, 1995). The OH• is formed from the combination of oxidants such as ozone and hydrogen peroxide and ultraviolet irradiation (UV) or catalysts such as metal ions or semiconductors. Depending on the structure of the organic contaminant, different reactions can occur involving OH•, such as the atomic hydrogen abstraction, electrophilic addition to substances containing aromatic rings and instaurations, electron transfer and radical-radical reactions (Nogueira et al., 2007).

A catalytic oxidation of tartaric acid in the presence of ferrous salts and hydrogen peroxide was reported by Fenton (Fenton, 1894). After 40 years it has been proposed that the OH• is the oxidizing species in the system, which is capable of oxidizing organic compounds in a lot of classes in which a spontaneous reaction occurs even in the dark (Haber, 1934). For the Fenton process, a sequence of reactions produces different radical with a higher-powered oxidant.

In the absence of a substrate, the OH• can oxidize other ion Fe^{2+} ($Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^-$). The Fe^{3+} can decompose H_2O_2 to H_2O and O_2 catalytically, also forming ferrous ions and radicals. On the other hand, the excess of H_2O_2, can also sequester OH•, forming hydroperoxyl radical (HO_2•), which has a lower reduction potential (E^0 = 1.42 V) than OH• (Paterline, 2005). The present work evaluated the oxidative degradation by Fenton reaction of yeast residue used as biosorbent for textile dyes employing a chemometric design to determine the ideal combination of H_2O_2, Fe^{2+}, organic matter and time to promote a most effective degradation of organic matter.

MATERIALS AND METHODS

Materials

The oxidative solutions were prepared from H_2O_2 50% m v^{-1} (Sigma-Aldrich, Germany) and $FeSO_4.7H_2O$ (Synth, Brazil). Quantitative nylon Filters Pro (0.45 µm, 33 DM) (Aprolab, Brazil) were used to filter the solid residue after oxidative treatment. A shaker TE-420 (Tecnal, Brazil) was employed for all experiments. Total organic carbon was determined by a TOC-VCSN (Shimadzu, Japan). The yeast residue was obtained from Cerradinho alcohol industry (Catanduva, São Paulo State, Brazil). The UV light source used in the process was a germicidal lamp 30W (Phillips, Brazil). Yeast residue post-dyes biosorption (red-FNR and blue H-RN-01 Cibacrom, Huntusman, EUA) were submitted to the Fenton best condition determination.

Experimental

Oxidative degradation of yeast residue employed as biosorbent by Fenton reaction. A blocked experimental design central composite-type (20 experiments) was performed to determine the best conditions for SR elimination (Table 1). The evaluated parameters were pH and initial concentration of H_2O_2, Fe^{2+} and yeast mass, in 4 levels. The initial concentrations of Fe^{2+} and H_2O_2 were based on the studies of Madeira (2011) who employed Fenton reaction for textile waste treatment. For the blocked experimental design central composite-type, with triplicate on the central point for yeast residue degradation, the pH was fixed at 3 (after a previous evaluation of pH 2) and the block times were fixed at 60 min (B1) and 90 min (B2). Levels -1, 0 and 1 were respectively: H_2O_2 = 500, 750 or 1000 mg L^1, Fe^{2+} = 25, 37.5 or 50 mg L^{-1} and mass of SR = 25, 112.5 or 250 mg. All experiments were carried out in triplicate, resulting in 60 experiments.

Masses of SR were weighted and suspended in solutions with H_2O_2 and Fe^{2+} at pH 3, according the experimental design (Table 1). The suspensions were shacked at 2400 rpm. After that, aliquots of 4 mL were collected and passed through filters previously weighted. The filters were dried until constant weight in an oven at 60 °C, cooled in desiccators and then weighted to determine the amount of SR remaining after Fenton treatment. In the next step, the pHs of remaining suspensions were adjusted to 8 to interrupt the Fenton process and an aliquot of 3 mL was filtered, diluted to 30 mL with deionized water and TOC was quantified. The TOC was determined after acidification with HNO_3 1 mol L^{-1} to guarantee the total solubilization of Fe^{2+} remaining on solution. The best conditions obtained from statistical treatment were employed on biosorbent after dyes biosorption.

RESULTS

The results of SR reduction and TOC (Table 1) were treated employing the software Statistica®. It is important emphasize that the SR reduction is the preponderant factor to denote the process efficiency, as the most important goal in this time is to reduce the SR after biosorption. For the statistical treatment it was employed the two-way model (double effect) that measures linear and quadratic variations with double effect. In the first evaluation, it was observed a loss of response when the block varied, with the best responses to SR reduction and TOC obtained for B1 (60 min). For B2 (90 min), time increasing was a critical factor.

One possible explanation is the fact that two reactions occur simultaneously, consuming the peroxide (Paterlini and Nogueira, 2005): a) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$ (k = 76 M^{-1} s^{-1}), b) $Fe^{3+} + H_2O_2$ $FeOOH^{2+} + H^+$ (k = 0,001-0,01 $M^{-1}s^{-1}$). The first reaction is initiated by OH•, resulting from the reaction of H_2O_2 with the Fe^{2+} ions. In this step, the H_2O_2 is intensely consumed beacuse of the catalytic formation of OH• radical. However, the Fe^{3+} produced can also react with H_2O_2, producing another kind of radicals (HO_2•)

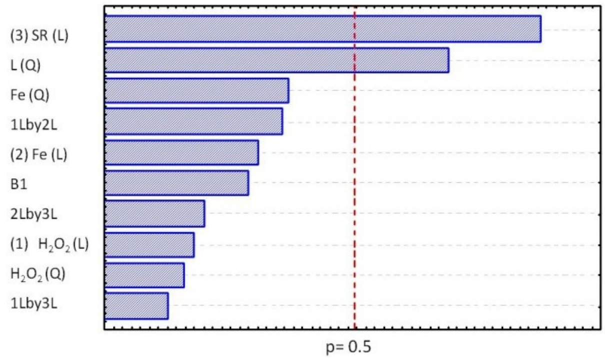
with less oxidizing power and reducing the quantity of H_2O_2 available in the medium. As the concentration of H_2O_2 is reduced, the formation of OH• is hampered. Thus, increasing time implies in increasing the formation of Fe^{3+} which interacts with H_2O_2, affecting negatively the SR reduction.

Considering the Pareto's graphic and the ANOVA values (Figure 1) for SR reduction, it is possible to observe that both components, linear and quadratic are statistically significant.

The ANOVA presented an error of 9.6% for the effects and the interaction media for the employed model. The error >5% could be related to the intrinsic nature of the experiment, which aims degradation of solid material by Fenton reaction, which is an innovation. The primary interaction of free radicals OH• with solid yeast residue would serve, in principle, to break the weakest chemical bonds which would convert into soluble species the polysaccharides macromolecules such as glucan, mannan and also chitin, which compose the yeast and spores cell wall (Lesage and Bussey, 2006). It is important to emphasize that, kinetically, the chances of a free radical meets a favorable chemical bond to cleave by hitting with a solid biological material is infinitely inferior to this phenomenon to occur when the same radical collides with a soluble organic molecule. This fact leads to the conclusion that with the generation of soluble molecules from the solid material, the action of free radicals on the solid sample would be reduced whereas the action on the soluble organic molecules would intensify, favoring the TOC reduction and limiting the SR.

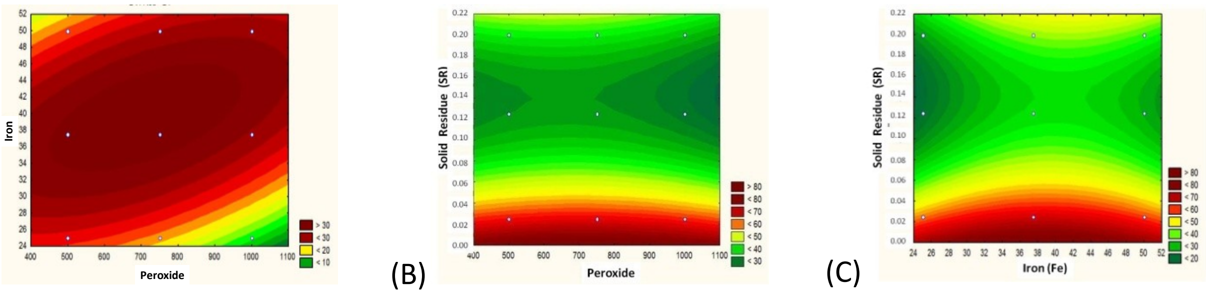
Table 1. Experimental design and results for SR reduction and TOC after Fenton treatment employing the blocked experimental design central composite with triplicate on the central point, pH = 3, B1 (60 min), B2 (90 min). Levels -1, 0 and 1 were respectively: H_2O_2 = 500, 750 or 1000 mg L^1, Fe^{2+} = 25, 37.5 or 50 mg L^{-1} and SR = 25, 112.5 or 250 mg.

	Parameters			*Answers*	
Block (B)	**H_2O_2 (mg)**	**Fe^{2+} (mg)**	**Mass (mg)**	**TOC (mg L^{-1})**	**SR reduction (%)**
1	-1	-1	-1	33.62	65.28
1	-1	-1	1	339.90	32.67
1	-1	1	-1	42.82	61.72
1	-1	1	1	291.40	[redacted]7.82
1	1	-1	-1	37.38	53.69
1	1	-1	1	291.80	18.06
1	1	1	-1	39.75	69.12
1	1	1	1	154.1	42.61
1	0	0	0	284.5	39.46
1	0	0	0	204.4	36.50
2	-1	0	0	175.9	31.96
2	1	0	0	123.9	31.68
2	0	-1	0	181.8	28.31
2	0	1	0	165	22.21
2	0	0	-1	39.51	57.95
2	0	0	1	241.2	50.98
2	0	0	0	182	14.65
2	0	0	0	160.2	33.63
2	0	0	0	129.7	41.55



Factor	SS	Df	MS	F	P
Blocks	102.553	1	102.553	1.21904	0.298293
(1) H2O2 (L)	19.862	1	19.862	0.23610	0638850
H2O2(Q)	11.863	1	11.863	0.14102	0.715968
(2) Fe (L)	121.615	1	121.615	1.44563	0.259908
Fe (Q)	198.550		198.559	2.36026	0.158837
(3) SR (L)	1577.885	1	1577.885	18.75620	0.001903
SR (Q)	919.649	1	919.649	10.93179	0.009137
1L by 2L	184.284	1	184.284	2.19057	0.172990
1L by 3L	3.443	1	3.443	0.04093	0.84175
2Lby 3L	31.577	1	31.577	0.37535	0.55266
Error	757.134	9	84.126		
Total SS	4416.390	19			

Figure 1. Pareto's graphic and variance analysis for SR reduction after Fenton treatment employing the blocked experimental design central composite with triplicate on the central point, pH = 3, B1 (60 min), B1 (90 min). Levels -1, 0 and 1 were respectively: H_2O_2 = 500, 750 or 1000 mg L^1, Fe^{2+} = 25, 37.5 or 50 mg L^{-1} and SR = 25, 112.5 or 250 mg, MS residual = 84.12604.



(A) (B) (C)

Figure 2. Contour surfaces for SR reduction after Fenton treatment for B1, 20 experiments, 3 factors, MS residual=84.126. A)Fe×H_2O_2 B) SR×H_2O_2 and C) SR×Fe (dark green=best conditions).

The surface responses graphics (Figure 2) suggests that the best responses for SR reduction can be obtained for the higher level for both H_2O_2 and Fe^{2+}. It was observed dependence between Fe^{2+} and H_2O_2, as they are limiting reagents for OH• production, and a efficiency loose for low concentrations of H_2O_2 and Fe. It was also observed that the SR residue was similar for both higher and lower concentrations of H_2O_2 and Fe^{2+} with a slightly better efficiency for higher concentrations. This behavior is similar for the two blocks evaluated (60 and 90 min). It is possible to conclude that the best response for SR reducing was obtained to the higher concentrations of H_2O_2 and Fe^{2+} (Figure 2). There is dependence between the reagents, as both limit the production of OH•.

The employment of minor SR masses produced a better SR reduction for all reagents levels. Two mathematical descriptions of the processes and prediction of response expressions were obtained, both using the Statistic® and using the model of Multivariate Adaptive Regression Analysis (MARS) with simplified expressions and 4 interactions (Time, Fe, H_2O_2 and SR mass). The reduced expressions for SR reduction and TOC, equations 1 and 2, respectively, are as follows:

Expression 1 – Degradation monitoring by SR reduction, significant interactions coefficients 5.516; 1.71 interposing on the minimum, average and maximum concentrations of the variables, H_2O_2, Fe^{2+}, SR mass, and time.

SR reduction = 5,51615070944104e+001 - 1,71026379615200e+002*max(0; Mi-2,50000000000000e-002) + 4,89485208829856e-003*max(0; H_2O_2 -5,00000000000000e+002)*max(0; Fe^{2+} -2,50000000000000e+001)*max(0; Mi-2,50000000000000e-002).

Expression 2- Degradation monitoring by TOC, significant interactions coefficients 4.41; 1.51 interposing on the minimum, average and maximum concentrations of the variables, H_2O_2, Fe^{2+}, SR mass, and time.

TOC = 4,41676363636365e+001 + 1,51142755158951e+003*max(0; Mi-2,50000000000000e-002) - 6,87273619631902e-002*max(0; H2O2 -5,00000000000000e+002)*max(0; Fe2+ -2,50000000000000e+001)*max(0; Mi-2,50000000000000e-002)

Simultaneous interactions among all components in the evaluated range were used to predict the best working condition (SR reduction of 100%). The ideal theoretical conditions were 25 g of SR, pH = 3, H_2O_2 = 2500 mg L^{-1}, Fe^{2+} = 250 mg L^{-1}, 60 min of reaction. The experiment employing these conditions was carried out and the results for SR reduction and TOC were respectively 62 ± 2% and 35 ± 2% for SR and 61 ± 3% and 29 ± 2% for SR post-dyes biosorption. We expected an increasing degradation when employing the predicted optimal conditions, which did not occur. Nevertheless, we viewed the SR in microscope and identified a predominance of yeast spores, which cell wall is composed primarily of chitin, a biopolymer resistant to degradation. Alternatives to intensify the SR reduction will be adopted in future experiments employing UV radiation and free radical production by electrochemical *in situ*.

CONCLUSIONS

The SR reduction higher than 60% is a promising result to achieve the proposed objective, reduces de SR of biosorbent. The chemometric design described the behavior of the parameters and how they are related, allowing us to identify the best range of responses in terms of SR reduction.

ACKNOWLEDGMENT: The authors are grateful to CNPQ, UNIFESP, FAPESP (2007/53860-6).

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(S47) Biotransformation of organic micro-pollutants by ammonia oxidizing bacteria

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Abstract

The biotransformation of five pharmaceutical compounds by ammonia oxidizing bacteria (AOB)was investigated. The pharmaceuticals studied were ibuprofen (IBP), ketoprofen (KTP), carbamazepine (CBZ), dexamethasone (DXM) and iopromide (IOP) at concentrations between μg/L range (environmental concentration) and mg/L range (above environmental concentration).

A full biotransformation was observed for IBP and KTP. The biotransformation product of IBP supports the assumption that the used bacterial culture was enriched AOB without heterotrophic bacteria. The results from the controls show that removal of pharmaceuticals by adsorption onto the biomass or intrinsic degradation can be neglected, and therefore, their transformation would depend only on the nitrifying activity. A competition between ammonium and the model compounds was shown at high ammonia concentrations. The metabolic succession of the compounds according to the biotransformation rate was: IBP ›KTP› DXM ›CBZ› IOP.

Our results support the concept that augmentation with nitrifying activity to achieve stable nitrification in the activated sludge system or during polishing treatment following activated sludge, can enhance the removal of trace organic pollutants.

Keywords

Pharmaceuticals biodegradation; Co-metabolism; Ammonia oxidizing bacteria; Ammonia monooxygenase.

INTRODUCTION

The occurrence and fate of pharmaceutical active compounds (PhACs) in the environment have received considerable attention from the scientific community during the last two decades. Their high-level persistence at environmental concentrations and low adsorption properties have led to PhACs being detected ubiquitously in water and wastewater environments and in some cases inwater distribution systems. Because these chemicals are often present in wastewater at concentrations ranging from 0.1 to 10^5 ng/L they cannot support growth or activity of microorganisms capable of mineralizing them during biological wastewater treatment (Ternes et al., 2007; Oulton et al., 2010).

The removal of PhACs from wastewater is essential to prevent environmental contamination and its possible adverse effects. A number of studies have shown that the biodegradation of PhACs in wastewater is likely to be due to co-metabolic activity (Tarn et al., 2009, Forrez et al., 2008). Studies published on co-metabolism of PhACs are currently limited. Several studies on the removal of xenobiotics have shown that the degradation can be enhanced by augmentation through the addition of organic carbon sources or other nutrient substances, such as nitrogen and phosphate, as well as mineral constituents (Tarn et al., 2009). Recent studies reported that the ammonia oxidizing bacteria (AOB) in a nitrifying activated sludge system were responsible for the elimination of these chemicals (Batt et al., 2006; Yi and Harper, 2007). The co-metabolism of PhACs may be important for their degradation because ammonium monooxygenase (AMO) has a relatively wide spectrum for the degradation of substrates (Tarn et al., 2009).

The data in this field are limited in the literature, and need more research and explanations, especially in terms of kinetics of degradation and effect of concentration. The main objective of this study was to establish the basis for the biotransformation of selected pharmaceuticals at environmental and above-environmental concentrations by ammonia oxidizing bacteria.

METHODS

Five selected pharmaceuticals ibuprofen(IBP), ketoprofen(KTP), carbamazepine(CBZ), dexamethasone(DXM) and iopromide(IOP), were applied as model compounds. The biotransformation of the PhACs was examined in a medium consisting of tap water supplemented with ammonium chloride at a concentration of 5 mg/L as N, 50 g/L sodium bicarbonate and 5 g/L potassium monophosphate. The bacteriostatic biocide sodium azide (2 g/L) and the AMO inhibitor allylthiourea (10 mg/L)were added to the controls. The ammonia-oxidizing bacterial enrichment was obtained from a continuousfluidized bed-nitrifying reactor operated for many years atlab conditionsat theTechnion and originated from activated sludge. Biotransformation of the model PhACs was tracked by liquid chromatography-multiple stage/mass spectrometry (LCMS/MS) .The concentration of N-NH_4 was determined by the colorimetric assay of Willis et al. (1996).

RESULTS AND DISCUSSION

The biotransformation of each of the model compounds by nitrifying bacteria was assessed in batch regime in cultivation flasks. An exponential decrease in concentration over time was observed for all model compounds, fitting a first order reaction. Figure 1 shows the removal percent of the PhACs after biotransformation by the nitrifying bacteria and their controls and Table 1 shows the initial concentrations of the PhACs and the biotransformation rates

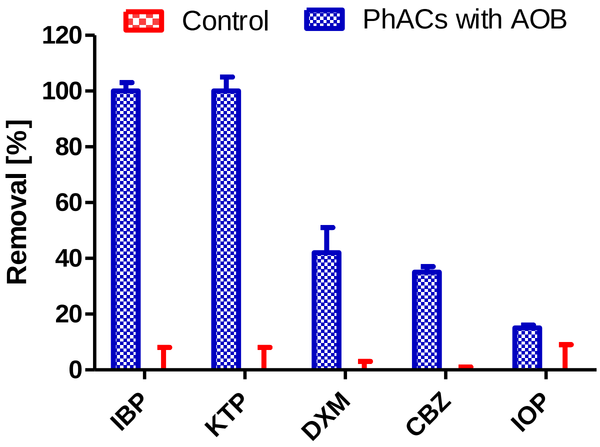

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Figure 1. Removal percentage of the PhACsby ammonia oxidizing bacteria and their respective controls.

Table1. Initial PhACsconcentration and biotransformation rates.

PhACs	**Initial concentration [µg/L]**	**Biotransformation rate [1/h]**
IBP	68	0.188
KTP	63	0.018
CBZ	77	0.0047
DXM	92	0.002
IOP	83	0.0002

From Figure 1can be seen that IBP and KTP were completely transformed. Similar results were reported for the removal of IBP by nitrifying bacteria in a recent report (Tran et al., 2009). This finding can be in part attributed to the relatively small size and structure of the IBP molecule. KTP was also completely transformed; however, a longer time was required for its complete biotransformation, which reflects a slower biotransformation rate as shown in Table 1. This can be at least partially attributed to the additional aromatic ring in the KTP molecule as compared to IBP. DXM was removed to about 48%. To the best of our knowledge, this is the first time biotransformation of DXM by enriched nitrifiers has been reported. Studies on DXM removal by conventional wastewater treatments have been reported, in many of which high levels of removal (more than 90%) were found (Outlon et al., 2010). CBZ was partially transformed to only approx. 40%. Despite the fact that the observed removal percentage of CBZ is low, it is still higher than that reported in the literature (Zhang et al., 2008; Tran et al., 2009). Most studies in wastewater treatment found that a low removal percentage was achieved by different biological treatments. Tran et al. (2009) reported about 25% removal efficiency for CBZ using nitrifying activated sludge. The recalcitrance of the CBZ can be attributed to its planar structure, which may lead to low diffusion across the cell membrane, or the presence of the nitro group that can make it less degradable. IOP displayed the lowest extent and rate of transformation (~10%). No significant removal of IOP (less than 10%) has been reported during conventional activated sludge process (Batt et al., 2006). IOP is the largest and most hydrophilic compound among the studied model compounds, with a MW of approximately 800 Da and pK_{ow} of -2.9, both of which properties could be attributed to its low biodegradation rate.

As can be seen from the results all model compounds displayed fairly good stability. These results clearly indicate that removal of pharmaceuticals by adsorption onto the biomass can be neglected, and therefore, their transformation would depend only on the nitrifying activity.

The effect of ammonia concentration on PhACs biotransformation by nitrifying bacteria was tested for IBP. The rate of biotransformation of IBP was tested at four different ammonium concentrations of the bulk (0, 5, 50, 100 mg/L as N) (Figure2).

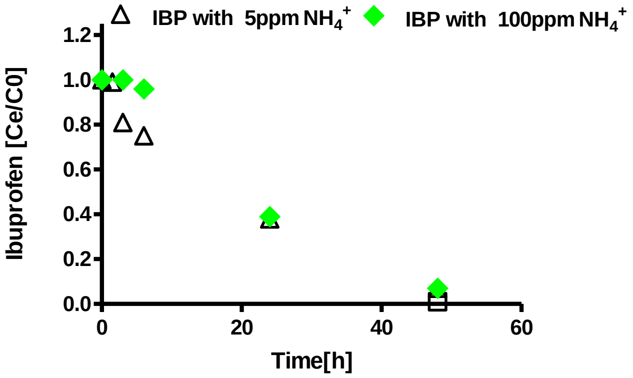

Figure 2. Changes in relative concentrations of IBPinthe presence of two different initial ammonium concentrations(5 and 100 mg/L, as N).

From Figure 2 can be seen that IBP was completely removed at the twoammonium concentrations at similar rate. However, a delay in the starting time of IBP biotransformation occurred until all ammonia was consumed which increased with the initial ammoniaconcenration. From these experiments, one can learn that a clear metabolic hierarchy exists for the nitrifying consortia in which ammonium is the primary electron donor followed by the PhACs.

Our findings help to explain number of basis for the biotransformation of selected pharmaceuticals by ammonia oxidizing bacteria, and support the concept thatenrichment of nitrifiers to achievestable nitrification during wastewater treatmentcan enhance the removal efficiency ofPhACs at trace concentrations.

ACKNOWLEDGEMENTS

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(S48) Enzymatic membrane reactor with covalently grafted laccase for tetracycline degradation

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Abstract

The presence of pharmaceutical residues and endocrine disruptors in environmental water resources is a tough challenge as it is difficult to evaluate the potential impact of long-term hazard that emerges from the contamination at below-activity levels on flora and fauna. With a limited efficiency of current wastewater treatment technologies to completely remove these contaminants, their treatment with an enzymatic membrane bioreactor appears as an interesting alternative. This work mainly describes the implementation of ceramic membranes grafted with laccase from *Trametesversicolor*in an enzymatic membrane reactor for the degradation of pharmaceuticals pollutants. The tetracycline was chosen as a model substrate to attest the grafting protocol optimization on two kinds of microfiltration membranes with pore diameters equal to 0.2 and 1.4 µm. The stability of different active membranes was tested to degrade a 20 ppm tetracycline solution during several cycles of 24 hours.

Keywords
Covalent grafting, degradation rate,enzymatic membrane reactor,laccase, tetracycline.

MATERIAL AND METHODS

Grafting optimization

The protocol for preparation of active tubular ceramic membranes (pore diameter of 0.2 and 1.4 µm) has been already described in a previous work(Chea et al. 2012). It is a 3-step procedure which starts with a cross-flow filtration of a gelatin solution prepared in 50 mM phosphate buffer at pH 7 in a tangential filtration pilot. In order to optimize the grafting process, several concentrations of gelatin were tested (0.5, 1, 5, and 10 g.L^{-1}). The gelatin deposited on the ceramic carrier was then cross-linked with a 4% (w/v) glutaraldehyde solution prepared in the same phosphate buffer solution. The aldehyde allowed alsothe covalently grafting of the laccase. Different enzymes concentrations (1, 5, 10, and 20 g.L^{-1}) were tested in order to optimize the amount of grafted enzyme. The optimized grafting was determined by degrading 2 L of a 20 ppm tetracycline solution prepared in osmosed water in a pilot unit at 25°C during 24 hours.

Pilot Unit and Enzymatic membrane reactor

The pilot unit was built with stainless steel and PTFE in order to avoid problems due to the possible adsorption of the pollutants. It was composed of a tubular reactorcontaining the active membrane, a heat exchanger connected to a cryothermostatin order to set the temperature and sensors for the measurement of transmembrane pressure and flow rate. The reactor can be operated in different configurations. In order to determine the stability of the grafted biocatalyst, several active membranes with different characteristics (channels, porosity and length) were prepared and used in the pilot unit to degrade 2 L of a 20 ppm tetracycline solution prepared in osmosed water at 25°C. The reactor was emptied, rinsed with osmosed water and filled with a fresh tetracycline solution periodically. The experiments carried out in batch configuration (retentate and permeate were both recirculated in the feeding tank)lasted for 4 cycles of 24 hours. High performance liquid chromatography coupled to mass spectrometry was used to quantify the residual tetracycline periodically.

RESULTS AND DISCUSSIONS

Optimized coating

The gelatin and enzyme concentrations were varied in order to determine the optimal grafting by degrading tetracycline in the membrane reactor. For ceramic supports of a mean pore size of 0.2 µm the best degradation rate was obtained by using 0.5 g.L^{-1} of gelatin, 20 g.L^{-1} of enzymes. Under these conditions the enzymatic reactor was able to degrade 0.34 mg/h of tetracycline. Moreover the degradation rate reached 0.84 mg/h of tetracycline when using ceramic supports with a mean pore size of 1.4 µm activated with a gelatin solution of 10 g.L^{-1} and 10 g.L^{-1} of the enzymatic solution.

Active membrane stability

The stability of active membranes was tested by measuring the reaction rate of tetracycline degradation in the pilot unit during several cycles of 24 hours. As it can be seen in Table 1, the degradation rates (mg.h^{-1}) seem different for each membrane. However the total active surface needs to be taken into account to properly compare the results. We can thus determine an average degradation rate equal to 124 mg.h^{-1}.m^{-2} with 0.2 µm membranes and 275 mg.h^{-1}.m^{-2} for 1.4 µm membranes. The results obtained with a long multichannel membrane with a high porosity seem very promising.

Table 1. Tetracycline degradation rate for different ceramic membranes.

Membrane	Length (cm)	Degradation rate (mg.h^{-1})	Pore size (µm)	Geometric surface (m²)	Degradation rate (mg.h^{-1}.m^{-2})
Monochannel	15	0.36	0.2	2.86×10^{-3}	125.74
Monochannel	25	0.61	0.2	5.06×10^{-3}	119.87
Monochannel	15	0.82	1.4	2.86×10^{-3}	287.30
7 channels	25	1.28	0.2	10.12×10^{-3}	126.78
7 channels	25	2.67	1.4	10.12×10^{-3}	263.42

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(S49) Degradation of Polycyclic Aromatic Hydrocarbons (PAHs) in Produced Water using Fenton Process

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) in produced water can have adverse effects on human health and environment due to their toxic, mutagenic and carcinogenic properties. This study determines the suitability of Advanced Oxidation Process using Fenton reagent for the treatment of PAHs-contaminated water. Produced water samples were adjusted to the selected pH value, range 2-5, and $FeSO_4$ and H_2O_2 were added at 1:4, 1:3, 1:2 and 1:1 ratios. After the desired reaction time, pH of reaction mixtures was raised to 10 to decompose H_2O_2 to stop further oxidation of organic matter prior to COD and TOC measurements. Gas Chromatography-Mass Spectrometer (GC-MS) was used for determination of PAHs after an enrichment step of Liquid-Liquid Extraction (LLE). The maximum COD and TOC removal achieved was 77.0% and 83.9% respectively, under operating condition of pH 3, 1.5mL H_2O_2, 0.5g Fe^{2+} and 180 minutes reaction time. Total PAHs removal was 72.5% under these operating conditions.

Keywords

Produced Water; Polycyclic Aromatic Hydrocarbons (PAHs); COD; TOC; Advanced Oxidation Process; Fenton Process

INTRODUCTION

The term ‘produced water’ refers to water that appears produced when oil and gas are extracted from the ground. It consists of a mixture of formation water naturally present in the reservoir, injected water used for the recovery of oil and/or chemicals added during production. Produced water is the largest volume waste stream associated with oil and gas exploration and production. Produced water has a complex composition; comprising inorganic and organic compounds including polycyclic aromatic hydrocarbons (PAHs). PAHs are a big class of compounds made up of more than two fused aromatic rings in a linear or clustered arrangement, usually containing only carbon (C) and hydrogen (H) atoms, although nitrogen (N), sulphur (S) and oxygen (O) atoms may readily substitute in the benzene ring to form heterocyclic aromatic compounds (Yap *et al.,* 2011). PAHs are persistent organic pollutants and are known to be toxic, mutagenic and carcinogenic. Out of more than 10,000 known PAHs; about 200 compounds are possible carcinogens (Pakpahan *et al.,* 2011). The U.S. Environmental Protection Agency (USEPA) has designated 16 PAHs priority pollutants (Pakpahan *et al.,* 2012; 2013), viz., Naphthalene/Np ($C_{10}H_8$), Acenaphtylene/Ace ($C_{10}H_8$), Acenaphthene/Acn ($C_{10}H_{10}$), Fluorene/F ($C_{13}H_{10}$), Phenanthrene/Ph ($C_{13}H_{10}$), Anthracene/An ($C_{13}H_{10}$), Fluoroanthene/Fl ($C_{16}H_{10}$), Pyrene/Py ($C_{16}H_{10}$), Chrysene/Ch ($C_{18}H_{12}$), Benzo[a]Anthracene/BaA ($C_{18}H_{12}$), Benzo[b]Fluoranthene/BbF ($C_{20}H_{12}$), Benzo[k]Fluoranthrene/BkF ($C_{20}H_{12}$), Benzo[a]Pyrene/BaP ($C_{20}H_{12}$), Indeno[1,2,3-cd]Pyrene/Ind ($C_{22}H_{12}$), Benzo[g,h,i]Perylene/BPer ($C_{22}H_{12}$), and Dibenzo[a,h]Anthracene/DbA ($C_{22}H_{14}$).

Advanced oxidation processes (AOPs) are used to oxidize complex organic constituents found in wastewater that are difficult to biodegrade. AOPs typically involve the generation and use of the hydroxyl free radicals (OH•) as strong oxidant to destroy complex organic compounds. Hydroxyl radicals are the most oxidative species that can be formed in aqueous solutions, and have been shown to degrade many organic compounds including PAHs, using different AOPs (Flotron *et al.,* 2004). AOP using Fenton reaction is based on the catalytic decomposition of hydrogen peroxide by Fe salts to produce hydroxyl radicals. Fenton process is a relatively economical treatment option as it requires no additional energy when compared to many other AOPs. Also, both iron and hydrogen peroxide are relatively cheap and safe. The overall reaction only produces water, oxygen, and carbon dioxide which are harmless by-products.

The objectives of this study were:

- to assess the feasibility of using Fenton process for the treatment of PAHs-contaminated water, and
- to optimize process parameters viz., Hydrogen Peroxide (H_2O_2) and Ferrous Sulphate ($FeSO_4$) dosages, pH and reaction time for organics removal.

MATERIALS AND METHODS

Produced water

Produced water collected from a local refinery crude oil terminal was transferred to the laboratory and kept in a cold room at 4 °C until being used in the experiments. The pH, COD and TOC of the produced water were 7.92, 1867 mg/L and 242 mg/L respectively. Only 12 of the 16 priority PAHs were detected in the produced water (Table 1).

Table 1. Concentration of the 12 PAHs in produced water

Compound Name	No. of Rings	Concentration (ppb)
Acenaphthene	3	13.610
Carbazole	3	9.070
Fluoranthene	3	9.150
Pyrene	4	10.830
Benzo (a) Anthracene	4	11.750
Chrysene	4	7.210
Benzo (b) Fluoranthene	4	11.860
Benzo (k) Fluoranthene	5	12.060
Benzo (a) Pyrene	5	7.310
Indeno (1,2,3-cd) Pyrene	6	8.910
Dibenzo (a,h) Anthracene	6	12.250
Benzo (g,h,i) Perylene	6	10.140
Low molecular weight PAHs (LMW-PAHs)*		31.830
High molecular weight PAHs (HMW-PAHs)		92.320
Total PAHs (TPAHs)		124.150

*Low molecular weight PAHs refers to 2 and 3 ring compounds

Experiments

Preliminary experiments. Preliminary experiments using 100 mL samples were conducted to determine the optimum operating conditions for treatment of PAHs contaminated water using Fenton reagent. For determination of reaction time, the experiments were performed by dosing 1.5 mL of H_2O_2 and 0.5 g of $FeSO_4$ and and pH of the sample was kept unadjusted at pH 7.92. Reaction times from 0 to 240 minutes were tried and treated samples were collected at 30 minute intervals for COD measurement. At the end of each reaction time, the treated sample pH was raised to 10 using 50% w/w NaOH solution to decompose H_2O_2 and stop further oxidation of organic matter. For determination of Fe^{2+} dosages, the optimum reaction time obtained was applied. Experiments were performed by dosing $FeSO_4$ in amounts 0.2g, 0.5g, 1.0g, 1.5g and 2.0g. The pH of the sample and H_2O_2 dosage were kept at 7.92 (unadjusted) and 1.5mL respectively.

Main experiments. For the main experiments, 1 L produced water was measured and poured into a beaker, and the pH was adjusted as necessary using concentrated H_2SO_4 solution. 100 mL solution was measured from the beaker and poured into a 125 mL conical flask. The sample was continuously mixed at 250 rpm at room temperature for 5 minutes. Fenton reaction was initiated by sequential addition of the required amounts $FeSO_4$ and H_2O_2 solution. Initiation of Fenton reaction time was by the addition of the first required amount of H_2O_2 to the reaction mixture. The mixture was continuously shaken using an orbital shaker. At the end of the reaction time, pH of reaction mixtures was raised to 10, followed by determination of COD and TOC for supernatants. PAHs analyses were conducted for raw produced water sample and sample treated under optimum operating conditions. Samples were extracted following method SW-846 Method 3510 C (Separatory Funnel Liquid-Liquid Extraction) using dichloromethane as solvent and dehydrated using anhydrous sodium sulphate for determination of PAHs concentration by gas chromatography-mass spectroscopy (GC-MS).

RESULTS AND DISCUSSION

Effect of reaction time

As shown in Figure 1, at reaction time of 30, 60, 90, 120 and 150 min, the COD removal efficiency was 29.0, 42.4, 47.3, 51.3 and 55.0% respectively. At 180 min and beyond, the COD removal efficiency remained constant at 58.8%; indicating no further degradation of organic matter.

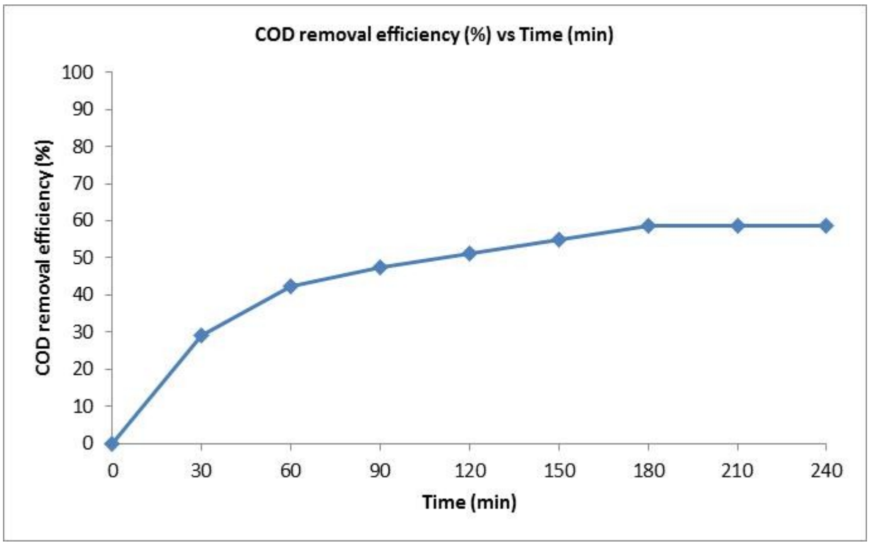

Figure 1. Effect of Fenton's reaction time on COD removal efficiency (H_2O_2=1.5mL, Fe^{2+}=0.5g, pH=7.92, T=298K)

Effect of pH, H_2O_2 dose and Fe dose

Following similar procedures as above, optimum pH, H_2O_2 dose and Fe dose were obtained as 3, 1.5mL and 0.5g respectively (results not shown). The pH result is corresponds to the 2-4 range typically reported in literature. Excess doses of H_2O_2 or Fe interferes with the chemistry of the reation mixture and results in lowered organic matter removal. Similar effects of operational variables were observed on TOC of the samples. The maximum TOC and COD removal efficiencies obtained at optimum conditions were 77 and 83% respectively.

Effect of Fenton Treatment on PAHs

Figure 2 shows the concentrations of PAHs in the treated sample under optimized conditions of pH 3, H_2O_2 1.5mL, $FeSO_4$ 0.5g and reaction time 180 min. Total PAHs removal efficiency was 72.5%. LMW-PAHs removal efficiency was higher (81.8%) compared to that of HMW-PAHs (69.1%). Owing to difference in physico-chemical properties of each compound, their degree of degradation varies. In general, PAH solubility in water decreases as the molecular weight increases. In other word, molecular weights of PAHs compounds are inversely proportional to their solubility (Pampanin and Sydnes, 2013) and would therefore affect their degradation.

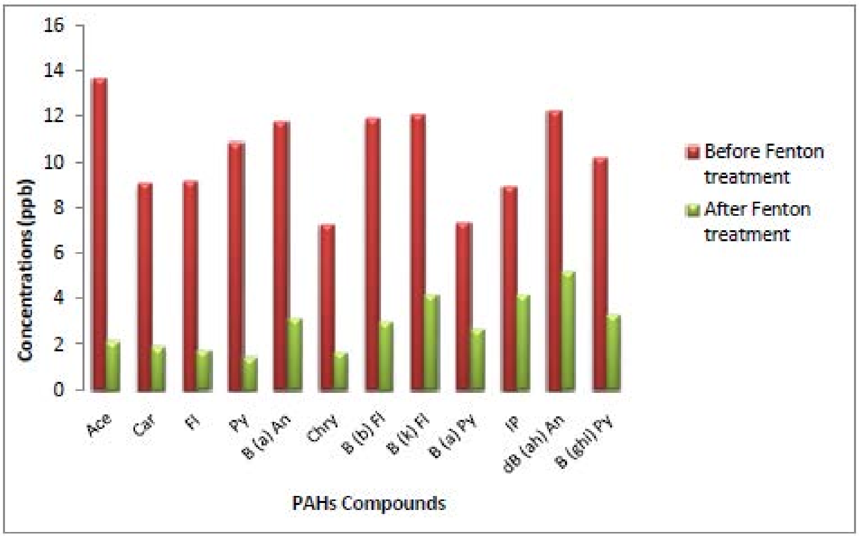

Figure 2. PAHs concentration in produced water before and after Fenton treatment (Fe^{2+}=0.5g, H_2O_2=1.5mL, pH=7.92, reaction time = 180 min, and T=298K)

CONCLUSIONS

Advanced oxidation process using Fenton reagent was shown to be effective for degradation of organic matter including PAHs. The main factors affecting the performance of the H_2O_2/Fe^{2+} process were H_2O_2 and Fe^{2+} dosages, pH and reaction time. Fenton process can mineralise organic carcinogenic compounds (PAHs) in aqueous solution.

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Innovative case studies

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(I9) Water reclamation and conservation in Greece: legal framework and public perception

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Abstract

Part of the research, presented in this paper, deals with social and economic aspects and public perception related to in-house water conservation measures and grey water technologies. On the basis of economical analysis it was concluded that a 40-60% reduction in water consumption can be achieved through the adoption of domestic water saving devices, at a cost of 300-1600 euros per household, with a recovery period of 1-6 years. Furthermore, on the basis of the results of a survey, involving replies to an extensive questionnaire, by more than 800 household representatives, interesting conclusions were drawn regarding familiarity with the issue, attitudes of different sectors of the population (age groups, income level, spatial distribution etc), main challenges and possibilities, major concerns.

Keywords

Hydropolis; urban water management; water conservation; grey water; public perception

THE NEED FOR EFFICIENT WATER MANAGEMENT AND THE POSSIBILITIES FOR IN HOUSE CONSERVATION

According to evidence from the European Environmental Agency (EEA, 2011) the Water Exploitation Index (WEI) for Greece is, on average, around 15%. This index represents the percentage of the available renewable water resources that are consumed in a year. Percentages below 20% are considered safe, while above 40% one faces drought conditions. The Index for Greece is lower than those of several Mediterranean countries, such as Cyprus, Spain or Italy with indices above the safe figure of 20%. Nevertheless, it has been rightly claimed that an overall index on a country level can be misleading, as it does not reflect possible strong spatial variations. For example it should be stressed that much higher WEIs can be found over extended River Basin Districts, such as the Thessaly District in central Greece, with an index to the order of 40-50%. Furthermore, the anticipated effects of the climate change, leading to higher future indices should not be overlooked. Finally, the Water Footprint of Greece, at is one of the highest in the world, second only to USA. There is therefore enough evidence to support firm action towards more efficient management strategies and conservation practices.

Irrigation water and in general water for agricultural practices represents in many Mediterranean countries the major consumer, with percentages as high as 70-80%. Greece is far from deviating, with a percentage of 86-87%. At first glance it is profound that major savings can and must be achieved in this sector, through sound and water efficient irrigation practices and leakage and/or evaporation control measures. Undoubtedly, this is a valid argument for the overall picture, at a country level. However, the benefits of urban and more specifically domestic water conservation can be very significant at specific local or river district levels, with a pronounced contribution of the urban/domestic section to the overall water consumption. Such areas include many of the Aegean islands but also significantly, the two metropolitan areas of Athens and Thessaloniki. In the greater Athens area domestic consumption represents 80% of the total, a figure approaching 90% if other urban uses are included.

LEGISLATIVE FRAMEWORK, CONSIDERATIONS AND INITIATIVES

The EU Water Framework Directive provides the reference point for the rational management and exploitation of precious water resources (2000/60/EC). The WFD introduces for the first time the concept of the full cost recovery of water services by all users. The 2007 Communication from the Commission entitled “Addressing the challenge of water scarcity and droughts" considers regulatory measures to save water in buildings. The "Blueprint to safeguard Europe’s waters" (2012) is an attempt to meet the European Union's policy about old and new challenges concerning water resources. Among others, the Blueprint argues that there is a lack of additional legislation required for the sustainable management of water resources. With the strategy "Europe 2020", the European Union has set targets to be achieved by 2020, involving the efficient use of resources. The "Roadmap to a Resource *Efficient Europe*" is one of the key elements of the "Europe 2020" strategy. The Roadmap, approved by the European Commission in September 2011, sets out a framework for the design and implementation of future actions. The Roadmap states that a “Communication on Sustainable Buildings” should be presented. Although no concrete actions on how to save water at home are provided, the “Communication on Sustainable Buildings” in 2013 , proposes actions to improve resource efficiency in construction, apart from energy efficiency.

The Eco-Design Directive (2009/125/EC) sets the context for mandatory requirements for energy using products and energy related products sold in all Member States. It covers more than 40 product groups, including products that use water, such as washing machines and dishwashers. The Regulation 1015/2010 on eco-design requirements for household washing machines determines performance criteria, including water consumption. The Regulation 1016/2010 on eco-design requirements for household dishwashers also includes benchmarks for water consumption. So far, these regulations have not been incorporated into our national legislation.

In Greece, the harmonization with the provisions of the WFD was performed by Law (3199) in 2003 and by a supplementary Presidential Decree (51/2007). Other legislation at national level include the presidential decree for rainwater tanks on islands, where according to the ministerial decision No. PD 05/10/2002 (Government Gazette 402/D/2002), the construction of rainwater tanks at new homes on islands is obligatory. In the New Building Regulations (Law No. 4067, 2012) there is a provision concerning the installation of water saving equipment in new residences, equipment which will be established by a decision of the Minister of Environment, Energy and Climate Change. In addition, the ministry of Environment, Energy and Climate Change through the Special Secretariat of Water considers (since 2011) the preparation and implementation of an Institutional Framework and a Program of Measures for household water conservation. The study, conducted to support this action, showed that simple interventions to equip a household can achieve significant water savings. Several institutional, regulatory and dissemination measures were proposed.

Regulations, programs and voluntary standards

Beyond the legislative acts of the European Union and related economic tools, saving water at home can be promoted through public awareness. The actions that can help raise awareness are campaigns, the labeling of products and technologies that offer efficient use of water, education of the society - students - teachers on matters of water, as well as acts of demonstration. Examples of such practices include: a) the mandatory labeling system WELS, applied in Australia since 2006. WELS is assigned to plumbing products, shower heads, tap equipment, equipment for toilets, washing machines, dishwashers. b) the obligatory “Code for Sustainable Homes” applied in the United Kingdom since 2008, according to which houses are classified into 6 levels, with level 6 referring to the most efficient and sustainable house, while level 3 is incorporated in the building Regulation.

COST BENEFIT CONSIDERATIONS

The economic analysis performed during the work was based on two scenarios. In the first scenario, there is no technology or product that offers water savings. In the second scenario old products are replaced with new which promote the efficient use of water (Table 1). The aim of the analysis was to calculate the payback period time of the investment in order to highlight whether there are incentives for consumers to replace existing equipment with new equipment that will deliver water savings, and to show the potential amount of water savings by the use of such new products and technologies. The analysis was based on the scaled tariff for water and sanitation services of the Water and Sewage Corporations of Athens (EYDAP) and Thessaloniki (EYATH).

Table 1. Characteristics of water saving devices used for the economical comparisons.

Product	Conventional	Water Saving	% Reduction
Shower	14 l/min	7,0 l/min	50,00 %
Tap	12 l/min	6,5 l/min	65,10 %
Toilet	10 l/use	4-6,0 l/use	56,70 %
Dishwasher	114 l/day	9,0 l/day	93,75 %
Washing machine	200 l/use	43,0 l/use	78,50 %

The main conclusion is that if all proposed products are bought and implemented (shower head, toilet, faucets, dishwasher and washing machine), the initial cost for a single household will be 1580€. However, the investment is still financially attractive with a payback period of 6 years. The water saving potential can be up to 61%. Namely, with an assumed water consumption for the first scenario of 208 liters per person per day, in the second scenario it is reduced to 81 liters per person per day. A more modest reduction, of about 40% can be achieved if dishwashers and washing machines are excluded. However, in this case the investment cost for a household is dramatically reduced to less than 300€ and the payback period to one year.

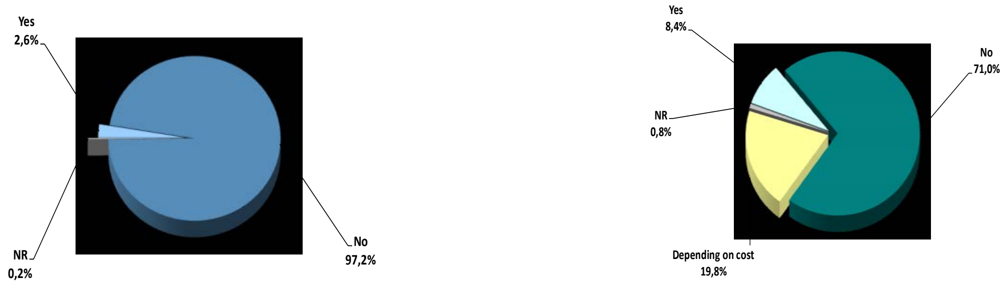
Furthermore, a separate analysis was conducted, to investigate the implementation of a gray water system in a residence. The findings were not equally encouraging. It seems that at 4000-5000€ per household, the installation of a grey water system is not attractive, at least without additional incentives for individual houses. Due to economies of scale, the investment for single buildings and individual facilities is higher than the investment for properties with several inhabitants and collective facilities.

Finally, the economic analyses for two cities (Athens and Thessaloniki) were compared for possible effects due to the different pricing regimes, but despite the slightly higher cost of the water in Thessaloniki, the main conclusions hold for both cases.

PUBLIC PERCEPTION

A survey aiming to investigate public perception regarding water issues and more specifically conservation and the use of alternative sources, such as grey water was conducted, involving a questionnaire of 118 variables with single and multiple questions. Following a pilot application in 50 households, a full scale investigation was performed, involving 800 households of the Greater Athens area and Aegean islands, during June and July 2013. The main findings can be summarized as follows.

The lack of familiarity with the relevant terminology, such as “grey water”, was evident, since 97% of the involved households were not familiar with the term, and even among the remaining 3% one third had the wrong conception (Figure 1a). Anyhow households in the island tended to be more familiarized, possibly due to traditional practices of rain water harvesting. Upon explanation and clarification, about 30% (mostly younger ages and higher incomes) indicated an unreserved or conditional (on cost considerations) willingness for the recycle possibilities offered (Figure 1b). Familiarity with high tech applications in general was positively correlated with the willingness to adopt such recycle technologies.



(a) (b)

Figure1. Familiarity with the concept of grey water (a) and willingness to adopt recycle possibilities (b)

A fairly high percentage (55%) believe that are adequately informed about environmental problems, with air pollution, energy conservation and solid waste management figuring among the main concerns (generally about 30-60% as top priorities). A lower percentage (10-14%) is concerned with water scarcity problems and climate change. Involvement with energy saving practices and solid recycle figures high (65-90%), with very low figures (less than 10%) related to water conservation practices. The top issues raised include health, public awareness and cost factors. More acceptable sources include desalinated and rain water (40-46%) with grey water and treated urban wastewater being less attractive (25-26%). Possible uses include washing clothes and showering (50-52%), tooth brushing and cooking (32-37% and even drinking (21%).

AKNOWLEDGEMENTS

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(I10) Optimizing the management of water services through inter-organizational network of public-owned water utilities: the case of VIVERACQUA in Veneto Region

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Abstract

VIVERAQUA is a publicly held company characterized by a stable not-for-profit collaboration among the Managers of the Integrated Water Services of the Region of Veneto (around 2,800,000 inhabitants in 437 municipalities).

The objectives of the company are to create synergies to jointly manage certain stages of business, the optimization and the reduction of operating costs, the improvement of the supplied service and the reduction of the costs for final users.

All the activities are developed using the establishment of Specific Offices with permanent technical personnel, Working Groups with a temporary character or by launching Ad-hoc projects.

VIVERACQUA represents an innovative bottom-up Veneto model for public management of water services, stretched, from one side, to maintain efficiency and relation with the territory and, from the other, to develop competitive capabilities typical for large companies.

Keywords

inter-organizational network; Viveracqua; Integrated Water Services; innovative.

THE START UP

The premises

Since 2009 some integrated water services company in the Veneto Region, created a new form of occasional cooperation, aimed at reducing costs for the acquisition of input resources. This cooperation was followed by a series of other economic and political relations of exchange, which soon promoted an inter organizational polycentric network between companies.

The constitution

Viveracqua scarl was formally constituted in 2011 as a consortium company with all public capital, in order to establish a stable collaboration between the integrated water services companies.

Its strengths are cost synergies, regional and national recognition and access to competitive opportunities normally reserved for large-sized companies. Viveracqua creates synergies for joint management of certain functions, to optimize and reduce operating costs, to improve the service, all with the goal of reducing the cost and increasing quality for users of water service.

The strategic objectives

The strategic goals are the affirmation of the model "in-house" in the water services management with innovative and highly territorial, strengthening the process of "aggregation operation" between the company and the achievement of the best performances of the national reference for the construction investment, compared to standard costs and staff productivity. Viveracqua aims to be a participant in the socio-economic recovery in the Veneto, a successful case in the "make network system" for engine and attractiveness to investors.

Method of work

All activities are developed with the use of one or more of the following operating modes:

- Permanent Constitution of internal functions to Viveracqua: to make the activities of some staff functions through the allocation of human resources full time;
- Creation of permanent working groups: to make the activities of some territorial functions (typically distributed) through collaboration between the resources of each company;
- Ad hoc projects: to make activities of specific projects using “external project management “.

ACTIVITIES

Activities undertaken

In the first three years of his life, Viveracqua have been undertaken the following activities.

Central purchasing stable for supplies and services

Viveracqua started a centralized and shared management of the procurement. It started a consolidated comparison of purchasing departments of each company to converge on common procedures and buying habits. It prepared also a common IT platform for the management of tenders and suppliers.

Health and safety at work

Viveracqua shared ways of organizing work and response to regulatory requirements, providing mutual and common areas for improvement and consistency between the individual companies.

It promoted an exchanged experiences to obtain benefit in terms of selection and testing of products such as personal protective equipment, working equipment and etc…

It started joint training programs on specific risks of the water services companies (eg access to confined spaces, biohazard, asbestos cement in the water pipe networks, etc..).

It established a group of security engineers, knowledgeable and equipped with direct experience in the multi-utility field, and they now conduct internal audits to evaluate the Management Systems Safety at Work (OHSAS 18001).

It started a new project to accredit Viveracqua at the Regional Responsible Authority as subject trainer, with the intent to propose and implement training measures financed with public funds, according to precise quality standards and minimum requirements.

Coordination office

Were initiated communal tables for analysis from the point of view of many legal regulations, including those relating to inconferibilità and incompatibility of positions in the public administration, the limits of the assumptions / Stability Pact, the constraints of personnel costs in society "in-house" bargaining 2nd level, regulation of the provision for New Investments, administrative transparency, spending review.

Regulation

Viveracqua set up a working group devoted to the analysis of the billing activities and in general the relationship with customers and the AEEG Authority (especially about the AEEG various consultation activities).

It studied the obligations resulting from the application of EU rules relating to banking domiciliation, the metrological checks on water meters, etc..

Hydrobond

Viveracqua is currently developing a project for raising funds to make the planned works in the programming documents of investments (Area Plan) of its members. The key objectives are to:

- Create a “task system" where elements of mutuality on the members give the financial dimensions that will attract the interest of institutional investors that have a specific focus in the field (like as

European Bank of Investments);
- Carry out the first step of funding for italian water sector companies through an “integrated system";
- Create a replicable financial structure with the involvement of institutional investors such as supranational and possibly insurance companies, pension funds and infrastructure funds;
- Provide alternative access to funds where there is currently a very hight difficult to obtain funds through other channels;
- Diversify the sources of funding of each shareholder.

Research and development

Viveracqua launched the following initiatives:
- join Aqua Publica, the International Association of water service public companies, which aims to bring to the attention of the offices of the EU on the needs for the public sector, and aims to access more effectively to funding from the European Community;
- analysis of initiatives and projects to present to the European public funding programs, with particular reference to the Horizon 2020 Water and Life +;
- promoting the formation of some of the resources of the individual companies through specific courses of Project Planning.

Planned Activities

Through the business plan scheduled for the next three years 2014/2017, Viveracqua aims to strengthen the cooperation already established between the individual companies and especially aims to strengthen the process of their "aggregation operations". Everything paying strong attention and commitment to activities typically transverse to all the companies and to large-scale projects, that would be well-approached only through an organizational dimension as important as that of Viveracqua. The main activities envisaged for this purpose is the establishment of permanent offices within Viveracqua such as Secretariat, Regulatory Affairs, Central Client ..., the organization of working groups stable for the Coordination of communication, dialogue jointly with the authorities and supervisory bodies, the development of training activities ..., the creation of ad hoc projects such as a new Call Center, a web portal based on social networks ...

VIVERACQUA: THE INSTITUTIONAL ROLE

Viveracqua is increasingly crediting as a serious and representative interlocutor with the institutional bodies of primary importance, for example:
- AEEGSI (Authority for Electricity Gas and Water Supply System), which is an independent body with the task of protecting the interests of consumers and to promote competition, efficiency and deployment of services with adequate levels of quality through the activity of regulation and control;
- FEDERUTILITY: which is the federation that brings together the local utility companies operating in the Electricity, Gas and Water;
- VENETO REGION;
- EUROPEAN INSTITUTIONS.

VIVERACQUA: CLOSING REMARKS

The experience of Viveracqua represents a model of “growth from below" in the water services, aimed on the one hand to maintain efficiency and link with the local territory, and the other hand to ensure the maturation of the capacity of competition typical of the large companies.

(I11) Project and realization of automation for the management of not manned wastewater treatment plants

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Abstract

Tea Acque srl society manages water cycle in 38 municipalities in Mantua territory, with 72 wastewater treatment plants with potentiality between 100,000 and 100 PE, spread on an extended territory.

Most part of plants are not manned and that implies two essential consequences: the first is the inadequate knowledge of characteristics of the single wastewater processes and the second is the way of intervention on different equipment made only depending on instantaneous conditions found during the inspection visits from operation staff in prearranged hours and days. In addiction to that we have to bear in mind that the organic charge actually treated from a plant and the characteristics of wastewater can be very different from a plant to an other depending on the afferent drainage system and on the type of users connected, changing significantly in load and composition in different daily time slot and in different periods of the year; an other important factor to consider is that a lot of plants have been correctly planned on the base of inlet ideal charged and for consequence they often result oversized. On these requirements Tea Acque srl based a new approach for wastewater treatment plants management that consists of:

- Installation of probes for continuous measure of principal parameters;
- Automation of different devices made on parameters measured on site;
- Communication on real time of measures, parameters, and alarms to have a remote control;
- Analysis and reporting of measures and working parameters through dedicated software able to alert operative staff automatically in case of any type of irregularity

All operation and regulation logics are studied from Tea Acque staff ad hoc for each single plant: so we can constantly modify logic depending on requirements of single plant changing even in different period of time. So we have a dynamic management of plant using an open system that we can modify in every moment and this is the true innovation of this approach.

Keywords

Wastewater treatment, probes, open system

INTRODUCTION

In this study, we show the case of a 8,000 PE potential plant, where we applied the new approach topic of this paper.

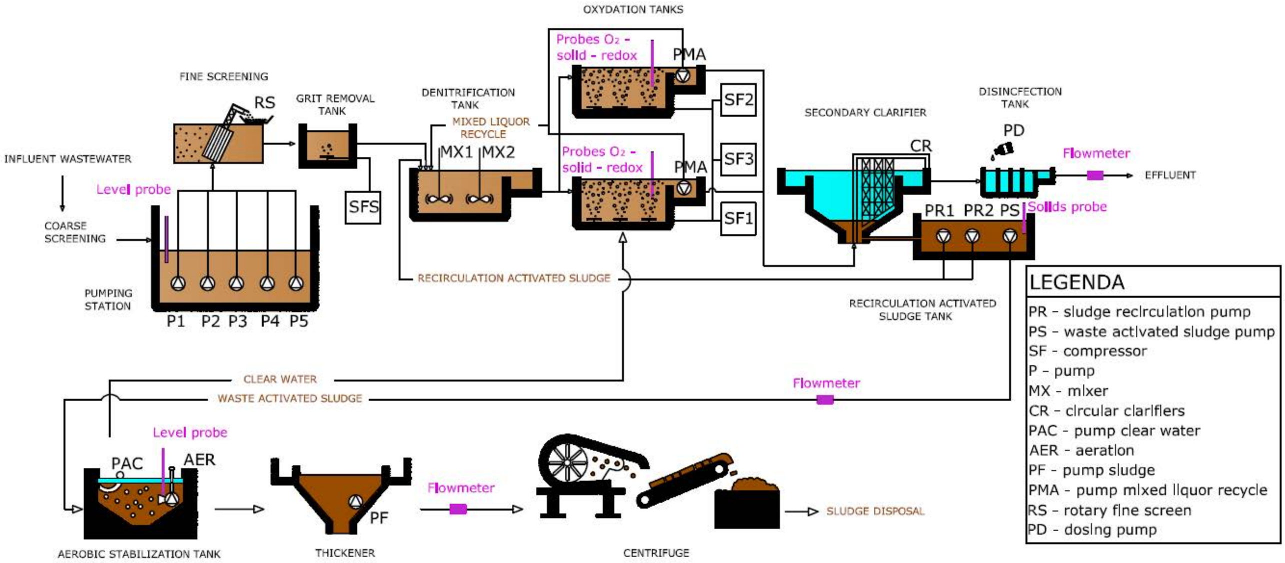
The plant, in service to 5,600 people, receives residential sewage and a low percentage of industrial sewage from a mixed sewer. It is structured like a classic wastewater treatment civil plant with the following units: coarse screening, pumping station, fine screening, denitrification tank, two oxidation tanks, secondary clarifier, disinfection tank, and, about the activated sludge an aerobic stabilization tank, a thickener and a centrifuge for sludge dewatering.

In this study we faced the following problems:

- control and management of operation of all electromechanical equipment installed, by monitoring continuously the main parameters such as electrical input, minutes of activation, state changes;
- check of the main operating parameters such as concentration of oxygen, solid concentration and redox value in oxidation tank, check of inlet flow rates, of flow to the centrifuge sludge dewatering, of level in pumping station and in the digestion tank;

- view in real-time from the control centre of all parameters measured on site, through graphs and tables, changing parameters and set points of different units at any time from any location, processing and reporting data collected;
- setting alarm thresholds that trigger alert messages on the operation of various devices (alarm absorption, high level alarm, lack flow alarm, etc ...) so that all irregular events are identified and communicated by remote;
- opportunity to provide a support to the management of system to staff working on site

MATHERIALS AND METHODS



The structure of wastewater treatment plant and its electromechanical equipment have not been changed, but system has been implemented simply with equipment shown in figure and listed below:

- two level probes, one in pumping station and one in digestion tank,
- two probes to measure oxygen, two probes to measure solids, two probes to measure redox potential in two oxidation tanks,
- one probe to measure solids in activated sludge recirculation tank,
- one flow meter in the pipeline of waste activated sludge,
- one flow meter in the pipeline of the centrifuge.

The main electromechanical equipment has been fitted with amperometric value for the detection of electrical input, and auxiliary contacts to detect changes of state.

The automation was carried out on a new PLC purchased ad-hoc and considered suitable by Tea Acque staff because it has the following features:

- complete with advanced Web interface to provide valuable support to operational staff,
- multi-protocol to act as a gateway with the instrumentation on site,
- complete with multiple ports and driver communication to the control centre.

RESULTS AND DISCUSSION

Operating mode before implementation

The control of different devices is fixed, not connected to the quality and quantity of the inlet wastewater; in particular:

Pumping station: control of pumps is made by dedicated starting and stopping floats. Pumps can be deactivated to avoid excessive flow rate only by definitely turning off; in this case plant has uncontrolled increase of flow rate.

Grit removal tank: compressor works continuously.

Oxidation tank: compressors work continuously, they are controlled by two control oxygen units (one in each different oxidation tank) changing between two set point inside inverters (working frequency at 30 hertz or 50 hertz).
Denitrification tank: mixers work continuously
Activated sludge pumping station: pumps work continuously
Thikener: all the operations can be conducted only by manual action based on instantaneous values of sludge concentration in oxidation tank.

Operating mode after implementation

The implementation consists of automation and remote control of the entire process through installation of a new electrical panel controlled by PLC, router UMTS for the transmission data phase, energy analyzer and probes listed above.

The software inside PLC has been entirely studied by Tea Acque staff, where process specific features for wastewater treatment plants were introduced, using a continuous communication with different measure equipments on site, turning the operation from static to dynamic. We have to underline that the quantity of wastewater treated and quality of water discharged are the same between the two different modes; a great room for improvement is in the better management of the plant and of malfunctioning and in significant energy saving observed.

Let's go to analyze what we made on the different sections of plant:

Pumping station: to guarantee a continuous flow rate without excessive variations, we installed an ultrasonic level probe inside pumping tank, which by regulation on PLC, allows to the submergible pumps activation and deactivation steps, following a rule that provides at most two pumps at the same time. With this regulation and with values coming from remote control, it was possible to control the pumping station so that one pump stay on for almost all the time while the other starts only following level increase.

Grit removal tank: compressor starts only if in presence of flow rate: when all pumps are off even compressor is disabled to avoid useless consumption

Oxidation tank: we provide an intermittent aeration to keep oxygen values in oxidation tank, with start and stop on base of oxygen measured value, providing a function to avoid the sedimentation of sludge in longest period. Compressors operation is controlled by two inverter with frequency between 35 and 50 hertz. From initial checks we can estimate that compressors can be completely off for 3,500 hours for year while before implementation compressors were continuously on.

Denitrification tank: since mixers ensure the flow of solids to the oxidation tanks, it was possible to adjust their operation through work-breaks as a result of the installation of solid probes in basins. The thresholds set can be modified and monitored at any time and allow currently working time of 6 minutes and pause times of 8 minutes to an estimated annual savings of at least 25,000 kWh per mixer.

Recirculation activated sludge tank: as for mixers also has been set up for recirculation operation a work-breaks. In this case breaks will be variable and adjusted according to the inlet flow. In case of high flow rates will be possible the simultaneous operation of both pumps to guarantee the conditions of sufficient recirculation sludge. By the trend we can estimate a savings of about 6,000 kWh per year for each pump.

Waste sludge thickening tank: solid probes in recirculation activated sludge tank and level measurement in thickening tank allow to operate automatically the waste activated sludge pump. This automatic function ensures the correct amount of activated sludge in the whole cycle of biological treatment and even a significant improvement of operating conditions for the process. Another valuable advantage of the automatic management is that it is no longer required the presence of an operator to perform this operation; the operator presence is indispensable only for the start of the dehydration step.

Through remote control all information is visible and editable directly from office.

CONCLUSIONS

The indicators of improvement obtained following the implementation carried out on the system, can be summarized as follows:

Decrease hours of management: being able to remotely control the operation of almost all the devices present on the system, and in particular being able to automatically perform operations that relate to the management of waste activated sludge and having all data that relate to the operation and breaks all the equipment, the hours due to management are reduced to manual operations that have to be conducted on the system.

Improving management of interventions to fault: through the visualization of trends of all parameters, measured on site and processed by the software and especially by sending alarms, we are able to keep under control the operation of all equipment systems and to provide immediate action to correct any deficiencies.

Energy savings: an analysis of energy costs for first months of 2013, the specific energy consumption of the system before implementation was 0.63 kWh/m³ of treated water, while in the early months of implementation (since August 2013), the specific energy consumption of the system is 0.40 kWh/m³ of treated water. This reduction means a monthly savings of approximately 1,200 €. The savings will allow a return of investment for deployment in less than three years. We are also considering the possibility of acquiring TEE to further reduce the payback period.

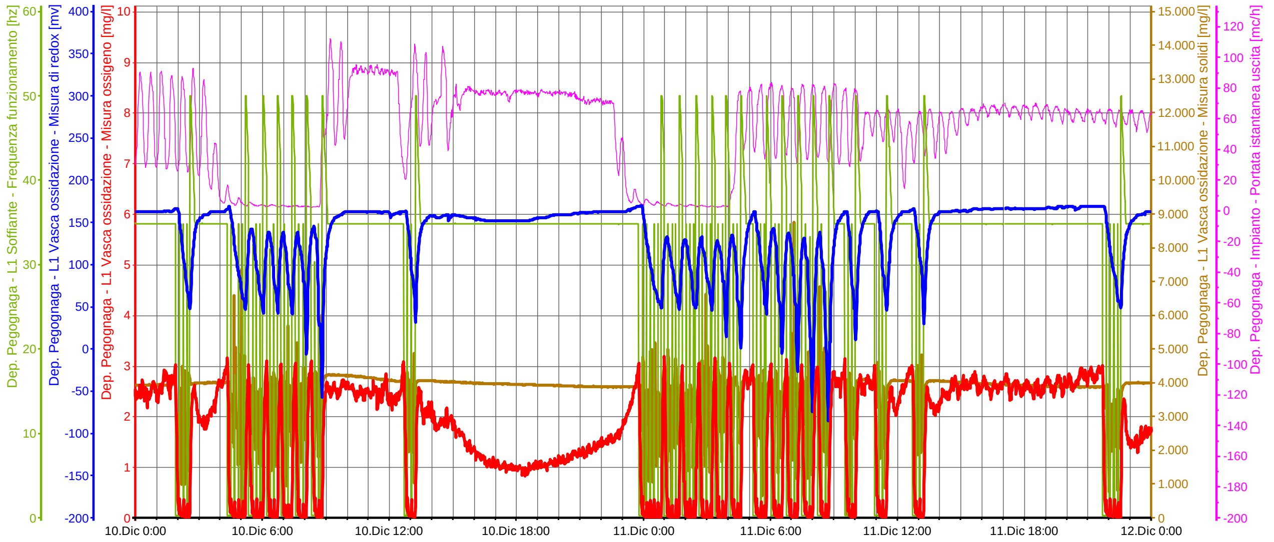


Figure 2. Value of principal parameters in oxydation tank

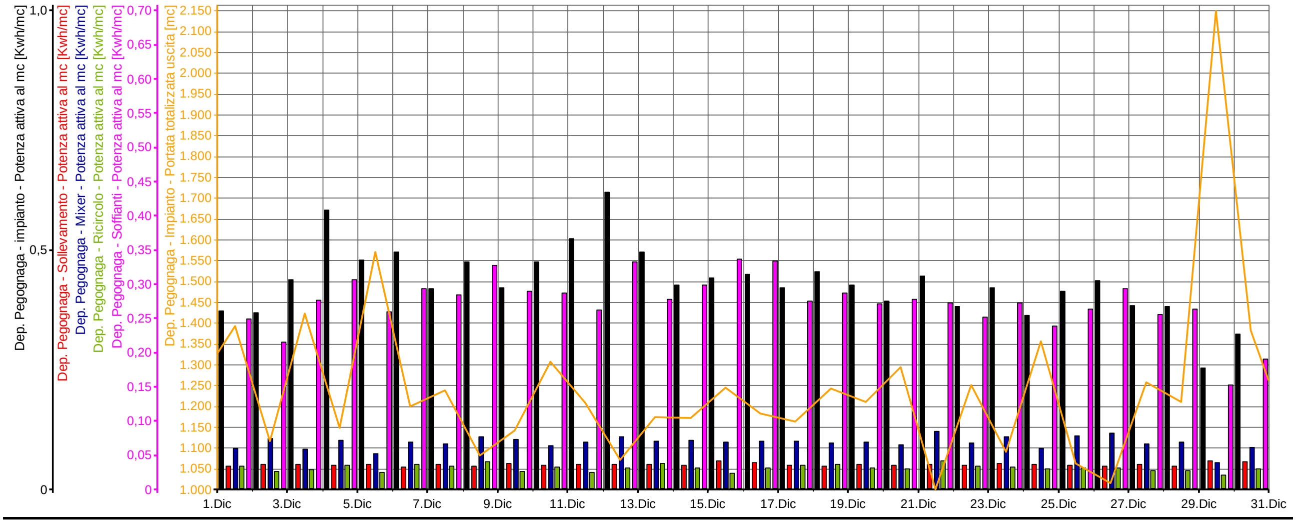


Figure 3. Specific energy consumption

(I12) Model-Based Methodology for Plantwide Optimization of WWTPs: A Case Study

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Abstract

This paper presents the application of a model-based methodology for improved understanding of the tight interplay between effluent quality, energy use, and fugitive emissions in WWTPs. Dynamic models inspired from the Benchmark Simulation Model No. 2 (BSM2) are developed and calibrated in an objective to predict the performance of a conventional activated sludge plant owned and operated by Sydney Water, Australia. A scenario-based approach is first applied to quantify the effect of key process variables under steady-state operation. An assessment of the operational strategy resulting in the least possible energy consumption at different nutrient discharge levels is also carried outthrough the application of systematic optimization techniques based on mathematical programming.

This improved understanding of the relationship between nutrient removal, energy use and emissions will feed into discussions with environmental regulators regarding nutrient discharge licensing.

Keywords
Modelling; plantwide simulation; effluent quality; energy consumption; operational strategy; retrofit; optimization

INTRODUCTION

Among the alternatives for the sewage industry to reduce their energy consumption without compromising effluent quality, improving operational and process control strategies holds much promise. These strategies may be particularly useful for energy intensive processes such as activated sludge aeration, which can account for 45-75% of a plant's energy expenditure [1]. Overall, it is estimated that energy consumption of most wastewater treatment plants (WWTPs) could be reduced by 10-40% [2]. Nonetheless, WWTPs are comprised of a large number of treatment and separation units, which involve a great variety of processes acting on different time scales and interacting with each other via recycling loops. Failure to account for these interactions, e.g. by optimizing in a unit-wise manner, may not lead to the largest possible improvements and can even be detrimental overall [3]. In this context, developing effective operational strategies can defy engineering intuition, and plant-wide simulation models, such as BSM2 [4], have started playing an increasingly important role [3, 5].

The main objective of this work is the application of a model-based methodology to provide a better understanding of the impacts of changing effluent quality targets on plant-wide energy use and fugitive emissions. Dynamic models based on commercial simulators or BSM2 are developed and calibrated in an objective to predict the performance of an activated sludge plant with sludge treatment owned and operated by Sydney Water. A scenario-based approach is first applied to quantify the effect of key process variables under steady-state conditions. An assessment of the operational strategy resulting in the least possible energy consumption at different nutrient discharge levels is then carried out through the application of systematic optimization techniques based on mathematical programming. This improved understanding of the relationship between energy use and nutrient removal will feed into discussions with environmental regulators regarding nutrient discharge licensing.

METHODOLOGY

The WWTP under investigation is a tertiary plant owned and operated by Sydney Water. The general layout is shown on Fig. 1. It operates two parallel primary/secondary treatment stages followed by a common tertiary treatment for nitrogen and phosphorus removal, while the secondary sludge is digested aerobically before disposal. The nutrient discharge limits currently in application are 5 mg L ^{1}, 45 mg L ^{1} and 5 mg L ^{1} for ammonia, total nitrogen and total phosphorus, respectively. This WWTP is flexible enough to explore a wide range of scenarios and presents excellent potential for optimization.

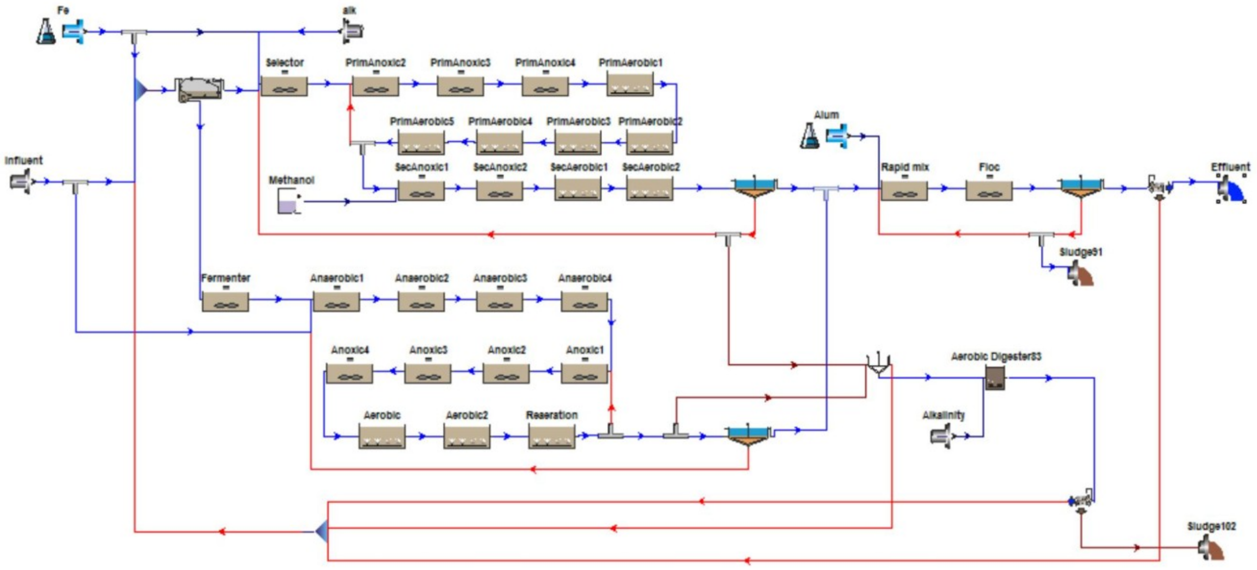

Figure 1: Activated sludge plant layout

Two modelling platforms have been considered, namely BioWin and gPROMS. BioWin is commonly used in the wastewater industry as a process analysis tool and to design or upgrade WWTPs. It features an active interface window for building WWTP flowsheets and allows analysis of different operational strategies and adjustment of the model parameters. gPROMS, developed by Process Sys-tem Enterprise Ltd, is an equation-oriented process simulator and features powerful process system analysis and optimization tools, both for steady-state and dynamic models. The unit models imple-mented in gPROMS are based on BSM2 and allow prediction of the energy consumption of the plant in addition to the effluent quality.

RESULTS AND DISCUSSION

A preliminary model calibration and validation has been conducted for both platforms using a com-bination of routine and non-routine monitoring data. The calibrated models are then simulated and optimised under various scenarios to quantify the links between energy use and effluent quality.

Model Fitting

The calibration has been conducted in an objective to capture the major trends in the plant, focussing primarily on mass conservation and flow splitting. In a first step, liquid and solid flows in the primary sedimentation tanks, DAF units, sludge dewatering units, tertiary clarifiers and dual media filters have been calibrated based on data from a 2-week non-routine monitoring campaign using the general-purpose simulator gPROMS, and validated with 12 months of data (April 2012-April 2013) from Sydney

Water’s data management system. In a second step, the bioreactors have been calibrated by adjusting a minimal number of kinetic parameters from their default values—based on sensitivity analysis—in order for the predictions to be in good agreement with the primary, secondary and tertiary concentrations from the non-routine monitoring campaign. These simulation results have been cross-validated in the wastewater simulator BIOWIN. Some comparison results are reported in Table 1 for the tertiary effluent, showing a good agreement between the measured and calibrated values.

Table 1: Comparison between averaged measurements during the non-routine monitoring campaign and predictions for both simulation platforms (after calibration).

	Measurements	BioWin	gPROMS
NH_4 N (mg$_N$ L^{1})	0.02	0.08	0.09
NO_3 N (mg$_N$ L^{1})	4.3	4.5	4.8
PO_4 P (mg$_P$ L^{1})	0.02	0.04	0.04
COD (mg L^{1})	34	31	30

Quantitative Analysis and Optimization

A simulation-based approach has been used to investigate two main aspects: (i) up to what point the effluent quality, especially nitrates, can be improved without causing a large increase in power consumption; and conversely, (ii) how large a reduction in power consumption can be obtained without significantly impairing the effluent quality or increasing fugitive emissions such as N_2O. A large number of scenarios have been investigated, which involve varying the influent split between both treatment stages, the separation efficiency in the primary sedimentation tanks, as well as the mixed-liquor recirculation (MLR) rate, the dissolved oxygen (DO) set-points and the sludge age in both stages. The results show a good potential for operational improvements, with large reductions in nitrate concentration in the tertiary effluent (down to 2-3 mg$_N$ L^{1}) being obtained by acting on the influent split, the primary sedimentation efficiency, and/or the MLR rate; see, for instance, Figure 2.

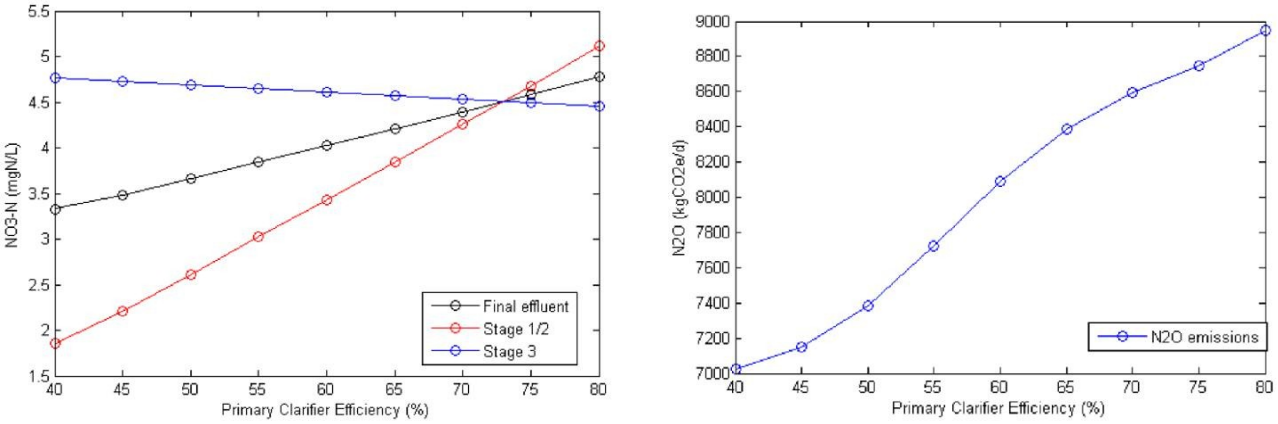

Figure 2: Nitrate concentration in secondary and tertiary effluents (left plot) and N_2O emissions (right plot) for different solids capture effciencies in the primary settler.

Quite expectedly, DO set-points have the largest influence in terms of power consumption, with a good potential for savings by decreasing the set-points. Nonetheless, too low a set-point can also cause a significant increase in fugitive emissions (N_2O) due to incomplete nitrification, as shown in Figure 3. These results illustrate well the tight interplay between energy consumption, effluent quality and fugitive emissions in this WWTP.Finally, Figure 4 presents a comparison of power consumption and emissions with respect to 4 scenar-ios that correspond to different levels of total nitrogen (TN) in the treated effluent: TN 5 mg_N L ^{1} corresponds to the current operation; TN 3 mg_N L ^{1} and TN 8 mg_N L ^{1} to an increased or decreased MLR rate in both stages, respectively. These results are to be compared with the scenario TN 0:3 mg_N L ^{1} corresponding to the implementation of a reverse-osmosis module.

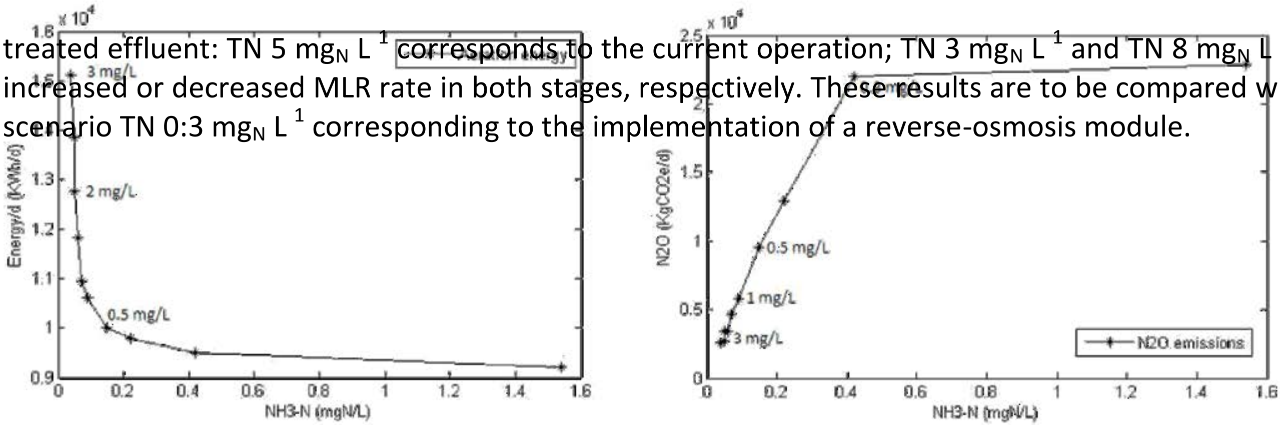

Figure 3: Power consumption (left plot) and N_2O emissions (right plot) as a function of the NH_3 N levels in the effluent at different DO set-points.

Given the good potential for effluent quality improvement and the high energetic penalty that would be incurred by a reverse-osmosis module, our on-going work aims at applying systematic, model-based opti-mization techniques to minimize the nu-trient content in the effluent. We con-sider operational improvements only, and we restrict the additional power consump-tion to be no greater than that of re-verse osmosis. These results will be presented at the EcoSTP'2014 confer-ence.

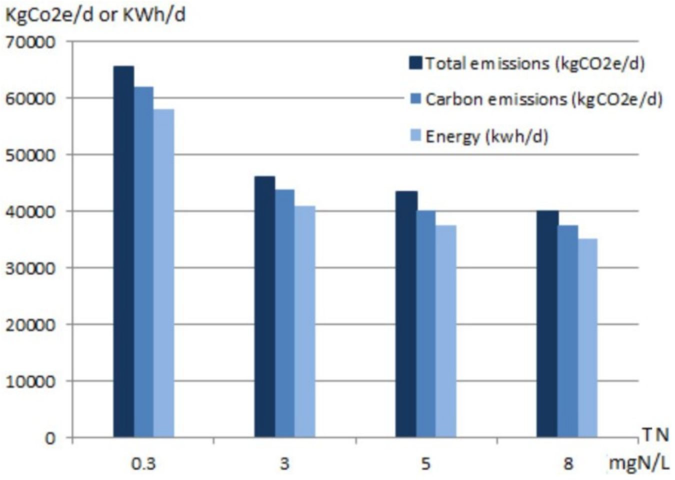

Figure 4: Comparison of plant updgrade scenarios.

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Poster Session

(1) Sewage Sludge And Fruit Wastes Anaerobic Co-digestion: Study Of The Co-substrate Change

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Abstract

The low organic load and the non-used capacity of the sewage sludge digesters are the driving forces behind its anaerobic co-digestion. The present article, where sewage sludge is co-digested with three different fruit waste (seasonality), focus on the transitory state when co-digestion starts, co-substrate is changed and co-digestion is stopped. Two lab-scale digesters were operated during 280 days, one as a reference and the other as co-digester. Co-digestion beginning led to an increase of the organic loading rate and biogas production together with a rise of the volatile fatty acids concentration, which recovered previous levels in 5 days. Co-substrate change did not disturb process stability; however, both biogas production and alkalinity varied depending on the fruit waste and sewage sludge characteristics. Finally, when co-digestion was stopped, the parameters conveyed, at different rates, to the values recorded in the reference digester.

Keywords

Anaerobic digestion, Co-digestion, Transitory state, Fruit waste, Sewage sludge

(2) Start-up of the Anammox Process in a two different Sequencing Batch Reactors

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Abstract

The Anammox process was developed and proposed as a technology for treating streams containing high concentration of inorganic nitrogen and low concentration of organic carbon. However due to very slow growth rate of the Anammox bacteria the start up of the process could be extremely long. This article shows the feasibility of successful fast start-up of single stage partial nitritation/Anammox process in the two laboratory scale Sequencing Batch Reactors (SBR). Both SBRs were treating real reject water with high ammonia concentration for over 100 days. The reactors differed in the feeding manner. The SBR-1 was fed with medium constantly whereas the SBR-2 was fed on the beginning of the cycle. In both reactors the nitrogen removal efficiency over 50% was reached within first two months of the reactor operation.

PCR-DGGE of total bacterial community and Anammox bacteria together with sequencing of the dominant Anammox genotypes were used as a tool for bacterial biocenoses analysis.

Keywords

Anammox start-up; nitrogen removal; reject water; SBR;

INTRODUCTION

Biological removal of high nitrogen concentrations from wastewater is very expensive when there is a lack of biodegradable organic carbon. Increasing requirements concerning nitrogen concentration in treated wastewater and increasing cost of the treatment exert a necessity of development a new method for biological nitrogen removal. The Anammox process was developed and proposed as a new technology for treating streams containing high concentration of ammonia nitrogen and low concentration of organic carbon. The main advantages of this process compared to the conventional nitrification/denitrification are: low sludge production, decrease of the aeration costs by almost 60% (only half of the ammonia is oxidized to nitrite in the nitritation process without further oxidation to nitrate), and no need for external organic carbon source addition (Anammox process) (Mulder, 2003; De Clippeleir et al., 2011). The low sludge production is another factor that contributes to the substantially lower operation costs compared to conventional denitrification systems. However, practical implementation of the Anammox process is still limited by its long start-up periods due to very low growth rates and biomass yields of the involved biomass (Fernandez et al., 2008) combined with the sensitivity of the microorganisms to inhibitory concentrations of some compounds that are often present in the industrial effluents.

The main goal of this study was to investigate the fast start-up of partial nitrification/Anammox process in two sequencing batch reactors (SBR) under different operation strategies.

METHODS

Both SBRs, volume of 10 L, were seeded with mixture of activated sludge and digested sludge from municipal wastewater treatment plant in Gliwice, Poland. They were working in the configuration for 3 cycles/day under temperature 25 ± 1.1ºC and 29.7 ± 1.1ºC for SBR-1 and SBR-2 respectively. Feeding medium was real reject water from municipal wastewater treatment plant in Gliwice, Poland. SBR-1 was fed with medium constantly for 6 hours 40 minutes, SBR-2 partially for 40 minutes.

The inflow to each reactor (2 ± 0.2 L/cycle) was provided by peristaltic pumps ISMATEC REGLODigitalMS (responsible for the inflow of wastewater and outflow of treated sewage). Additionally, the system was equipped with aeration and mixing devices and was controlled by electronic and analog timers. The standard physic-chemical parameters such as: ammonium, nitrite, nitrate nitrogen concentration, TSS, VSS, alkalinity, phosphates, COD, temperature, pH were measured once a week. NH_4^+-N, NO_2^--N, NO_3^--N as well as COD, phosphates and alkalinity was measured according to MERCK methodology on spectrophotometer Spectroquant NOVA320. For physical parameters (pH and temperature) the pH-meter WTW 340i with electrode was used. TSS and VSS were measured according to Standard Method APHA (1998). PCR-DGGE of total bacterial community and Anammox bacteria together with sequencing of the dominant Anammox genotypes were used as a tool for bacterial biocenoses analysis.

RESULTS AND CONCLUSIONS

During the first 30 days of experiment the nitrogen removal efficiency not exceeded 20% in both reactors. After 40 days of SBR-1 operation the nitrogen removal efficiency exceeded 60% whereas in the SBR-2 it took over 60 days. However, the nitrogen removal was much more stable in the SBR-2 reactor and it was possible to increase the nitrogen in the inflow to this reactor over 200 g m^{-3} whereas the in the SBR-1 the nitrogen concentration in the inflow was around 160 g m^{-3}. After the process start-up the average nitrogen removal efficiency was equal to 58.5 ± 10.9% and 79.7 ± 7.1 for SBR-1 and SBR – 2 respectively (Figure 1).

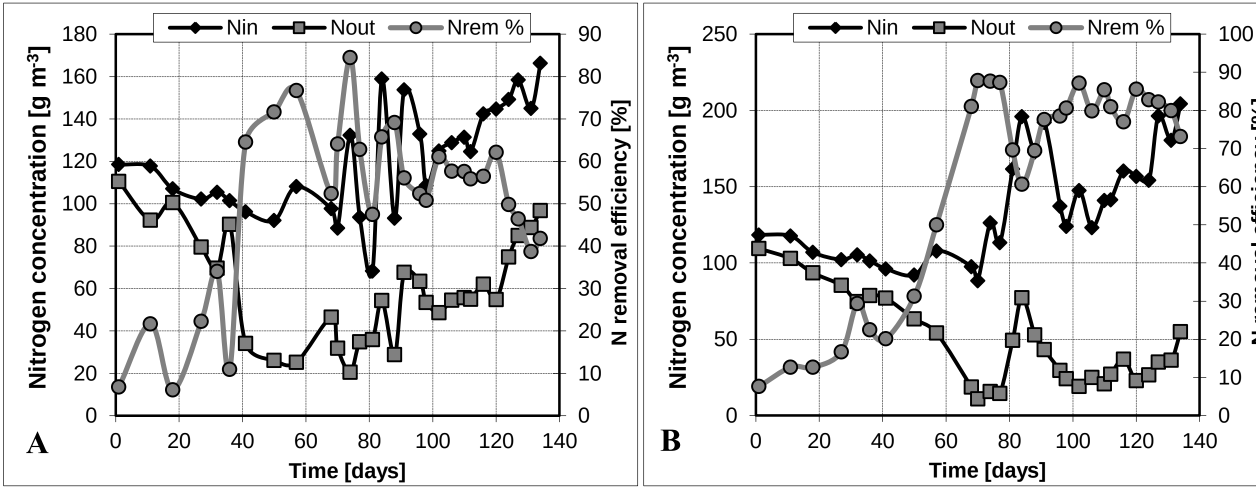

Figure 1. Nitrogen conversion and nitrogen removal efficiency in A) SBR-1 and B) SBR-2

It seems that the seeding condition as well as the temperature has the high influent on the start-up time and the process stability. PCR-DGGE monitoring enabled to present the biodiversity shifts linked with community rearrangement and bacterial biocenoses qualitative change.

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(3) Characteristics of Media Implied Anaerobic Membrane Bioreactor for Domestic Wastewater Treatment

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Abstract

In this study, media implied anaerobic membrane bioreactor was used for treatment artificial domestic wastewater to investigate organic matter removal efficiency and biogas generation by monitoring water quality parameters and methane concentration for estimate reactor performance.

The anaerobic bioreactor could achieve excellent treatment performance in terms of COD removal and biogas production even at a short HRT (6 h). COD concentration of effluent was maintained lower than 20 mg/L and average removal efficiency was 95%. TOC and VFAs consumed through anaerobic treatment it means organic matters transformed to biogas. Membrane fouling was successfully controlled by scouring effect induced by media rotation. The anaerobic membrane bioreactor could be adapted to domestic wastewater treatment.

Keywords
Anaerobic membrane bioreactor; domestic wastewater treatment; media; biogas; membrane fouling

INTRODUCTION

Anaerobic wastewater treatment had been unusually used owing to the sensitive operation parameters until the advantage of anaerobic treatment which less consumption of electricity and methane production, resurfaced by global warming. The major site of electricity consumption in aerobic biological treatment systems is the aeration equipment, which consumes above 40% of whole facility consumption. The anaerobic treatment system could be adapted in traditional treatment system as a solution for energy saving. Contrary to the treatment of high-strength wastewater, the difficulty in retaining slow-growth microorganisms with short hydraulic retention time (HRT) has been concerned in the treatment of low-strength wastewater (Haandel and Lettings, 1994). The use of membrane can retain high biomass concentration in the bio-reactor without any sludge loss irrespective of short HRT. Thus, anaerobic membrane bioreactor (MBR) has been studied to treat low strength wastewater (Huang et al., 2008). However, to control fouling development in the anaerobic membrane bioreactor is an issue of concern. The Anaerobic MBR has more serious membrane fouling tendency, comparing to aerobic MBR (Pattanayak, 2007). Although of energy consumption, bio-gas recirculation is usually used to control membrane fouling in submerged type anaerobic MBR. Therefore, in this study, a media implied anaerobic MBR was attempted to reduce energy consumption for control of membrane fouling in the anaerobic MBR, and investigated the performance of the reactor on organic matter removal efficiency and biogas generation by monitoring water quality parameters and methane concentration for artificial wastewater.

MATERIALS AND METHODS

Anaerobic membranr bioreactor and media

The anaerobic MBR system was composed of two reactors, an anaerobic expended bed reactor (AEBR) and an anaerobic rotary media membrane bioreactor (ARMBR). Two rotary disks connected to the motor via a shaft were installed in the ARMBR, and the membrane (0.25 μm, PVDF) was located between the rotary disks. Both of the reactors were filled with fibrous ball media made of polypropylene. The water treated was sucked out through membrane at 11 LMH. The synthetic wastewater with 350 mg/L of COD was fed. The reactors were maintained at 30℃. The AEBR and the ARMBR were operated at 2-3h and 4h HRT, respectively.

Artificial domestic wastewater

Table 1. shows the component and concentration of artificial wastewater.

Table 1. The artificial wastewater composition and concentration

Components	Concentration (mg/L)	Component	Concentration (mg/L)
$FeCl_2$	2.92	$C_6H_{12}O_6$	100
$MgSO_4$	2.5	CH_3COONa	138.96
$CaCl_2$	3.13	Peptone	50
NH_4Cl	76.04	Beef extract	50
KH_2PO_4	20	$NaHCO_3$	100
NH_2CONH_2	10	$MnSO_4 \cdot H_2O$	0.031
ZnC_{l2}	0.021	$NiCl_2 \cdot 6H_2O$	0.041
$CuCl_2 \cdot 2H_2O$	0.027	H_3BO_3	0.056
$Na_2MoO_4 \cdot 2H_2O$	0.025	$CoCl2 \cdot 6H_2O$	0.041

Analytical methods

The COD_{Cr} and TOC were measured for organic matter removal efficiency using Hach DR-5000 spectrophotometer (Hach, USA) and TOC-V CPN (Simadzu, Japan). The biogas volume and component analysed by water substitution method and gas chromatograph HP 6890 (HP, USA) equipped with Carbonex™ 1004 stainless steel micropacked column(Supelco, USA). The VFA was detected by LC-10 AVP HPLC system (Simadzu, Japan) DO, pH, ORP, SS and alkalinity was analysed to confirm bioreactor condition

RESULTS AND DISCUSSION

Effect of rotating media on membrane fouling

Fig 1 shows changes in trans-membrane pressure (TMP) under various rotation speed and media volume condition in the ARMBR. TMP rapidly increased at no rotation and no media condition. However, under the same condition, when only the rotation was applied at 40 rpm, increase of TMP was reduced to half level. And under that condition, if 10% of media was added in the reactor, TMP was additionally decreased to half level of no media condition, which was a quarter TMP level of no rotation, no media condition. This TMP was the same level of the TMP achieved at 100 rpm without media. It indicate that rotating media could effectively control membrane fouling since rotating media swept out fouling matters from the membrane surface.

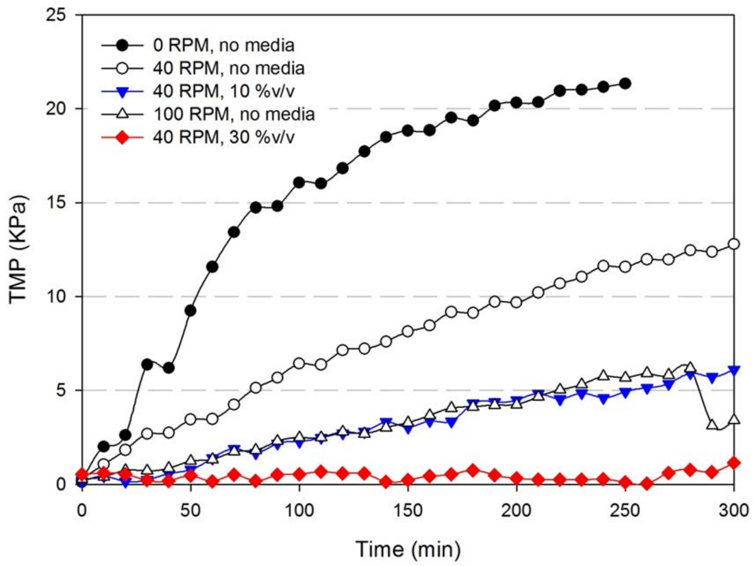

Figure 23. Effect of media rotation on membrane fouling

Characteristics of organic matter removal and biogas production

As shown in Fig. 2, the AEBR stably treated wastewater. COD concentration of effluent was maintained about 55 mg/L and average removal efficiency was 85%. To reduce reaction time, the HRT was reduced from 3h to 2 h. Even when HRT was reduced to 2hr, removal efficiency was kept about 85%.

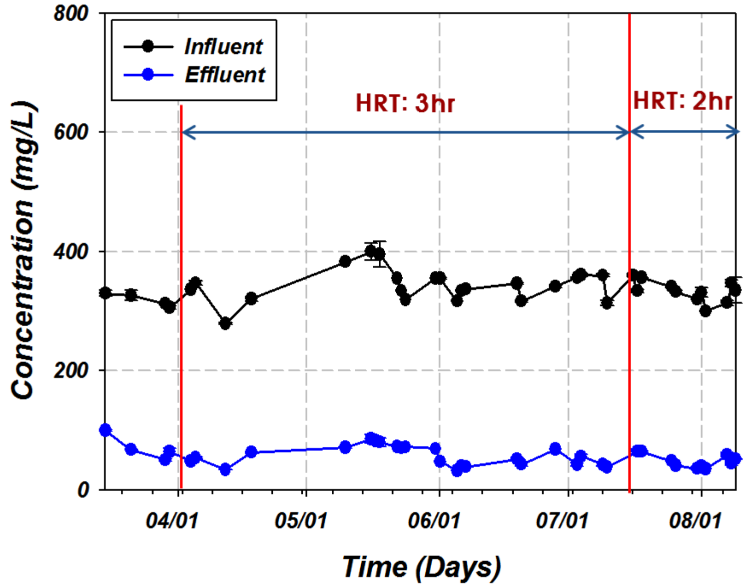

Figure 2. Changes in COD concentration of influent and effluent

Figure 3. shows methane production during the experiments. Regardless of HRT, the methane production rate and methane yield were maintained about 2.3 mol/m^3/d and 0.18 L/gCOD, respectively. The methane content was kept around 95%, regardless of HRT.

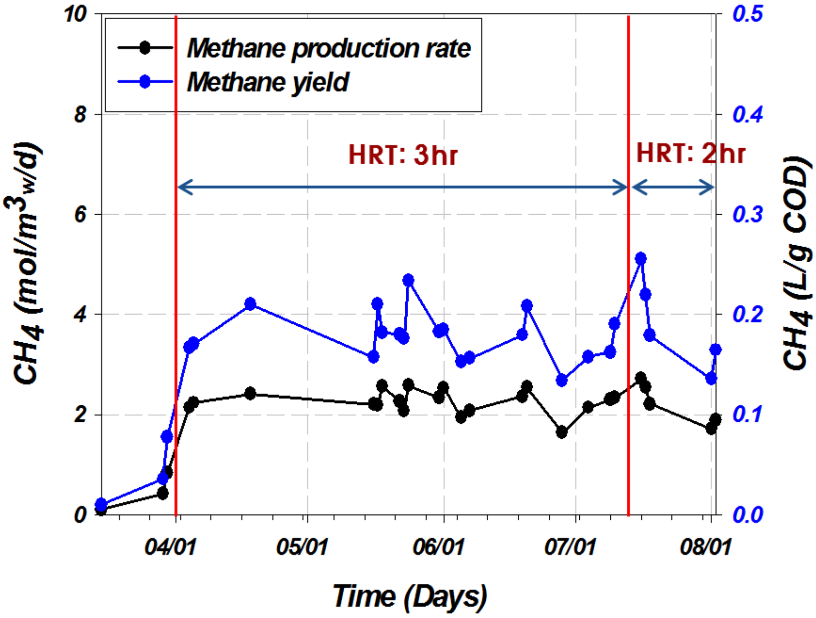

Figure 3 Changes in methane production

CONCLUSIONS

AEBR could achieve excellent treatment performance in terms of COD removal and biogas production even at a short HRT (3-2 hr). In the ARMBR, membrane fouling was successfully controlled by scouring effect generated by media rotation. ARMBR could be used for polishing of the AEBR effluent, reducing 50 mg/L of COD down to 10 mg/L and nearly zero for TSS. It is feasible to treat municipal wastewater with the anaerobic MBR system.

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(4) Developing Efficient Photo-active Media Filters for the Removal of Dissolved Metals

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Abstract

Storm water pollution has been the various concerns over the past decade. Best management practices (BMP) were utilized to mitigate the pollutants found in storm water to protect the water quality of water bodies, and has been augmented to existing water treatment facilities to provide additional resources for potable water usage. This paper describes the use of nanoparticle–coated sand media filter to remove dissolved Cu and Zn. Possible mechanism of the metals degradation was presented in the study.

Keywords

Dissolved metals, media filters, photocatalysis, water treatment, WO_3–TiO_2 nanoparticles

INTRODUCTION

Urban storm water runoff has been encountering problems regarding contaminations from various sources and has since been actively studied by various research groups around the world (Lau, *et*. *al*., 2009). Decreasing the contamination levels of runoffs to the minimum accepted levels to protect the water quality of rivers, estuaries, streams, lakes, seas, and other bodies of waters have been the objectives of various storm water best management practices (BMP) implemented in the United States and other parts of the world, and has been integrated to other existing water and sewage treatment facilities to provide additional water resource for potable or domestic usages. Among the BMP's commonly used for improving water runoff quality is the media filter that removes pollutants in storm water such as suspended solids and phosphorus, and sand is the most common filter material used (Lai, *et*. *al*., 2001). Novel filter materials are used also to improve the performance of media filters and extend their capabilities to removing other pollutants such as organic/aromatic hydrocarbons and heavy metals (Demirel, *et*. *al*., 1999). Among the novel materials being considered are photocatalyst nanoparticles coated into the sand media filter. Photocatalysts especially TiO_2 have been studied during the last 30 years and saw applications in the degradation of organic pollutants with the help of visible light irradiation (Fu, *et*. *al*., 1999; Hashimoto, *et*. *al*., 2005). In this paper, sand coated with WO_3–TiO_2 nanoparticles were used as the filter material and were tested for the removal of dissolved copper (Cu) and zinc (Zn).

MATERIALS AND METHODS

The WO_3–TiO_2 nanoparticles were synthesized by the wet chemistry method wherein TiO_2 powder was added into a beaker containing the appropriate amount of aqueous solution of H_2WO_4 (tungstic acid), and were stirred for two hours. The resulting solution was dried for 72 hours in an oven at 105 ^{0}C. Then, the bone–dried particles were calcined in air at 300 ^{0}C for 4 hours. After calcination, the particles were grounded by mortar and pestle and were milled. The sand was coated with the synthesized nanoparticles by first soaking sand with 10M NaOH for 24 hours and then, washed with concentrated nitric acid and finally with distilled water. The nanoparticles were added after washing. The mixture of sand and nanoparticles were heated in a furnace for 4 hours at 300 ^{0}C temperature. Batch kinetic studies were performed by placing an ample amount of the nanoparticle–coated sand in a beaker with water containing appropriate amounts of nitrate salts of Cu and Zn equivalent to a metal concentration of 10 ppm. The resulting mixture was stirred for 30 minutes and afterwards was irradiated with white fluorescent lamp for 2 hours. Water samples were collected every 5 minute interval for one hour (samples were collected then for every 15 minute interval thereafter) and analysed for heavy metal concentration using inductively coupled plasma–mass spectrometer (ICP–MS).

RESULTS AND DISCUSSION

Batch kinetic study results showed that the degradation of the heavy metals have been decreasing through time, and from Figure 1, metal concentration tends to start decreasing significantly after 15 minutes and the concentration almost reached equilibrium and it can be inferred that the dissolved metals were almost removed totally after 1 hour.

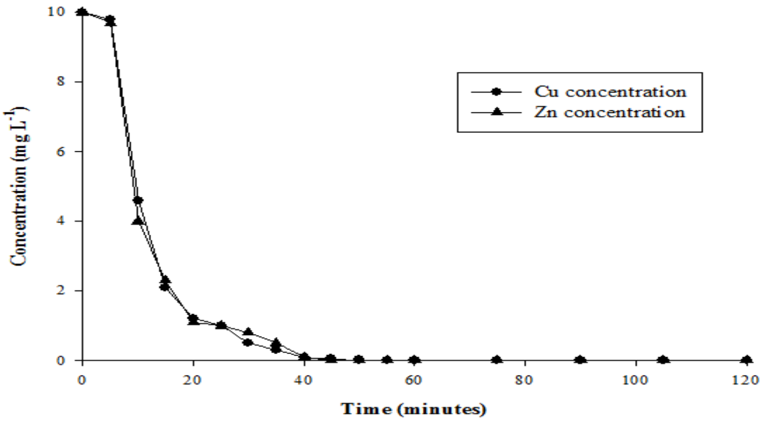

Figure 1. Kinetics of the dissolved metals degradation.

After the initial batch experiments were conducted, the sand particles were separated from the synthetic wastewater, and was dried in the oven for 24 hours at 105 ^{0}C. Afterwards, the sand particles were repeatedly used twice for the same batch experiment procedures outlined above, and the performance was relatively unchanged as shown in Figure 2 and 3. This result shows that the sand particles coated with the WO_3–TiO_2 can be utilized repeatedly without decreasing its effectiveness in removing dissolved metals.

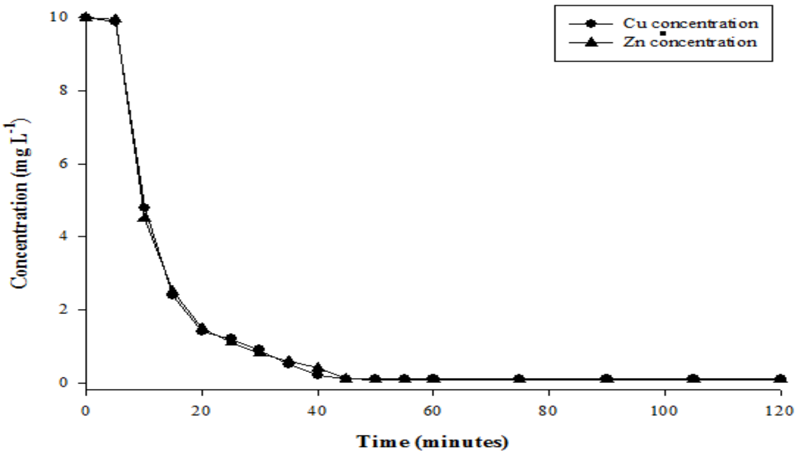

Figure 2. Metals concentration had decreased over time after first cycle of reuse.

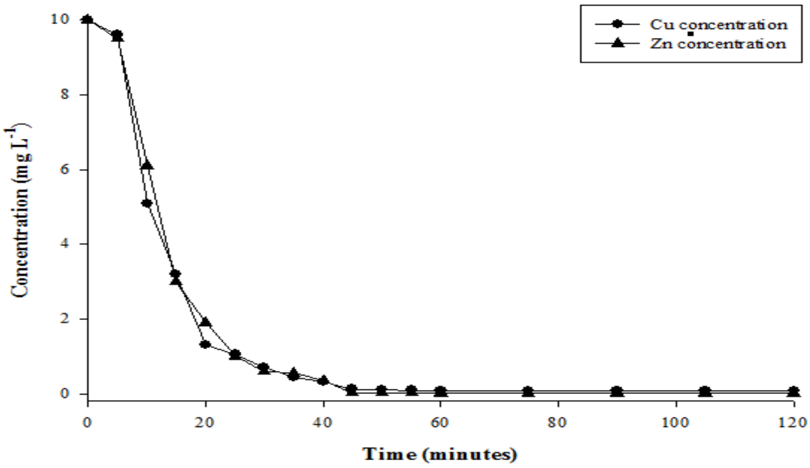

Figure 3. Metals concentration had decreased over time after second cycle of reuse.

This ability of the nanoparticles can be attributed to its high surface area therefore having more pollutant metals could be adsorbed into the catalyst particles' surface, and that the nanoparticles are not actually consumed in the degradation mechanism but it only aids in the reduction process were the semiconductor particles, when irradiated, donates electrons to the metals adsorbed in the catalyst surface. Water including the dissolved oxygen that could be present donates electrons back to the metal oxide catalyst particles that would appear as if it was not consumed in the reaction. The proposed reaction mechanism is presented in Figure 4. Further examination of the catalyst particles' surface are currently being undertaken to evidently validate the mechanism of the degradation of the dissolved metals in the catalyst particles' surface.

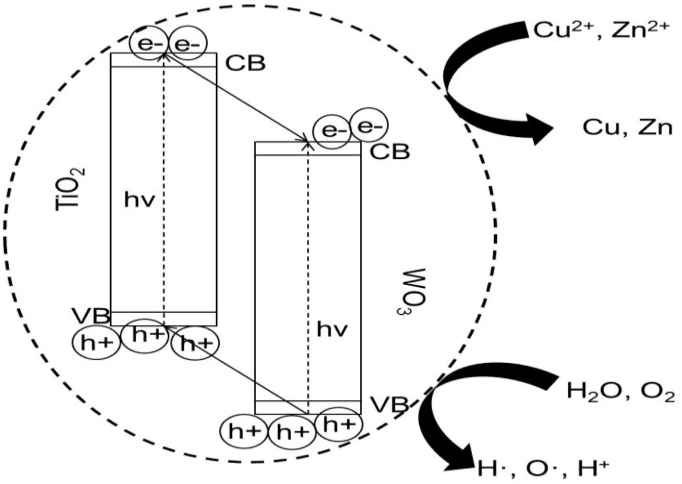

Figure 4. Proposed mechanism of the degradation process of dissolved metals.

CONCLUSION

Novel and efficient photo-active media filters made from sand particles coated with WO_3–TiO_2 nanoparticles were developed for the removal of dissolved metals particularly found in urban storm water runoffs. However, use of these media filters can also be subsequently used for the treatment of industrial wastewater and for reuse into potable or domestic usage. Among the advantages of using nanoparticles is that it is not fully consumed in the degradation process therefore reducing the need for regeneration as compared with traditional filters used for removing dissolved metals. Further surface analysis of the catalyst particles' surface is being undertaken currently to verify the fate of the dissolved metals in the nanoparticle–coated sand media filter.

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(5)Effect of fluidized media on fouling control and organic removal in anaerobic fluidized MBR

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Abstract

A laboratory-scale staged anaerobic baffled/fluidized membrane bioreactor system was operated at 25 °C and fed with complex synthetic wastewater with chemical oxygen demand averaging 250 mg/L. The anaerobic baffled reactor first stage was operated at a 3 h HRT and was followed by an anaerobic fluidized membrane bioreactor (AFMBR) operated at 0.93 to 1.16 h HRT. Granular activated carbon (GAC) was used as the fluidizing media in the AFMBR for biofilm attachment and to control membrane fouling. Polyethylene tetraphthalate (PET) plastic beads were also applied as fluidized media alternative to GAC particles to compare membrane fouling and system performance. The AFMBR under GAC fluidization was operated for 200 d at permeate flux between 8 and 10 $L/m^2/hr$. However, when using a flux of 10 $L/m^2/hr$, sudden rise in suction pressure was observed. With PET beads as fluidized media, the sustainable flux of the AFMBR was observed at 12 $L/m^2/hr$, suggesting that mechanical cleaning effect to reduce membrane fouling should be more beneficial than GAC fluidization. In the AFMBR, particle size distribution and compressibility measured were similar between GAC and PET media fluidization. Although fouling control was better with plastic PET beads than GAC particles as fluidized media, overall COD removal by the two-stage system at a sustainable flux was higher with GAC fluidization than PET media fluidization (96 vs. 84 %). Energy requirement for complete fluidization with both media was lower than the energy required for biogas sparing. However, PET media fluidization showed higher energy requirement than GAC fluidization (0.032 vs. 0.0087 kWh/m^3) due to bigger uniform size range characterized by PET media

Keywords

Anaerobic fluidized bed membrane bioreactor, granular activated carbon, polytethylene tetraphthalate (PET) media, membrane fouling

Introduction

Application of anaerobic bioreactor has been attractive particularly for treating a relatively dilute wastewater. However, anaerobic treatment efficiency of the dilute wastewater is not effective enough to meet the discharge limit because of the difficulty of maintaining sufficient active biomass in the reactor. In addition, membrane fouling is still major obstacle because it can reduce membrane performance. Our previous study showed that combining membranes with anaerobic GAC fluidized bed reactor, termed as “AFMBR”, provided promise to improve organic removal efficiency while reducing membrane fouling which is a long-standing problem in membrane technology (Kim et al., 2011). However, elucidating activities of GAC particles and other media alternative to GAC particles in terms of the improved organic removal and fouling control during the long-term operation of AFMBR still require further works. Comparative study between various types of fluidized media will lead to better understanding and improvements in the design and operation of AFMBR to optimize the system performance. In this presentation, our results on comparing membrane fouling during the operation of the AFMBR as the post treatment for the anaerobic baffled reactor (ABR) will be presented. GAC particles and polyethylene tetraphthalate (PET) beads were used as fluidized for comparative study.

Material and Methods

The AFMBR having an effective volume of 1.0 L was developed as a polishing unit to treat the effluent from the anaerobic baffled reactor (ABR) at 25 °C. The feed to the ABR consisted of sugar and yeast extract at equal SCOD concentration of 250 mg/L and filtered supernatant (0.57 volume %) was added as source of micronutrient. The effluent of SCOD and SS from ABR averaged 50 mg/L and 20 mg/L, respectively. A module with microfiltration hollow-fiber membranes (PVDF, 0.1 μm as nominal pore size) was developed and applied for the AFMBR. A 225 g of 10x20 mesh GAC particles were fluidized in the AFMBR by recirculating bulk solution through the column reactor under an upflow rate of 1.2 L/min. Alternative to GAC particles, polyethylene terephthalate (PET) beads were selected as fluidized media for comparison. Properties of each fluidized media tested in this study are summarized in Table 1.

Table 1. Properties of GAC particles and PET beads as fluidized media

	GAC	PET beads
Specific gravity	2.3	1.3
Particle size (mm)	1-2	3

Results

Granular activated carbon (GAC) and plastic PET bead were compared as fluidized media to reduce membrane fouling and organic removal in the long-term operation of the AFMBR polishing ABR effluent. Results showed that the both media provided effective tool to control membrane fouling by mechanical cleaning action along membrane surface. Hydraulic shear caused by upflow rate only on membrane surface through recirculation line in the AFMBR was not effective to reduce membrane fouling. Under media fluidization, microbial flocs were disaggregated by the movement of media in size from 0.1 to 1.0 μm and there was no significant difference in particle size distribution in the AFMBR between GAC fluidization and PET media fluidization. Sustainable flux at which membranes are operated for about three months without chemical cleaning was higher with PET media fluidization than GAC fluidization (12 vs. 9 L/m^2/hr). However, overall COD removal was 96 % with effluent COD of about 11 mg/L under GAC fluidization while the effluent COD from the AFMBR was about 20 mg/L under the fluidization of PET media. The electrical energy required for complete fluidization were 0.0087 kWh/m^3 with GAC fluidization, much less than that of an anaerobic MBR combined with biogas sparging to control membrane fouling. The use of PET media required less electrical energy than gas sparging to control membrane fouling, but the energy consumption for fluidization was higher than the GAC particles (0.032 kWh/m^3).

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(6)Removal properties of ammonium ion with surface modified zeolite

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Abstract

The magnetic zeolite was synthesized by hydrothermal process and the adsorption properties for ammonium ion were examined. The pH of ammonium ion solution affected the characteristics of magnetic zeolite and the decrease ratio of adsorption capacity is 10 to 20% between magnetic zeolite and non-treatment one, where showed 2.5mmol/L and 2.1 mmol/L, respectively. The magnetic zeolite saturated with ammonium ion was regenerated by substitution and thermal desorption methods. In addition, it is easily able to be separated by magnetic force.

Keywords

Adsorption; ammonium ion; Langmuir isotherm; regeneration; zeolite

INTRODUCTION

Ammonia is mainly used for the materials of chemical fertilizer or nitric acid. Ammonia exists in the form of ammonium ion in water and causes eutrophication when it is accumulated into the water environment. It is significant to remove ammonium ion. Zeolite as cation exchanger is drawing the interest to remove ammonium ion from the water environment. But this method does not spread widely due to the high cost of equipment and/or low adsorption capacity. Therefore, we synthesized magnetic zeolite in order to make easy withdrawal of zeolite from water with simple magnetic process and evaluated the adsorption properties.

MATERIALS AND METHODS

Magnetic zeolite

Magnetic zeolite was synthesized by depositing Fe_3O_4 on zeolite surface, which is A-3 type. The protocol for magnetic zeolite is as follows; 20g of $FeCl_2 \cdot 4H_2O$ and 13.5g of $FeCl_3 \cdot 6H_2O$ was added to 50mL of distilled water, respectively; 1mL of $FeCl_2 \cdot 4H_2O$ solution and 4mLof $FeCl_3 \cdot 6H_2O$ solution were mixed and heated at about 70°C; 50mL of 2% NH_4^+ solution was added to the mixed solution to adjust pH of the solution about 12, and 1.5g of zeolite was added to the solution; synthesized magnetic zeolite was separated by magnetic separation. The collected zeolite was dipped to 20 mass% NaCl solution to remove and wash Fe^{2+} and/ or Fe^{3+}. The Fe_3O_4 content of magnetic zeolite is 36 mass%.

Adsorption experiment and analytical methods

The adsorption characteristic for ammonium ion was examined by batch type experiment, where the solutions were prepared with NH_4Cl adjusted to 5 mmol/ L. Ammonium and sodium ion concentrations were detected by ion chromatography equipped with Metrosep C4-150. The magnetic zeolite in the reaction mixture was removed by filtration with membrane filter. The surface morphology of magnetic zeolite was observed by a scanning electron microscope equipped with an energy dispersive X-ray analyzer. The thermal behavior was also measured by thermogravimetry/ differential thermal analyzer.

RESULTS AND DISCUSSION

Influence of solution pH

The adsorption amount (q_e) of zeolite is influenced by solution pH as shown in Fig. 1. The q_e presents the maximum value in neutral pH condition. Under acidic condition, the q_e decreases sharply. Magnetic zeolite shows the same adsorption behaviour as non-treatment zeolite. The q_e of magnetic zeolite is about 30 % smaller than non-treatment zeolite. The deposition of Fe_3O_4 has little influence on the adsorption capacity compared with Fe_3O_4 content.

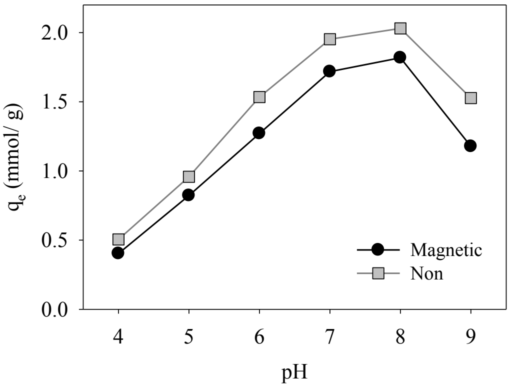


Fig.1 Influence of pH on adsorption amount (q_e).

Adsorption isotherm

The adsorption isotherm was shown in Fig.2, and the equilibrium adsorption concentration was about 1.60 mmol/g. The value of solution pH was not controlled and increased to 8.3. The adsorption isotherm for ammonium ion is approximated by Langmuir equation as follows;

$$q_e = \frac{3.200C_e}{1 + 1.464C_e}$$

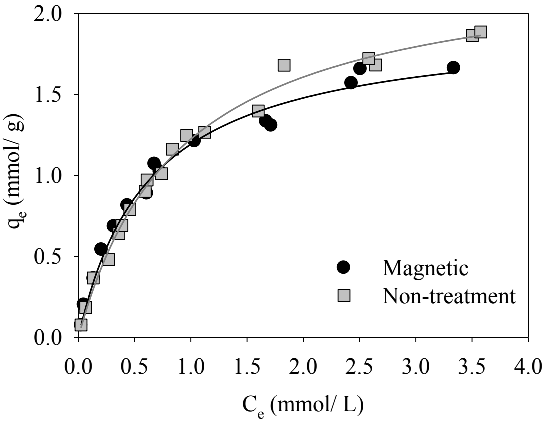
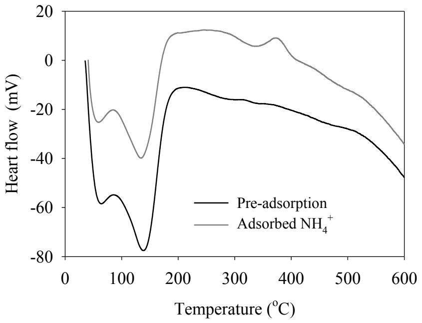


Fig.2 Adsorption isotherm.

Regeneration

The zeolite saturated with NH_4^+ was regenerated by substitution and thermal desorption methods. In the substitution method, the saturated zeolite was dipped in 30 mass% NaCl solution at 24 h and 25 ºC for the release of NH_4^+. As shown in Fig. 3 for the behaviour of thermal desorption, the peak from thermal desorption was observed in around 350 ºC in Ar gas atmosphere, and that was different between before and after adsorption of NH_4^+. The temperature of thermal deposition was decided 400 ºC at 4 h. The influence of regeneration number for q_e is shown in Fig. 4. In the both method, qe was decreased with the increase of regeneration number. Fig.5 shows the surface morphology of magnetic zeolite, which was treated by thermal desorption. The cubic crystal of zeolite was decomposed, and that was agglomerated with each treatment.



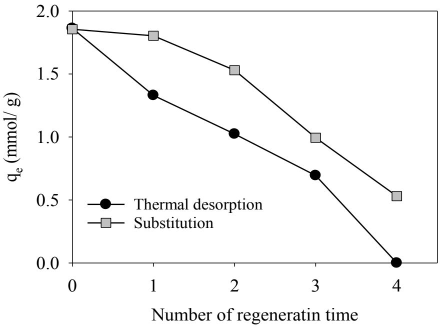


Fig. 3 The behaviour of thermal desorption.

Fig. 4 Decrease of qe with regeneration treatment.

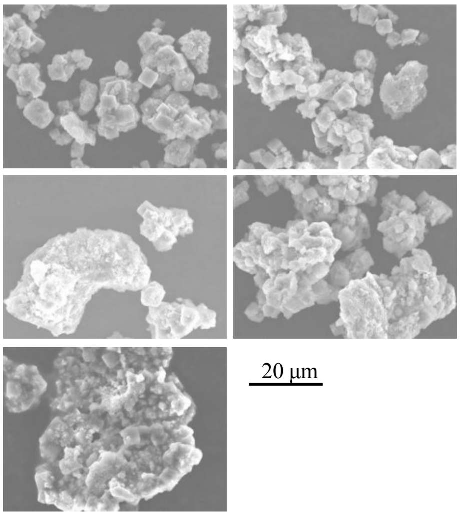


Fig. 5 Surface morphology of magnetic zeolite with each thermal desorption.

CONCLUSION

The magnetic zeolite was successfully synthesized by hydrothermal process and examined the adsorption properties for ammonium ion. The adsorption amount is influenced by solution pH and shows the maximum value in neutral pH condition. The deposition of Fe_3O_4 gives little influence on the adsorption capacity which was followed by Langmuir equation. The surface morphology treated by thermal desorption showed that the cubic crystal of zeolite was decomposed and agglomerated with each treatment. Magnetic zeolite was easily separated by magnetic force.

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(7) Modelling NOB activity under different dissolved oxygen, ammonia and nitrite concentrations

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Abstract

Batch tests were conducted on sludge samples drawn from a nitrifying/denitrifying SBR fed on a synthetic wastewater to search for causes of the observed nitrification unbalancing, focusing on the effects of dissolved oxygen and ammoniacal and nitrous nitrogen concentrations on nitrite oxidising bacteria. Ammonium and nitrite oxidation rates were assessed by pH/DO-stat titration, i.e. by measuring the rate of addition of an alkaline solution and of an oxygen-reach solution required to maintain constant, at a selected set-point level, both pH and dissolved oxygen (DO) concentration of the sludge sample. According to experimental results, nitrite oxidising bacteria (NOB) were penalised under DO limitation (DO half saturation constant for ammonia and nitrite oxidation were 0.1 and 0.4 mg l^{-1}, respectively). Several inhibition functions were found to describe the effect of increasing nitrite and ammonia concentrations on NOB allowing to assess the EC50 values for both chemical species.

Keywords
dissolved oxygen, free ammonia, free nitrous acid, inhibition functions, nitrite oxidising bacteria

INTRODUCTION

Nitrite is known to be a common intermediate in the biological nitrogen oxidation/reduction cycle. While nitrite accumulation within conventional nutrient removing wastewater treatment plants has to be avoided, favouring nitrite production *versus* oxidation plays a relevant role in novel processes for nitrogen removal, like the short-cut nitritation/denitritation and the fully autotrophic N removal process (partial nitritation/anammox). The nitrite level is mostly defined by the activity of nitrite oxidising bacteria (NOB). Several environmental parameters have been appointed for playing a role in affecting the NOB activity. The pH of the mixed liquor is also known to affect bioprocesses by influencing ionisation of weak acid/bases and thus their possible inhibiting effect on bacterial activity. Free ammonia (FA) is known to be more toxic to NOB than the ionised ammonium form, while inhibition of NOB by nitrite is a typical example of substrate inhibition as firstly described by Anthonisen et al. (1976). These authors identified the un-ionized nitrous acid (FNA) as the inhibiting form, which prevails at low pH values and reported a threshold inhibiting level as low as 0.2 $mg_N\ l^{-1}$, although higher concentrations were later suggested (e.g. Carrera et al., 2004). However, even ionised nitrites were found to have an inhibiting effect on nitrite oxidisers (Buday et al., 1999; Jeniček et al., 2004, Mosquera-Corral et al., 2005). As for dissolved oxygen (DO) concentration, several authors claim that AOB have a higher affinity for oxygen (Hanaki et al., 1990 among others).

Aim of this work was to study the effects of some relevant conditions (dissolved oxygen, ammonia and nitrite concentrations) on activity of NOB in sludge samples cultivated in a SBR fed on a synthetic wastewater. Batch tests were performed in order to get sufficient experimental data to test mathematical models describing the effect of those factors on NOB activity.

MATERIAL AND METHODS

A 20-litre volume SBR was operated according to 4 cycles per day, fed on a synthetic influent (OECD, 2001) having a COD and N content of 880 mgCOD l^{-1}, and 100 mgN l^{-1}. The organic and nitrogen loading rates were 0.53 kgCOD $m^{-3}\ d^{-1}$, and 0.06 kgN $m^{-3}\ d^{-1}$, respectively. The aerobic sludge age was 20 to 24 d. Temperature and pH were respectively 20-22°C and 7.2-8.3 pH units.

Nitritation rates were determined by applying the pH/DO-stat titration technique (Ficara et al. 2000, Artiga et al., 2005), which allowed easy calculation of the reaction rates, which are directly related to titration rates, under careful control of DO and pH. Specifically, NaOH addition rate is used to assess the activity of ammonium oxidising bacteria (AOB), while nitrite oxidation rate is assessed from O_2 addition rate. Tests were performed at constant temperature (22±0.5°C). The titration instrument (MARTINA) has been provided by SPES s.c.p.a. (Fabriano, AN, Italy). Set-point titration tests were performed to determine AOB and NOB activity under various environmental conditions. An initial set of environmental parameters was fixed and a test was performed by adding the appropriate substrate for the bacteria group whose activity had to be determined (ammonium or nitrite, 5 mgN l^{-1}). When the added nitrogen was fully oxidized, all parameters were kept constant but the one whose influence was under study, which was increased or decreased. The appropriate substrate was spiked again to assess the nitrification activity under the new condition. From a minimum of two up to five different conditions were tested on one sludge sample. The maximum nitrification activity was measured after each substrate spike and, then plotted against the level of the varied parameter.

RESULTS

First, the effect of DO concentration between 1 and 7.5 mg/L on nitrification activity was considered. pH was set at the optimal value for the bacteria group under study, i.e.: 8.3 for AOB and 7.5 for NOB. Results are plotted in Figure 1 where horizontal error bars indicate that DO concentration oscillated around the set-point value during the activity test. The best-fitting Monod curves are plotted, and estimated parameters are: maximum AOB activity = 3.0 $mg_N\ g^{-1}_{VSS}\ h^{-1}$; half saturation constant for AOB: $K_{O,AOB}$ = 0.1 $mg_{O2}\ L^{-1}$; maximum NOB activity = 2.6 $mg_N\ g^{-1}_{VSS}\ h^{-1}$; half saturation constant for NOB: $K_{O,NOB}$ = 0.4 $mg_{O2}\ L^{-1}$. These results confirm the higher affinity of AOB for oxygen.

In the second experimentation, the effect of the free ammonia concentration on NOB activity was assessed by measuring the decrease in NOB activity under increasing free-ammonia (FA) concentration and constant nitrite concentration (5 mgN L^{-1}). Allylthiourea was added to inhibit ammonia oxidisers. The FA level was modified either by increasing the total ammoniacal nitrogen (TAN) up to 1000 mgN/L, or by increasing the pH value (from 7.5 to 8.3). The FA molar concentration was assessed from that of TAN By taking into account the dissociation equilibrium of ammonium. By plotting the percentage inhibition of NOB activity against both TAN and FA concentrations similar inhibition responses were detected in the presence similar FA concentrations (S_{FA}), confirming that FA more than TAN is responsible for the observed inhibition. For data interpretation, inhibition (I) versus data were fitted with several inhibition functions (Kroiss et al., 1992). General dose-response functions were considered: linear: $I = a \cdot S_{FA} + b$; exponential: $I = 1 - e^{-a \cdot S_{FA}}$; S-curve: $I = 1 - 1 \Big/ \left[1 + \left(\frac{S_{FA}}{a} \right)^{b} \right]$ where: *a* and *b* are the fitting parameters. Moreover, the non-competitive and competitive inhibition model were also tested: $I = \frac{1}{1 + K_{I,FA} / S_{FA}}$; $I = S_{FA} \Big/ \left[K' + K_{I,FA} \cdot \left(1 + \frac{S_{FA}}{K_{I,FA}} \right) \right]$ where: $K_{I,FA}$ and K' are fitting parameters. Fitting results are plotted in Figure 2. According to the adjusted coefficient of determination (R^2_{adj}), all tested models appear to satisfactorily fit experimental data (R^2_{adj} included between 0.8714 and 0.9716), the exponential curve appears to be the best one. On this curve, the estimated EC_{50} (50% effect concentration) is 45.3 $mg_N\ L^{-1}$.

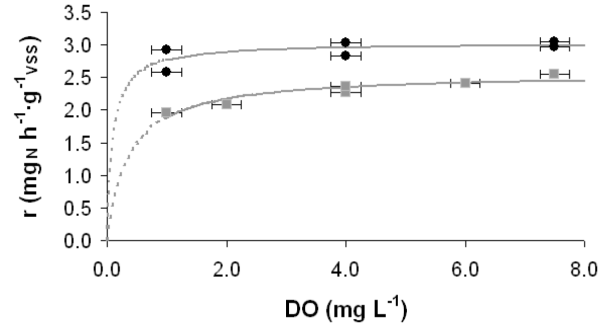

Figure 1: Effect of DO on the oxidation rate of AOB (●) and NOB (■).

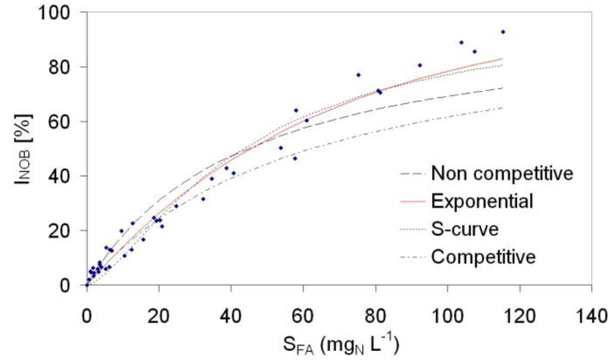

Figure 2: Fitting experimental data by several inhibition curves.

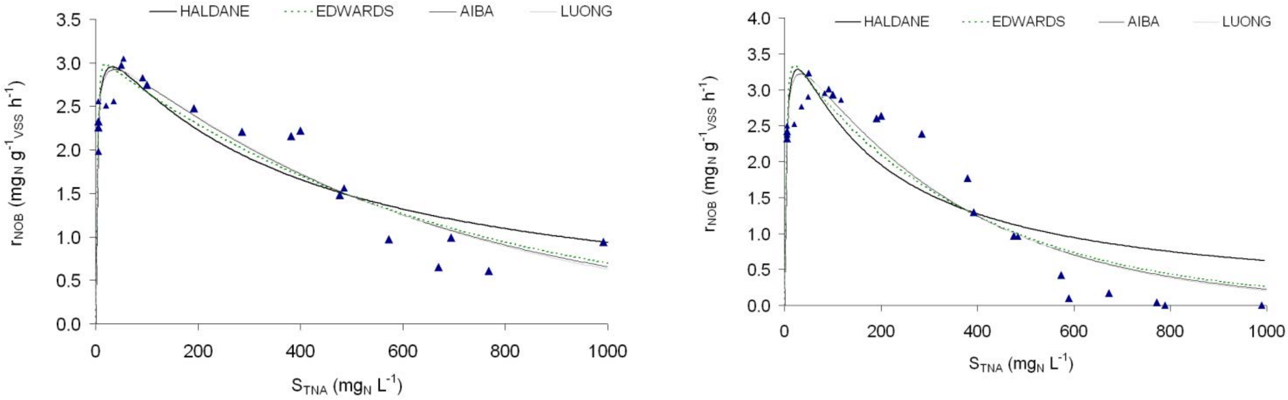

Figure 3: Fitting experimental data by several inhibition curves (pH = 8.3 on the left and at pH = 7.5 on the right).

In the third experimentation, the effect of total nitrous acid (TNA) concentration and of the un-ionized nitrite acid (FNA) concentration was evaluated by measuring the decrease in NOB activity under increasing total nitrite concentration, achieved by spiking nitrites at 30-50 min intervals under DO-stat conditions and by working at two pH values (7.5 and 8.3). The actual TNA during the test was computed by taking into account the total amount of nitrite added and the amount of nitrite oxidised to nitrate, as estimated from the oxygen dosed by titration. TNA was increased from 0 to 1000 mg$_N$ L^{-1}. The FNA concentration was calculated from that of TNA, by considering its dissociation equilibrium. The NOB activity was plotted against both TNA and FNA concentrations. Contrary to what observed with FA concentration, the TNA and not the FNA concentration appeared to correlate with the observed inhibition. Possibly, at the tested pH, FNA concentrations were too low (<0.01 mg$_N$ L^{-1}) to be relevant for inhibition. Thus, NOB activities versus TNA concentrations data were fitted with four inhibition functions known to describe substrate inhibition, namely Haldane, Edwards, Aiba and Luong (for more details on these functions please refer to: Carrera et al., 2004). The R^2_{adj} values varied between 0.7892 and 0.8987, suggesting that all models could explain data trends satisfactorily. The Aiba model provided the best fit (Figure 3). This model can be written as:

$r_{NOB} = \hat{r}_{NOB} \cdot \frac{S_{TNA}}{K_S + S_{TNA}} \cdot e^{\left(-\frac{S_{TNA}}{K_{I,TNA}}\right)}$, where r$_{NOB}$ is the nitrite oxidation rate, *S$_{TNA}$* is the concentration of total nitrous acid and *K$_{I,TNA}$* is the inhibition coefficient. According to this model, the EC$_{50}$ TNA concentration is 430 mg$_N$ l^{-1} at pH 8.3 and 240 mg$_N$ l^{-1} at pH 7.5.

CONCLUSIONS

The experimentation lead to the following conclusions:

(1) The applied pH/DO-stat titration technique proved to be a simple and convenient technique to assess the activity of nitrite oxidising bacteria (NOB) under various operational conditions.

(2) The tests revealed that the half saturation constant of NOB for dissolved oxygen in Monod kinetics was $K_{DO,NOB} = 0.4$ mg_N l^{-1}, and confirmed it is higher than that of ammonia oxidising bacteria ($K_{DO,AOB} = 0.1$ mg_N l^{-1}).

(3) Data of NOB activity under various free ammonia (FA) concentrations could be best-fitted by an exponential-like dose-response curve ($R^2_{adj} = 0.9716$) with an EC_{50} of 45 mg_N l^{-1}.

(4) The effect of nitrite concentration (substrate inhibition) on NOB was assessed; total nitrous acid (TNA) more than free nitrous acid (FNA) was found to correlate well with the observed inhibition; Aiba model provided the best fit of the experimental data, with an EC_{50} TNA concentration of 430 mg_N l^{-1} at pH 8.3 and 240 mg_N l^{-1} at pH 7.5.

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(8) Food industry wastewater treatment plant with dissolved air flotation (DAF) and membrane bioreactor (MBR)

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Abstract
This paper deals with an Italian food industry wastewater treatment plant that was projected for 100 m3/d, 440 kgCOD/d, 290 kgBOD/d and 4 kgN/d. The plant is made of an accumulation tank (50 m3), a dissolved air flotation tank (footprint 6.5 m2), two serial accumulation tanks (50 m3 and 70 m3), a fine screen (2 mm), an activated sludge oxidation tank (196 m3) followed by a tank (196 m3) where sludge is separated from water by plane membranes (porosity 0.04 um). Total filtration surface is 500 m2, project flux is 7.4 L/m2h, maximum flux is 25 L/m2h, maximum suction pressure is 400 mbar. The plant was started in 2013; this year it has treated 113 m3/d, 1682 kgCOD/d, 1231 kgBOD/d, 53 kg/d oils and greases, 13 kgN/d and 4.3 kgP/d. The flotation has removed 74% of COD, 72% of BOD, 99% of oils and greases and 55% of nitrogen and phosphorus; the whole plant has removed more than 99% of all pollutants and has respected limits. Sludge concentration is 8.9 kgTSS/m3, permeate flux is 9.4 L/m2h.

Keywords
Wastewater treatment, Activated sludge, Food industry, Flotation, Membrane bioreactor

PLANT DESCRIPTION

This paper deals with a plant that treats wastewater of an Italian food industry. The industry has three sites in an unique area, they produce different wastewater which main parameters are listed in tab. 1; each site has an accumulation tank and a pumping station. The plant was projected to treat all wastewater altogether, it was dimensioned for 100 m^3/d, 440 kg_{COD}/d, 290 kg_{BOD}/d and 4 kg_N/d. The final effluent is discharged into public sewer network and must respect limits stated by the national law 152/2006: TSS ≤ 200 mg/L, COD ≤ 500 mg/L, BOD ≤ 250 mg/L, oils and greases ≤ 40 mg/L. The plant (fig. 1) is made of a common accumulation tank (50 m^3), a pumping station, a dissolved air flotation tank (footprint 6.5 m^2), two serial accumulation tanks (50 m^3 and 70 m^3), a drum fine screen (2 mm holes), a biological section and a sludge storage tank (50 m^3). The biological section is based on a membrane bioreactor: an activated sludge oxidation tank (196 m^3) followed by a tank (196 m^3) where sludge is separated from treated water by ultrafiltration membranes. In this tank 5 modules Bio-Cel plane polyetheresulfone membranes are installed to give a total filtration surface of 500 m^2; membrane porosity is 0.04 um, project flux is 7.4 L/m^2h, maximum flux is 25 L/m^2h, maximum suction pressure is 400 mbar. Every working cycle is 600 s, of which 510 s for filtration, 60 s for relaxation and 30 s for backwashing. Once a month membranes are chemically washed with sodium hypochlorite solution (250 mg/L). The oxidation tank is aerated by two 530 Nm^3/h blowers controlled by inverter; membranes are cleaned continuously with aeration by a 250 Nm^3/h blower. It was estimated that flotation should remove 35% of COD and BOD, so the biological section was projected for 286 kg_{COD}/d and 188 kg_{BOD}/d; project sludge concentration is 10 kg_{TSS}/m^3.

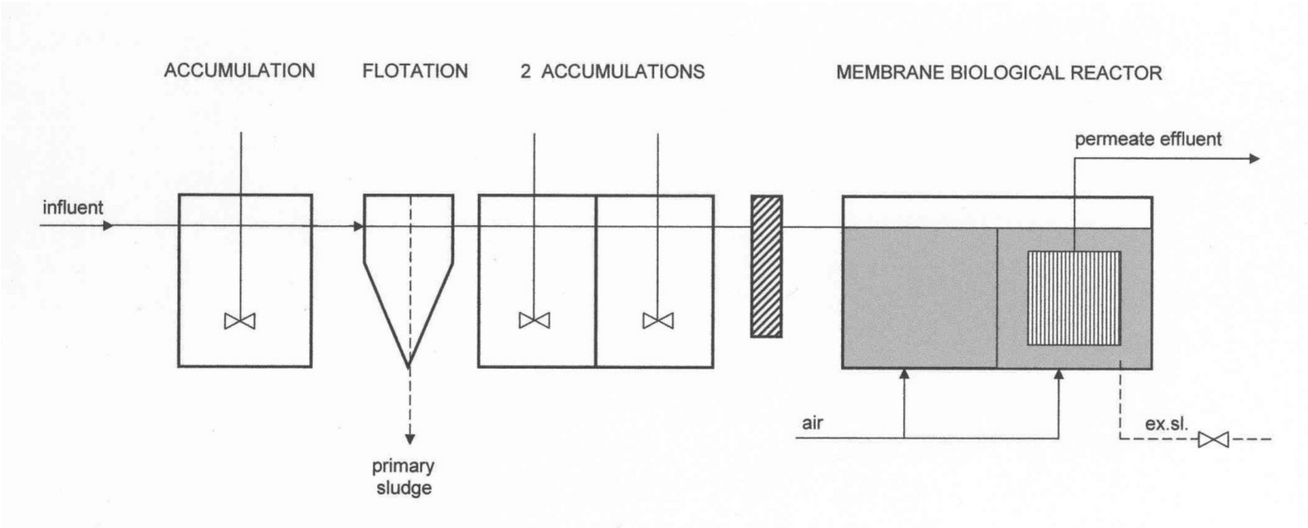

Figure 1: Scheme of the food industry wastewater treatment plant.

Table 1: Average characteristics of wastewater produced by the three sites.

		Site nr. 1	**Site nr. 2**	**Site nr. 3**	**Total w.w.**	**Project**
Hydraulic load	(m^3/d)	20	29	42	91	**100**
COD	(mg/L)	3440	5290	4180	4373	**4400**
BOD	(mg/L)	2294	4000	2390	2886	**2900**
NH_4^+	(mg/L)	104	16	22	38	**38**

RESULTS AND DISCUSSION

The plant was started in April 2013 and has been studied during the following six months. In this year the hydraulic load has varied between 100 – 125m^3/d (average value 113 m^3/d); pollutant concentrations in raw influent wastewater, after flotation (average values) and in final effluent are listed in tab. 2. On average basis, effective pollutant loads are respectively 1682 kg_{COD}/d, 1231 kg_{BOD}/d, 53 kg/d oils and greases, 13 kg_N/d and 4.3 kg_P/d. These values are much higher than expected ones; the plant is significantly overloaded because of a recent important production increase, but it was dimensioned with a good margin of safety, and the final effluent respects emission limits. The flotation unit removes 74.0% of COD, 72.6% of BOD, 99.4% of oils and greases and ca. 55% of nitrogen and phosphorus. Thus the biological section treats 438 kg_{COD}/d, 337 kg_{BOD}/d, 7 kg/d oils and greases, 6 kg_N/d and 1.9 kg_P/d. The plant removes more than 99% of COD, BOD, oils and greases, nitrogen and phosphorus. Average sludge concentration in biological reactors is 8.9 kg_{TSS}/m^3, of which 7.9 kg_{VSS}/m^3; effective organic load factor is 0.10 $kg_{BOD}/kg_{VSS}d$. Average permeate flux is 9.4 L/m^2h and maximum value is 10.4 L/m^2h.

Table 2: Pollutant concentrations at the wastewater treatment of the food industry.

Parameter		Raw influent			after DAF	Final effluent			Removal %	
		min	average	max		min	average	max	DAF	Plant
COD	(mg/L)	7150	14883	34700	3877	< 25	123	500	74,0%	99,2%
BOD	(mg/L)	5100	10890	25600	2980	< 5	6	15	72,6%	99,9%
Oils greases	(mg/L)	156	465	890	64.2	< 0.5	0.8	3.7	99,4%	99,8%
NH_4+	(mg/L)					< 0.5	< 0.5	< 0.5		
NO_2-N	(mg/L)					< 0.1	< 0.1	< 0.1		
NO_3-N	(mg/L)					< 1	< 1	< 1		
Tot-N	(mg/L)	93,0	119	170	53.0	< 1.5	< 1.5	< 1.5	55,5%	99,3%
Tot-P	(mg/L)	19.4	37.7	78.1	16.9	< 0.5	5.6	6.6	55,2%	99,3%

Note: when values were lower than detection limits, for calculations of average values and removal efficiencies they were considered as half of detection limits

CONCLUSIONS

These results confirm that concentrated food industry wastewater can be treated with dissolved air flotation and membrane bioreactors, with high pollutant removal efficiencies. This plant is much overloaded (organic loads are almost 4 times higher than project values), but it was dimensioned with a good margin of safety and the final effluent respects emission limits. The DAF unit removes more than 70% of organic load 99% of oils and greases, and the whole plant removes more than 99% of all pollutants. Effective organic load factor is 0.10 $kg_{BOD}/kg_{VSS}d$; average permeate flux is 9.4 L/m^2h and maximum value is 10.4 L/m^2h.

(9) Upgrading of a wastewater treatment plant with hybrid MBBR

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Abstract

A municipal wastewater treatment plant was projected for 2200 p.e.; expected loads were 550 m3/d, 264 kgCOD/d, 132 kgBOD/d and 26 kgN/d. The plant was based on a circular oxidation tank (395 m3) and a circular crown settler (315 m3); other units were built but not yet in use in 2008: fine screen, sand and grit removal, another settler (570 m3), disinfection, sludge thickening. Effective hydraulic load was 245% higher, organic load was 46% lower and nitrogen load was 39% higher than project values. So the circular crown settler was divided into two sectors: a predenitrification tank (100 m3) and a hybrid oxidation MBBR (180 m3) with 50% AnoxKaldnes K3 carriers; units not yet in use were also re-started. Suspended sludge concentration in biological reactors was 2.0-2.8 kgTSS/m3; biofilm showed oxidizing and nitrifying ctivities two months after plant re-starting and its concentration reached 1.1 gTS/m2.The upgraded plant removed 56% of COD, 74% of BOD, 85% of TKN.

Keywords

Wastewater treatment, Activated sludge, Nitrogen, Biofilm, Moving bed, Hybrid

PLANT DESCRIPTION

The wastewater treatment plant of Porto Tolle (RO, Italy) was originally projected for 2200 p.e.; expected loads were 550 m^3/d, 264 kg_{COD}/d, 132 kg_{BOD}/d and 26 kg_N/d. Emission limits were stated by the Regional Plan for Water Resanation and were: TSS ≤ 35 mg/L, COD ≤ 125 mg/L, BOD ≤ 25 mg/L, NH_4^+ ≤ 20 mg/L, NO_2-N ≤ 1 mg/L, NO_3-N ≤ 30 mg/L, P ≤ 10 mg/L. The plant was originally made of a pumping station, a circular activated sludge oxidation tank (395 m^3) aerated by a 1480 Nm^3/h blower and fine bubble diffusers, a sedimentation unit in the external circular crown (315 m^3), and two drying beds for sludge (fig. 1A). Other units were built but not yet in use in 2008: fine screen, sand and grit removal, a circular settler (570 m^3), a disinfection tank with peracetic acid and a sludge thickener. According to average data of 2007, the plant treated 1898 m^3/d with 35 mg/L TSS, 75 mg/L COD, 37 mg/L BOD, 19.1 mg/L TKN; hydraulic load was 245% higher, organic load was 46% lower and nitrogen load was 39% higher than project values. Wastewater was (and is) very dilute because of infiltrations of rain waters and clean water from the river Po. Even if the plant respected emission limits, the regional environmental law was near to be modified with more strict emission limits for nitrogen, the plant had no denitrification, and higher pollutant loads were expected for following years. So it was decided to modify the plant and to start units not yet in use; the choice to convert part of existing volume into a hybrid MBBR was justified with the possibility of reducing activated sludge concentration. So the circular crown was divided into two sections (fig. 1B): a sector of 180 m^3 was converted into a predenitrification tank, a sector of 100 m^3 was converted into a hybrid MBBR oxidation tank. This reactor was filled with 50% AnoxKaldnes^{TM} K3 carriers (tab. 1) and aerated by a new 1000 Nm^3/h blower and medium bubbles air diffusers.

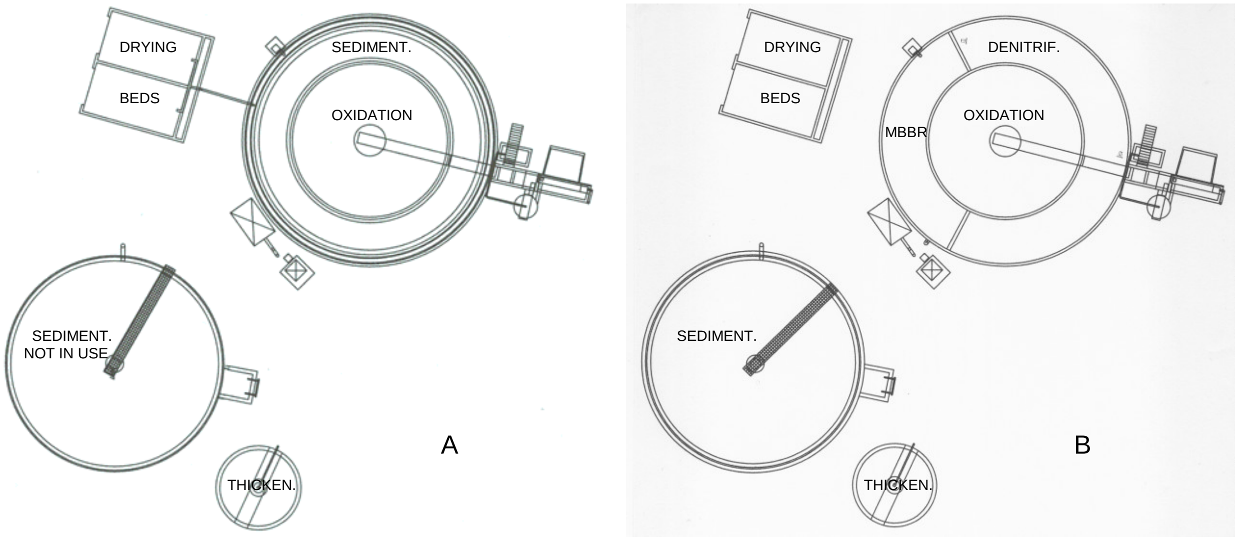
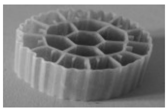


Figure 1: Plant of Porto Tolle in first configuration (A) and after upgrading (B).

Table 1: Characteristics of AnoxKaldnes^{TM} K3 carriers.

Shape	
Length (mm)	12
Diameter (mm)	25
Density (g/cm^3)	0.95
Nr. carriers pr. m^3	144000
Maximum filling degree	66%
Effective specific surface (m^2/m^3 carriers)	500

RESULTS AND DISCUSSION

The plant was modified in July 2013 and restarted with all units in August; carriers were introduced in the MBBR tank in two phases (75% in August and 25% in September). The modified plant was studied in the period 12 August – 22 November; hydraulic load was measured daily and samples were taken every week form raw wastewater and final effluent; results are listed in tab. 2. Average pollutant loads were 90.5 kg$_{COD}$/d, 36.5 kg$_{BOD}$/d and 21.1 kg$_{N}$/d; the plant was modified in order to treat up to 180 kg$_{COD}$/d, 90 kg$_{BOD}$/d and 60 kg$_{N}$/d, so it has still significant residual capacity. Since 15 September, samples of carriers were taken from MBBR every two weeks to determine biofilm concentration, oxidizing activity and nitrifying activity with laboratory batch tests. Biofilm showed significant activity (67 mg$_{COD}$/g$_{TS}$h and 13.8 mg$_{N}$/g$_{TS}$h) since the end of October; its concentration reached 1.1 g$_{TS}$/m^2 (0.27 kg$_{TS}$/m^3 tank); in the same period activated sludge was 2.0-2.8 g$_{TSS}$/m^3.

Table 2: Hydraulic load and pollutant concentrations at the wastewater treatment of Porto Tolle.

Parameter		Raw influent			Final effluent			
		min	average	max	min	average	max	Removal
Hydraulic load	(m^3/d)	306	1587	2208	306	1587	2208	
TSS	(mg/L)	< 10	15	28	< 10	11	32	63%
COD	(mg/L)	< 25	57	214	< 25	25	49	56%

BOD	(mg/L)	< 5	23	111	< 5	6	15	74%
TKN	(mg/L)	6.0	13.3	41.3	< 4	< 4	< 4	85%
NH_4-N	(mg/L)				< 0.5	< 0.5	< 0.5	
NO_2-N	(mg/L)				< 0.1	< 0.1	< 0.1	
NO_3-N	(mg/L)				7.3	10.7	12.4	
Tot-N	(mg/L)	6.0	13.3	41.3	7.3	10.7	12.4	20%

Note: when values were lower than detection limits, for calculations of average values and removal efficiencies they were considered as half of detection limits

CONCLUSIONS

These results confirm that hybrid MBBR is a suitable technology to upgrade existing activated sludge wastewater treatment plants without new tanks. Biofilm showed significant oxidizing and nitrifying activity two months after first carriers introduction. In this plant incoming wastewater is still very diluted, so the plant has significant residual capacity that will be useful during next years, since pollutant load increasing and more strict emission limits for nitrogen are expected.

(10) Food Industry Wastewater Treatment Plant Based On Flotation And MBBR

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Abstract

This paper deals with a plant that treats wastewater of an Italian food industry. The plant was projected to treat 240 m3/d, 1870 kgCOD/d, 1080 kgBOD/d and 96 kg/d oils and greases. The plant is made of a fine screen, an accumulation tank (182 m3), two parallel dissolved air flotation tanks with lamellae (each with footprint 5.6 m2, projected surface 14.4 m2, volume 3.4 m3), a hybrid MBBR oxidation tank (148 m3) filled with 35% AnoxKaldnes K3 carriers, an activated sludge oxidation tank (292 m3) and a sedimentation tank (surface 33 m2, volume 73 m3); sludge is sent to thickening an filter belt press. The plant in 2013 has treated 152 m3/d, 1468 kgCOD/d, 1193 kgBOD/d and 47 kg/d oils and greases; flotation has removed 64% of COD, 70% of BOD and 65% of oils and greases; the whole plant has removed 92% of COD and 96% of oils and greases; it has always respected emission limits and has a significant residual capacity.

PLANT DESCRIPTION

This paper deals with a plant that treats wastewater of an Italian food industry. The plant was projected to treat 240 m^3/d with 7800 mg/L COD, 4500 mg/L BOD, 400 mg/L oils and greases; so expected pollutant loads were 1870 kg_{COD}/d, 1080 kg_{BOD}/d and 96 kg/d oils and greases. Nitrogen and phosphorus were only a few mg/L, so they must be added as chemicals in biological section. The final effluent is discharged into public sewer network, so it must respect these limits stated by the national law 152/2006: TSS ≤ 200 mg/L, COD ≤ 500 mg/L, BOD ≤ 250 mg/L, oils and greases ≤ 40 mg/L. The plant (fig. 1) is made of a pumping station, a drum fine screen (2 mm holes), a stirred accumulation tank (182 m^3), two parallel IFS15 VWST dissolved air flotation tanks with lamellae (each tank with footprint 5.6 m^2, projected surface 14.4 m^2, volume 3.4 m^3), a biological section and the sludge treatment line (thickening, filter belt press). The biological section is made of a hybrid MBBR oxidation tank (148 m^3) followed by an activated sludge oxidation tank (292 m^3) and a sedimentation tank (surface 33 m^2, volume 73 m^3). The hybrid MBBR is filled with AnoxKaldnes^{TM} polyethylene carriers (characteristics in tab. 1) with filling degree 35%. Each biological reactor is aerated by a 480 Nm^3/h blower controlled by an inverter; air is sent to the hybrid MBBR through medium bubble diffusers, to the activated sludge tank through micro bubble diffusers. It was estimated that flotation should remove ca. 50% of COD, 40% of BOD and 75% of oils and greases; therefore the biological section was designed to treat 900 kg_{COD}/d, 600 kg_{BOD}/d and 24 kg/d oils and greases. The first-stage hybrid MBBR was dimensioned to remove ca. 50% of this amount of COD and BOD, thus the second-stage activated sludge reactor was dimensioned to remove ca. 85% of COD and BOD so that the final effluent could respect emission limits.

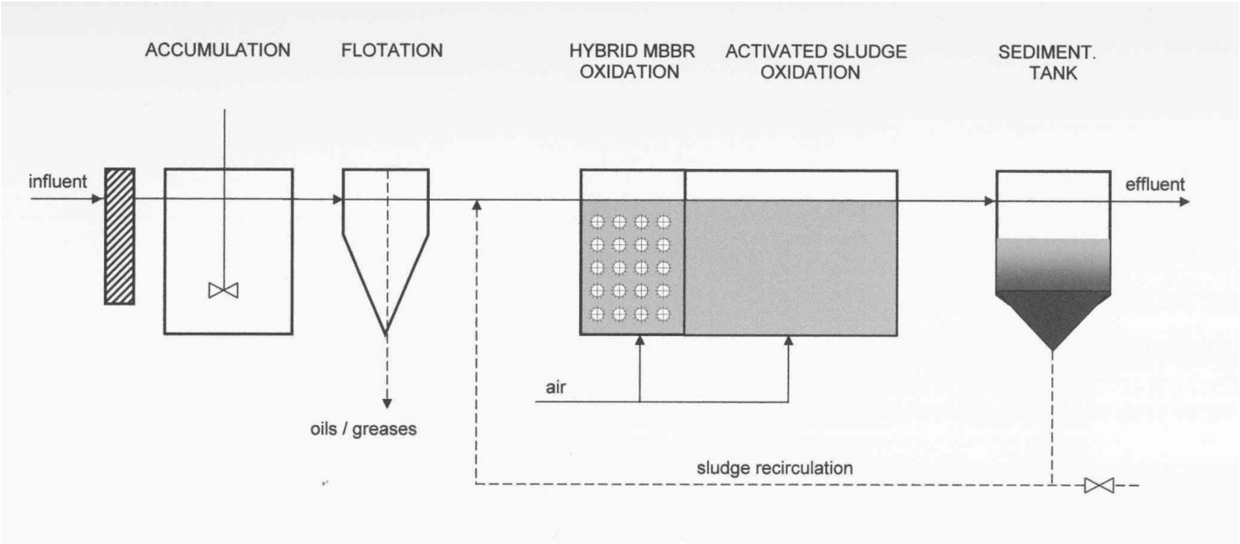
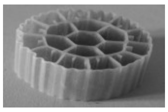


Figure 1: Scheme of the food industry wastewater treatment plant.

Table 1: Characteristics of AnoxKaldnes^{TM} K3 carriers.

Shape	
Length (mm)	12
Diameter (mm)	25
Density (g/cm^3)	0.95
Nr. carriers pr. m^3	144000
Maximum filling degree	66%
Effective specific surface (m^2/m^3 carriers)	500

RESULTS AND DISCUSSION

The plant was started in 2012 and has been studied during year 2013. In this year the hydraulic load has varied between 55 – 237 m^3/d (average value 152 m^3/d); pollutant concentrations in raw influent wastewater, after flotation (average values) and in final treated effluent are listed in tab. 2. On average basis, flotation has removed ca. 64% of COD, 70% of BOD and 65% of oils and greases; the whole plant has removed 97% of COD and 99% of oils and greases, and the effluent has always respected emission limits. Effective pollutant loads are 1468 kg_{COD}/d, 1193 kg_{BOD}/d and 47 kg/d oils and greases; the biological section treats 535 kg_{COD}/d, 354 kg_{BOD}/d and 16 kg/d oils and greases. These values are lower than expected ones, so the plant has a significant residual capacity. The biological section removes 92% of COD and 96% of oils and greases that it receives; but it is not possible to evaluate performances of the hybrid MBBR alone since no intermediate data are available. Average sludge concentration in biological reactors is 12.0 kg_{TSS}/m^3, sludge recirculation rate varies between 100% – 150% of influent hydraulic load.

Table 2: Pollutant concentrations at the wastewater treatment of the food industry.

Parameter		Raw influent			After flotat.	Final effluent			Removal %	
		min	average	max		min	average	max	Flotat.	Plant
COD	(mg/L)	2260	9657	22100	3520	70	280	437	64%	97%
BOD	(mg/L)	1660	7848	15600	2325				70%	
Oils greases	(mg/L)	120	308	560	108	< 0.5	3.8	21.6	65%	99%
NH_4-N	(mg/L)	< 0.5	3.8	33.0		< 0.5	2.9	5.3		
NO_2-N	(mg/L)					< 0.1	< 0.1	< 0.1		
NO_3-N	(mg/L)					< 1.0	< 1.0	< 1.0		
Total P	(mg/L)	3.2	18.3	29.8		< 0.5	4.8	12.8		

Note: nitrogen and phosphorus are added as chemicals after flotation, so removal efficiencies are not calculated; no data are available for BOD in final effluent

CONCLUSIONS

These results confirm that flotation and MBBR in combination with activated sludge are suitable technologies to treat concentrated food industry wastewater. In this plant, flotation had removed 64% of COD, 70% of BOD and 65% of oils and greases, and the remaining amount has been removed with very high efficiencies by the biological section. Effective pollutant loads are lower than expected values, so this plant has a significant residual capacity.

(11) Sludge Reduction Mechanism in Anoxic-Oxic-Settling-Anaerobic Process Based on Carbon Balance

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Abstract

The sludge reduction mechanism of Anoxic-Oxic-Settling-Anaerobic (A+OSA) process, a modification of the anoxic/oxic (A/O) process via insertion of sludge holding tank into the sludge return line, were investigated. The A+OSA process reduced sludge yield by 48.98% under the sludge retention time (7.14 h) in sludge holding tank. The carbon element balance in terms of its solid (S), aqueous (A), and gas phases (G) in the A+OSA process and the AO process were close to 100% for the sludge reduction and reference systems (97.80% and 97.15%, respectively). The carbon percentage in the solid phase of the sludge reduction system was nearly 50% higher than in that of the reference system. The insertion of a sludge holding tank in the sludge return circuit was effective in sludge reduction. Loss of solid-phase carbon was the major portion (over 90%) of the carbon balance in each tank. On the other hand, gas production was the major source (about 60%) of sludge reduction in the carbon balance for both systems. The utilization of aqueous-phase carbon content in the anoxic and oxic tanks (main reaction zones) of the A+OSA system was more efficient than that in the reference system. The amount of carbon consumed for biosynthesis in the main reaction zones of the A+OSA system was higher than in that of the AO system. Sludge decay was observed in the sludge holding tank. The results suggested that excess sludge reduction in the A+OSA system could be a result of the combination of sludge decay in the sludge holding tank and sludge compensatory growth in the main reaction zones.

Keywords

Sludge reduction; Anoxic-Oxic-Settling-Anaerobic process; carbon balance; sludge decay

INTRODUCTION

Municipal and industrial wastewater treatment both domestically and abroad are mainly based on activated sludge process. However, one of the draw backs of during this process is the generation of a large amount of excess sludge. In 2005, 11 million tons dewatered sludge cake (water content of 80%) was produced in China, and it was anticipated that the number will rise to 35 million tons in 2015(Ye et al, 2010; Yang et al, 2011). Huge excess sludge production in wastewater treatment plants (WWTPs) has become a serious problem due to the higher energy consumption and higher treatment cost, so methods of excess sludge reduction are of great interest(Gao et al, 2011). Excess sludge disposal methods that are widely used today may be classified into two broad approaches: post-treatment methods and process reduction methods. The advantage of the latter approach is that it may minimize excess sludge through processing and avoid affecting the efficiency of sewage treatment (Yang et al, 2011). For the process reduction methods, the excess sludge reduction based on classification as: (a) Biological lysis-cryptic growth (High oxygenation), (b) Biological uncoupling of metabolism (High So/Xo, Oxic-Settling-Anaerobic), (c) Maintenance Metabolism (MBR), and (d) Eco-manipulation (Predation) (Khursheed et al, 2011). The OSA process was first developed by Westgarth in 1964. It is a modification of a conventional activated sludge process by inserting a sludge holding tank in the sludge return circuit. The OSA process has been demonstrated to be capable of achieving good sludge reduction without any chemical addition, while effluent quality and settle ability of activated sludge were improved. And it also has a low-cost of capital construction (Wang et al, 2008). Such a sludge holding tank retains thickened sludge from the settling tank under the no air supply condition, which results in an ‘’anaerobic’’ sludge zone in an OSA process (Chen et al, 2003). So inserting a sludge holding tank creates an alternative oxic and anaerobic cycle and a fasting/feasting condition to the exposed biomass, which reduces the excess sludge production effectively (Khursheed et al, 2011).The mechanism of the OSA process has been investigated by various researchers. Chudoba et al (1992) attributed the sludge reduction to the uncoupling mechanism between catabolism and anabolism. Saby et al (2003) and Chen et al(1999; 2003) systematically investigated energy uncoupling, domination of slow growers, and SMPs as possible cause of sludge reduction during the OSA process. Wang et al (2008) concluded that sludge decay in the sludge holding tank of the OSA process is the main reason for the sludge reduction. All these works studied the mechanism of the OSA process only focus on the sludge holding tank, few attentions was paid to the oxic tank and the connection between them. Therefore, further investigation on the carbon balance is needed in order to understand the mechanism of sludge reduction in the OSA process.

The Anaerobic–Aerobic (AO) process receive great attention over the past decades due to its numerous advantages such as high nitrogen removal efficiency, high process stability and reliability, low energy consumption, low chemical consumption, less equipment required and high operational simplicity(Chan et al, 2009). But it still has the problem of generation of excess sludge daily that needs to be processed and disposed of. According to our previous research (Lu et al, 2008), The A+OSA process, a modification of the AO process, may achieve significant excess sludge reduction and nutrient removal efficiency is not severely affected. It seems that OSA process based on different wastewater treatment technology will result in different percent reductions and mechanism of excess sludge reduction. For the A+OSA process, it will be necessary to determine the mechanism of minimize excess sludge production. And the investigation of the carbon balance can be a better way to explain the mechanism of the A+OSA process.

In this work, the carbon element transport in terms of its solid, aqueous, and gas phases in the A+OSA process and the AO process were investigated to assess the fate of carbon during the treatment process. The cause of sludge reduction in the A+OSA system was evaluated through carbon element balances.

MATERIAL AND METHODS

Experimental set-up and operation

Two identical reactors with an anoxic tank having an available volume of 4.0 L, an aerobic tank having an available volume of 12 L and a settling tank having a volume of 4.0 L were used in the two continuous systems. With the A/O system as reference, an anaerobic sludge holding tank with an available volume of 25 L was inserted into the sludge return line in the A+OSA system. The sludge holding and anoxic tanks were mixed by the magnetic stirrer with a speed of 120r/min. The sludge holding tank was also covered with a gas release outlet to keep the gas pressure balanced. No injection of pure nitrogen for ORP control of the sludge holding tank is provided, which was to make the technology more suitable for full scale application. The influent flow rate in both systems was maintained at 48.96*L*/day by peristaltic pumps, with return sludge recycle ratio of 100% and internal recycle ratio of 200%. Sludge discharges in the sludge reduction and reference systems were permitted daily to maintain the MLSS content in both oxic tanks at 2500 *mg*/L. The temperature of two systems was controlled at 25±1 °C using a water bath. The dissolved oxygen (DO) concentration in the anoxic was kept at 2.5–3.5 *mg*/L by air flow meter with the air pumps to supply air. The HRTs in the anoxic, oxic, and sludge holding tanks were 1.92h, 5.56h, and 7.14 h, respectively. The COD loading rate, DO, HRT, and MLSS in the anoxic and aeration tanks of the A+OSA system were all maintained at the same levels in the two systems. A diagram of the systems is shown in Fig. 1.

The seed sludge was taken from a local sewage treatment plant (Chongqing, China). The synthetic wastewater was continuously fed to the two systems. The composition of the nutrients in the synthetic media were same as flow: glucose (300 *mg*/L), sucrose (166.7 *mg*/L), peptone (100 *mg*/L), $NaHCO_3$ (675 *mg*/L), NH_4Cl (225 *mg*/L), $MgSO_4 \cdot 7H_2O$ (113.6 *mg*/L), $CaCl_2 \cdot 2H_2O$ (75 *mg/*L), KH_2PO_4 (219.4 *mg*/L), and nutrient solution (1.25 *ml*/L). The nutrient solution consisted of the following compounds per liter: 1.3 g of $ZnSO_4 \cdot 7H_2O$, 0.28 g of $CuSO_4 \cdot 5H_2O$, 0.6 g of $MnCl_2 \cdot 4H_2O$, 0.1 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.05 g of $FeCl_3$, and 0.003 g of $CoCl_2 \cdot 6H_2O$. The characteristics of the synthetic wastewater were shown in the Table 1.

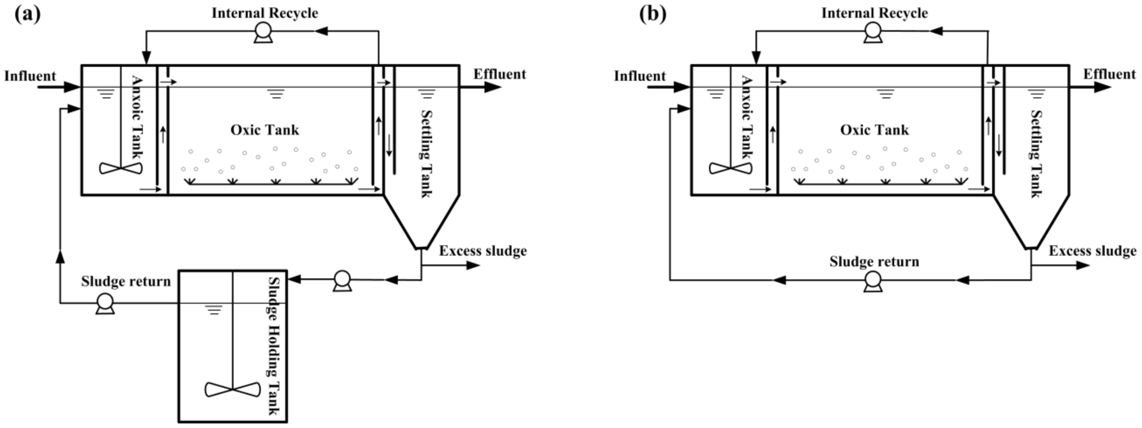

Figure 1.Schematic diagram of A+OSA (a) and AO (b) experimental setups

Table 1. Characteristics of the influent

Parameter	Value (*mg*/L)
COD	430–620
pH	6.5-7.5
Total nitrogen	48–62
Ammonium nitrogen	49–58
Total phosphorous	5–8

Batch experiments

The bath experiments were conducted in the reactor with 1.0 L volume with sludge taken from the anoxic and toxic tanks in both system and sludge holding tank in A+OSA systems, respectively(as shown in Fig.2). The contents of the anoxic and anaerobic batch reactors were well mixed using a magnetic stirrer at 25±1°C. Batches of 1#, 2#, 3#, and 4# were controlled by check valves, which were appropriately adjusted to well maintain the reaction condition during the experiment. Prior to and after biogas collection, pure argon was continuously injected into each batch reaction for about 5 min. The purpose was to remove or collect completely CO, CO2, and CH_4 inside the reactor. The sludge of the first batch experiment was taken from the influent, uniform mixed liquor in the sludge holding tank, and return mixed liquor in the A+OSA system. The ratio of the components was 1:1:2. The sludge of second batch experiment was inoculated from the influent, uniform return sludge, and return mixed liquor in the AO system and the ratio of the components was 1:1:2. The sludge of third and fourth batch experiment was taken from the uniform mixed liquor output of the anoxic tank in the A+OSA and AO systems, respectively. The sludge of fifth and sixth batch experiment was taken from the uniform return sludge in the A+OSA system. The reaction times were in accordance with the designed HRT in each tank. The gas emitted from each reactor was collected in gas bags for COD analyses. To ensure data accuracy, liquid samples before the experiments were collected from the reactors. These samples were used to analyze parameters related to sludge and sewage, which would be the same with those in the systems when compared. The possible fate of elemental carbon in both systems should include that discharged with the final effluent and waste sludge (aqueous and solid phases), as well as the emission of gaseous products. The fate of elemental carbon was calculated based on the following mass balance:

$$m_{in} = m_{out} + m_{sludge} + m_{gas}$$

m_{in}, m_{out}, m_{sludge} are the carbon masses in the influent, final effluent, and waste sludge, respectively (in g), calculated based on the relevant carbon concentrations. m_{gas} is the carbon mass released from the systems (in g).

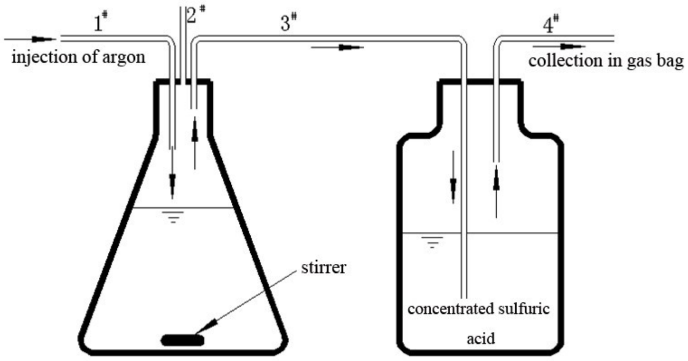

Figure 2. Experimental setup of the biogas collection

Analytical methods

Chemical organic demand (COD) was determined using a HACH COD kit and meter. The total carbon (TC) in the filtrate was measured using a TC analyzer (Liqui TOC, Elementar, Germany). The carbon content in the dry biomass was detected by an element analyzer (Vario EL III, Elementar, Germany). All samples were immediately filtered through a vacuum filter with a 0.45 µm prewashed membrane, and the filtrate was collected. The filtered sludge was oven dried at 103–105 °C until a constant weight was reached. The dried samples were then crushed into a powder using a mortar and pestle. For the analytical application, the particle size included did not exceed 200 meshes. The concentration of CO, CO_2, and CH_4 was assayed by a gas chromatograph (Agilent Technologies, Avondale, PA, USA) equipped with a thermal conductivity detector. The GC column was 8 ft × 1/8 in. × 0.085 in. Suspended solids packed with Haye Sep Q (80/100 mesh) designed for reactive gas mixtures of air, methane, and carbon dioxide were used. Helium was used as the carrier gas at a constant flow of 30 mL/min. A mixture with a certified composition of CH_4, CO_2, and CO gases of known purity was used as the standard for calibration. A sample volume of 2 mL was injected for analysis.

RESULTS AND DISCUSSION

Excess sludge reduction in the A+OSA system

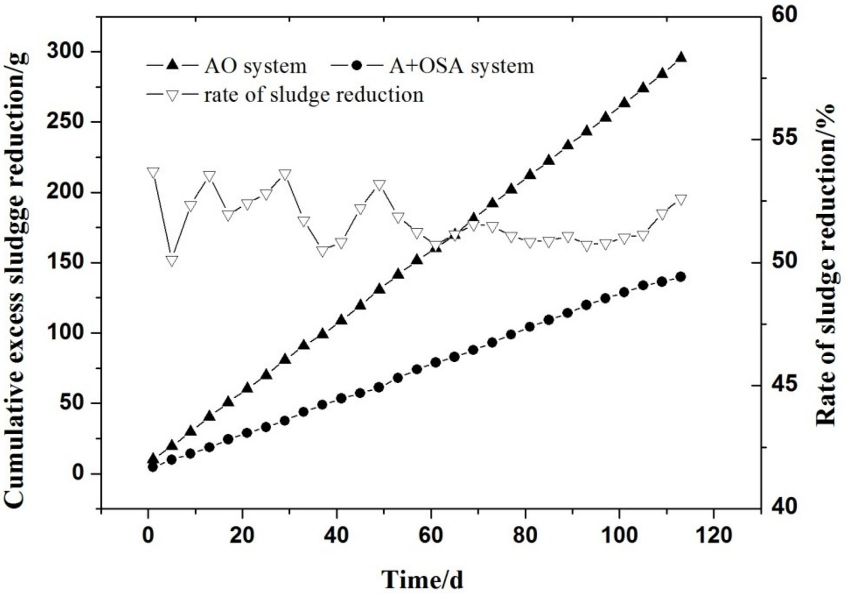

Figure 3. Cumulative sludge productions in the A+ OSA and the AO systems

Fig.3 summarizes the cumulative reduction of sludge under 7.14 of HRT in the sludge holding tank. The excess sludge was discharged when MLSS levels of oxic tanks were above 2500 mg.L^{-1} in the two systems. And the cumulative excess sludge discharged was recorded. Compared with the AO system of excess sludge production rate of 2.46 g SS/day, the excess sludge production rate averaged 1.17g SS/day (reduced by 49.98%)in the A+OSA system. It can be concluded that the A+OSA system can reduce excess sludge effectively under 7.14 of HRT in the sludge holding tank. In precious studies, OSA systems based on different wastewater treatment system on the excess sludge reduction have been studied. Saby et al(2003) studied the effect of ORP levels in the sludge holding tank on the sludge reduction efficiency of the MBR-OSA system. They found when the ORP level was up to -250 mV and 10.4h of HRT in the sludge holding tang, the sludge reduction efficiency can reach 58%. But to maintain ORP level, the injection of pure nitrogen was necessary to provided. Chudoba et al (1992) also found that the SBR-OSA process can reduce excess sludge by 40%-50% when sludge is retained in the anaerobic tank for 3h when the ORP level kept at -250 mV. Due to the different experimental conditions of the OSA system, it is difficult to compare the results with obtained from this study with the others. But in our study, we confirm that the A+OSA system can reach an acceptable sludge reduction without pure nitrogen injection. And this can save the cost and be facilitating for application at an industrial scale. In our previous research (Lu etal, 2008), the A+OSA technology, can achieve significant biomass reduction and nutrient removal simultaneously. But the sludge reduction mechanism about this system needs to be clarified further.

Carbon balance in the A+OSA and AO systems

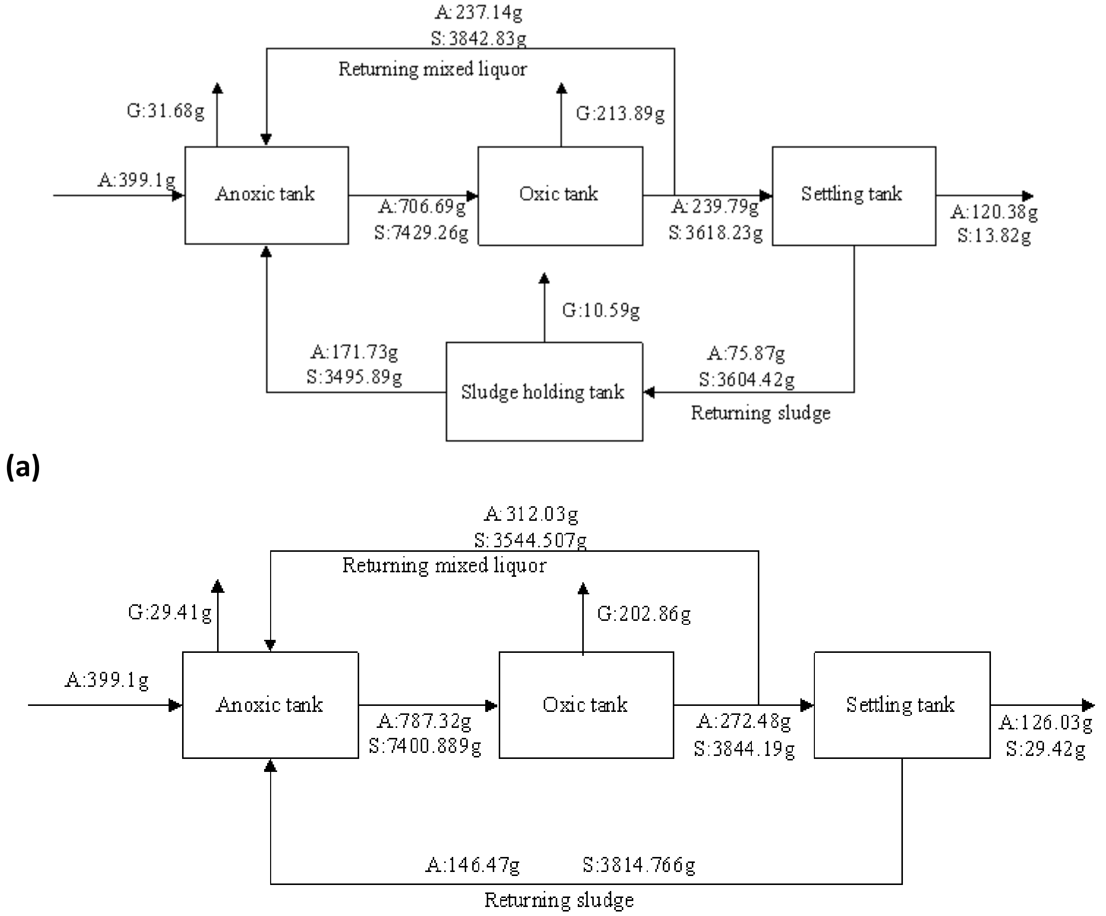

Figure 4.Carbon distributions in the A+OSA (a) and AO (b) systems(30d).

The carbon transfer flow in the A+OSA and AO systems for 30 d of stable operation was shown in the Fig.4. Except for the influent, return sludge, and return mixed liquor, a sample of mixed liquor in each reactor was collected. The carbon contents in the aqueous and solid phases were separately determined. The gas production was also calculated during the batch experiments. The cumulative biogas from the A+OSA system was the sum of the gas emissions from the anoxic, oxic, and sludge holding tanks. The biogas from the reference system was the sum of the biogas emissions from the anoxic and oxic tanks. Initially, carbon in the inlet sewage was the sole carbon source in the two systems. However, with the degradation and sorption by the activated sludge in the systems, carbon was either converted into biogas or discharged in the final effluent and waste sludge. By comparing the initial and final total carbon masses in both reaction systems, only 2.2% and 2.8%, respectively, of the carbon source could not be accounted for. The missing carbon may be attributed to measurement errors from the use of different analytical methods. Similar results have been reported in an earlier research (Lee et al, 2008) where 4.5%, 3%, 4.5%, 0.5%, and 4.5% of the nitrogen input is lost in the nitrogen balance of a sequencing batch reactor system for five runs, respectively. In another study(Ross et al, 2008) on the COD balance in two batch experimental reactors simulating the anaerobic conditions in the sludge holding tank of an OSA sludge reduction process, 6.6% and 4.3% of COD levels are also unaccounted for. Therefore, the measurement errors in the present experiments were acceptable, and the carbon was considered to be balanced.The balances were obtained by estimating the total amounts of carbon input and output in each tank of the A+OSA and AO systems in the aqueous, solid and gas phases, respectively, for 30 d of steady operation. The results of the mass balance calculation in each tank indicated that approximately 91.22%–94.99% remained in the solid phase output, 4.67%–8.68% remained in the aqueous phase output, and only 0.003%–2.63% accumulated in the gas phase. The percentage of carbon mass balance for each tank was calculated from the ratio of the amount of carbon output to input. The results for the anoxic, oxic, and sludge holding tanks were 100.29%, 100.19%, and 99.66%, respectively. Hence, the fate of carbon in each tank of the A+OSA system could be accounted for, with mass balances close to 100%. The carbon of 90.07%–90.24%, 7.10%–9.58%, and 0.36%–2.48% (with respect to the total carbon input in each tank) remained in solid, aqueous, and gas phase outputs in each tank in the AO system, respectively. The results in the anoxic and oxic tanks were 100.01% and 99.82%, respectively. Carbon was considered to be balanced in the anoxic and oxic tanks. Therefore, carbon loss in the solid phase was the major portion in each tank. With respect to each entire system, the carbon balance results revealed that gas production was the major cause of sludge reduction.

Cause of sludge reduction in the A+OSA system

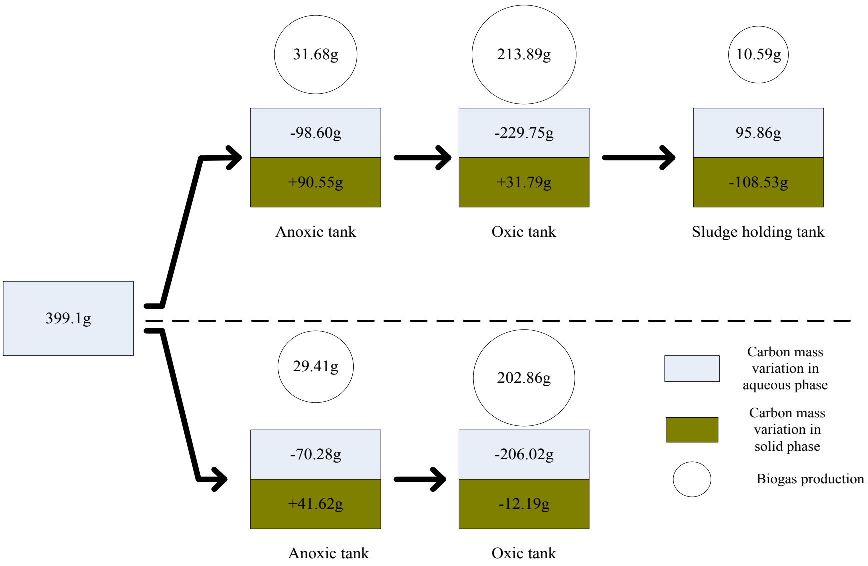

Figure 5. Carbon transfer in the A+OSA and AO systems

As shown in the Fig. 5, Carbon content in the aqueous phase in the anoxic tanks of A+OSA and AO systems was decreased by 98.60 and 70.28 g, respectively. These values accounted for 12.2% and 8.2% of the total carbon content in the anoxic tank in the aqueous phase input, respectively. Clearly, the removal capability of the A+OSA system for carbon content in the aqueous phase in the anoxic tank was greater than that of the reference system. Carbon content in the aqueous phase in the oxic tanks of two systems was decreased by 229.75 and 206.02 g, respectively. These values accounted for 32.5% and 26.2% of the total carbon content in the oxic tank in the aqueous phase input, respectively. The percentages of escaped gaseous products produced under anoxic (0.39% and 0.36%, respectively) and oxic (2.63% and 2.48%, respectively) conditions in both the sludge reduction and reference systems were nearly the same. The utilization of carbon content in the aqueous phase in the anoxic and oxic tanks (main reaction zones) of the A+OSA system was more efficient than that in the AO system. Obviously, the amount of carbon consumed for the biosynthesis in the main reaction zones of the A+OSA system was higher than in that of the AO system. The content of total carbon increase in the solid phase in the two systems (13.81 and 29.43 g, respectively) was consistent with the carbon contents in the excess waste sludge (13.82 and 29.42 g, respectively). For 30 d of stable operation, the carbon quantities in the sludge holding tank and main reaction cells of the A+OSA system were -108.53 and 122.34 g, respectively. The carbon quantity in the AO system was 29.43 g. These data suggested that sludge decay occurred in the sludge holding tank, resulting in increased carbon content in the aqueous phase. The increased carbon mass in the main reaction zones was significantly higher than in the AO system. Hence, carbon accumulation in the solid phase was evident in the main reaction zones of the A+OSA system under the cyclic anoxic/oxic/anaerobic environment. Compared with the reference system, the insertion of a sludge holding tank in the sludge return pipeline may have resulted in the formation of a special microbial population. This phenomenon could account for the obvious difference between the sludge reduction and reference systems. Methanogens and other hydrolytic-fermentative bacteria may develop in the sludge holding tank. These microorganisms could influence sludge disintegration to a certain extent and lead to sludge decay. These phenomena warrant further studies. From the carbon balance of the A+OSA and AO systems, 64.18% and 58.20% of carbon in the influent were converted to biogas, respectively. On the other hand, 30.16% and 31.58% were converted into aqueous forms, respectively. Meanwhile, solid-phase carbon was produced in very small proportions (3.46% and 7.37%, respectively). Compared with the reference system, an almost 50% decrease in the solid phase was found. This finding supported the conclusion that a sludge reduction rate of 49.98% could be achieved in our experiment. In a previous study (An et al, 2003), the excess sludge production rate was only 2.3 g/d, almost half that of the reference system (4.7 g/day). Therefore, the A+OSA system effectively reduced excess sludge.

Regarding the main reaction zones, sludge production compensated for the loss of decay via exposure in the sludge holding tank. Sludge growth yield in the main reaction zones of the A+OSA system was higher than in that of the AO system, referred to as “growth.” The so-called “compensation” was relative to the sludge decay in the sludge holding tank. With respect to the reference system, sludge growth substantially increased in the main reaction zones of the A+OSA system following sludge decay in the sludge holding tank. This phenomenon of sludge growth is denoted as “compensatory growth” in the present study. Compared with the conventional AO process, the amount of sludge reduction in the A+OSA system should be the difference of the amount of sludge decay in the sludge holding tank and sludge compensatory growth in the main reaction zones. The amount of sludge compensatory in the main reaction zones in the A+OSA system is the difference of sludge production in the main reaction zones of the A+OSA system and the overall sludge production in the AO reference system. Consequently, when the sludge was exposed to the starved and stressful environment in the anaerobic tank, the sludge degraded. In turn, compensatory growth was generated in the subsequent anoxic/oxic environment in the presence of adequate food in the main reaction zones. The anaerobic reactor inserted in the recycling bypass of the sludge was the key unit of the OSA process. Therefore, the excess sludge reduction by the A+OSA system was caused by sludge decay in the sludge holding tank and sludge compensatory growth in the main reaction zones.

CONCLUSIONS

The effect of inserting a sludge holding tank into a sludge return pipeline on the fate of carbon in its solid, liquid, and gas phases in the A+OSA process was studied. The main results obtained were as follow: (1) the carbon balances in the sludge reduction and reference systems were 97.80% and 97.15%, respectively. (2) The solid-phase carbon loss comprised a major portion (over 90%) of the carbon balance of each tank. Gas production was the major source (about 60%) of sludge reduction for the entire systems. (3) The utilization of carbon content in the aqueous phase in the anoxic and oxic tanks of the A+OSA system was more efficient than that in the reference system. The amount of carbon consumed for the biosynthesis in the main reaction zones of the A+OSA system was more than in that of the AO system. Sludge decay was observed in the sludge holding tank. (4) Excess sludge reduction in the A+OSA system could be caused by sludge decay in the sludge holding tank and compensatory growth in the main reaction zones.

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(12) Water Denitrification by Using Wheat Straw and Sponge Iron

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Abstract

A heterotrophic/autotrophic denitrification (HAD) approach supported by wheat straw and sponge iron was proposed for nitrate removal from nitrate rich water. Four parallel up-flow laboratory column reactors made of PVC (90 cm height and 10 cm internal diameter) were employed in this study. The first reactor was solely packed with 200g wheat straw (wheat straw supported denitrification, WSSD) , the other three HAD reactors were packed with 200g wheat straw as well as 20g sponge iron at different levels of the reactor (bottom, middle and top). The results showed that all of the four reactors had significant performance on water denitrification. They all can reduce the concentration of nitrate from 22.6mg N/l to below 0.04 mg N/l within three days, and can maintain high denitrification performance for nearly two months. Comparing with the WSSD reactor without sponge iron, the HAD reactors with sponge iron had an obvious better deoxygenation performance. However, there was not much difference in denitrification performance among the three HAD reactors with sponge iron packed at different levels.

Keywords
Denitrification; HAD; nitrate; wheat straw; sponge iron

INTRODUCTION

Nitrate pollution of water constitutes an important and rapidly growing environmental problem in developed and developing countries (Hiscock et al., 1991). Among various methods (physical, chemical, physico-chemical and biological) available for the removal of nitrate, biological denitrification (BD) is considered to be the most economical and environmentally sound and to be feasible on a large scale (Soare et al., 1998). Biological Denitrification (BD) falls into two groups: (1). heterotrophic denitrification (HD) which requires an anaerobic and organic carbon-rich environment, and (2). autotrophic denitrification (AD) which requires an anaerobic and inorganic carbon-rich condition (Soare 2000). Some previous studies have shown that the HAD approach had a very good performance in removing nitrate from nitrate rich drinking water and groundwater (Della Rocca et al. 2006, 2007; Huang et al. 2012). The objectives of this study were to: (1) examine the HAD performance by using wheat straw and sponge iron; (2) compare the denitrification performance among the four different column reactors, and determine if the position of packing sponge iron affect the HAD performance; (3) investigate deoxygenation capacities of the HAD and the change of TOC and IC value in the systems.

MATERIAL AND METHODS

Chemicals and Reagents

Granulated spongy iron (Fe0, 60.60 %; 0.425–1.000 mm in diameter) was obtained from Kaibiyuan Co., Beijing, China. Wheat straw was obtained from Sandersons Grain & Fodder Store in Adelaide, Australia. Sodium nitrate and dipotassium phosphate were used to spike tap water, and the inlet nitrate (as N) and phosphorus concentration was 22.6mg/l and 3mg/l (N: P =22.6:1), respectively.

Analytical Measurements and Sampling

Inorganic nitrogen (NO3-N, NO2-N, and NH4-N) was analyzed using a FOSS-Tecator FIAStar 5000 flow injection analyzer (Sweden) equipped with a FOSS 5027 Auto Sampler. DO and pH were measured using a digital DO meter (Model 9143, Hanna, Italy) and a pH meter (Model 8417, Hanna, Italy). TOC and IC were measured using a TOC analyser (Model TOC-L CSH, Shimadzu, Japan). Four parallel up-flow laboratory column reactors were employed in this study (fig. 1). The first reactor was solely packed with 200g wheat straw, the other three reactors were packed with 200g wheat straw as well as 20g sponge iron at different levels of the reactor (bottom, middle and top). The flow rate of the four reactors was maintained at 1.2ml/min. Samples were taken from the outlet on a regular basis and stored in the cool room at around 3 Celcius degree before analysing.

RESULTS

All of the four reactors had significant performance on water denitrification. They all can reduce the concentration of nitrate from 22.6mg N/l to below 0.04 mg N/l within three days, and can maintain high denitrification performance for nearly two months (fig. 2). However, there was not much difference in denitrification performance among the three HAD reactors with sponge iron packed at different levels during the experiment period (fig. 3). Comparing with the WSSD reactor without sponge iron, the HAD reactors with sponge iron had an obvious better deoxygenation performance (fig. 4). TOC value was expected to decrease during the whole experiment period as the organic carbon was washed out from the reactors continually. However, on the third day, TOC of all the four reactors reached the maximum value. The value began to drop until the 20th day, then it increased again until the end of the experiment (fig. 5). Meanwhile, IC value had considerable fluctuations during the whole experiment period (fig. 6).

CONCLUSIONS

The HAD reactors supported by wheat straw and sponge iron had significant performance in removing nitrate from nitrate rich water. Sponge iron had an obvious effect of deoxygenation in the HAD systems. The population of denitrification bacteria in the HAD systems needs to be investigated in the further study.

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(13) Integrated technology for improved energy balance and reduced greenhouse gas emissions at WWTPs

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Abstract

State of the art solutions for WWTPs call not only for meeting stringent effluent quality standards but also for maximum energy recovery. Typically aeration consumes over 50% of total plant energy requirements where nitrification is one of the most energy consuming processes. The increasing sludge production is causing serious problems with its management. The aim of the project is to develop a novel sustainable technology that combines increased biogas production with enhanced nutrients removal from reject water. Through the enhanced primary treatment by organic coagulant/flocculant addition the organic load of biological treatment is reduced while the primary sludge production for digestion is increased. To prevent carbon shortage for denitrification and phosphorus removal, the nitrogen load can be reduced by using partial nitrification and anammox processes, whereas, remaining nutrients in the effluent can be reduced in algae or wetland system.

Keywords

Environmental engineering; process optimisation; wastewater treatment plant;

INTRODUCTION

The current regulation for wastewater treatment plants (WWTPs) focuses almost entirely on local water quality, at the unrecognised life cycle impacts mainly through energy consumption and greenhouse gas (GHG) emissions. In the face of the progressing global warming effect, there has also been a change of thinking within the wastewater treatment sector. The conflict has been identified and tackled with respect to protection of receiving water bodies by all technical means available and the high energy input (use of resources) and GHG emission. Optimization of existing treatment processes and development of new innovative, energy-efficient processes, especially for nitrogen removal, have been the key objectives during the last years.

DISCUSSION

The aim of the project is a practical application of sustainable management in municipal WWTPs by energy recovery and reduction of GHG emissions. The project focuses on both increasing the energy production in a WWTP by enhanced primary treatment with organic coagulants and the development and implementation of a novel technology of nutrient removal from sludge digester liquors in order to reduce the energy consumption. This technology includes the anammox (Anaerobic Ammonium Oxidation) process followed by algae or wetland systems. The technology is completed by the processes leading to an increased biogas production by coagulation/flocculation of organic colloids and particulates in the primary clarifier and additional sources of biomass from the algae growth. The results obtained in the experimental part of the project will be the basis for an energy balance and an estimation of the GHG emissions from wastewater treatment processes. It is expected that implementing this integrated technology will lead to a major reduction in consumption of natural resources and non-renewable resources as well as reduction of air and water pollution emissions. The structure of the project is presented on the Fig. 1.

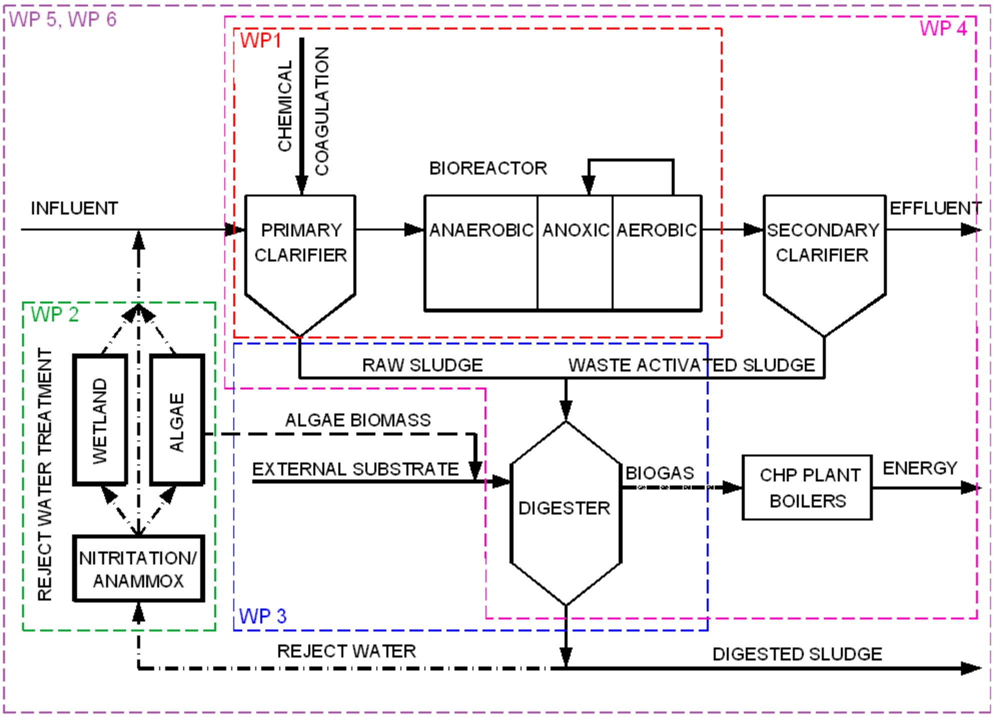

Figure 1. Graphical structure of the Baritech project

CONCLUSIONS

The outcome of the project will be practical application of sustainable management including technology, energy, greenhouse gases emission and economy aspects of WWTP activity. It is expected that the implemented technology will lead to a major reduction in consumption of natural resources and changes in application of non-renewable resources in technological processes, reduction of air and water pollution emissions and reduction of environmental degradation.

Acknowledgments

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(14) URWASTECH: Innovative urban waste treatment by using hydrodynamic and biological technologies

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Abstract

The results presented in this paper refer to an innovative environmentally friendly strategy that merges both urban rest fraction and wastewater management. Concretely, URWASTECH, which is developed within the EU LIFE+ Program, uses a hydro mechanical separation where the effluent from mixing the rest fraction of urban solid waste (RF-USW) and urban wastewater (UWW) goes to a biological treatment. This biological treatment is based on anaerobic digestion (AD) for organic matter valorization followed by a membrane biological reactor (MBR) and wetlands technology for wastewater treatment.

URWASTECH demonstrates that an alternative more efficient USW treatment can be performed. Lab scale trials with the mixture of RF-USW and UWW gave some trends (COD removal (62%) and high quality biogas (58% CH_4)) to determine the adequate conditions to optimize the process. This information has been used for the designing and construction of a complete demonstration pilot plant focused on obtaining (1) more production and quality of biogas compared to conventional treatments, (2) depurated water ready for further applications, (3) other valorizable fractions such as plastic metals and biomass waste as a potential compost and, as a consequence of the abovementioned, (4) to reduce the amount of organic matter disposed to landfill.

Keywords
Urban solid waste; urban wastewater; biogas; depurated water; waste disposal reduction

The selective collection and separated management of the organic matter, plastics and packaging, glass, paper and cardboard and other special fractions as profitable and recyclable residues are already well established in several countries. On the other side, the remaining waste named rest fraction, a mixture of wastes non-originally separated, is usually sent to landfill or incineration. The amount of organic matter in the rest fraction is considerable, so mechanical treatments are used to recover the organic matter that composes the rest fraction. However, such "organic matter" still contains an important amount of undesirable materials such as plastics, metals, textile, etc.

URWASTECH's main goal is the development of an eco-innovative and integrated pilot plant for the efficient management of this rejected fraction of urban solid wastes (RF-USW), based on the joint treatment of both solid waste and urban wastewater (UWW).

The proposed process (Figure 1) is based on the hydro-mechanical separation of materials contained in the RF-USW by using UWW as a solvent. This process will transfer the organic fraction of the RF-USW to the UWW via suspension/dilution. From this currently underused organic matter that is nowadays disposed in

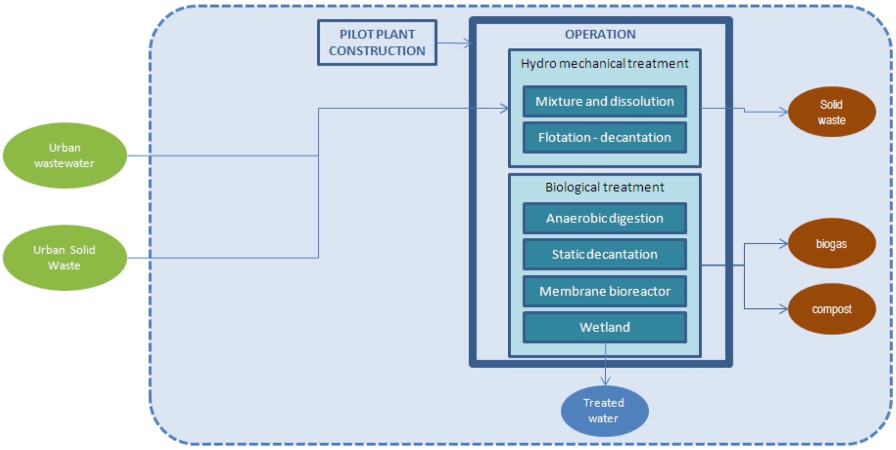

Figure 1. Urwastech strategy

landfill, further anaerobic digestion (AD) process will permit energy recovery. Aqueous effluent from the digester will be subsequently treated by a MBR and a wetland assuring depurated water for further applications.

Table 1 summarises the wastewater composition before and after its mixing with RF-USW during lab scale trials. The hydro-mechanical process increased the organic matter content and conductivity in UWW. Ammonium and metal contents (data not shown) in resulting UWW were found to be below the values reported to be inhibitory towards the different types of anaerobic microorganisms (Chen et al., 2008). Hence, the resulting wastewater was suitable for further anaerobic treatment.

Table 1. Composition of wastewater before and after the hydro-mechanical separation unit.

	H	Conductivity	ST	SV	COD	BOD_5	NH_4^+	Total-C	Total-N
		(µS/cm)	(mg/L)				(%)		
Raw UWW	7.68	2.60	n.d.	n.d.	1,104	717.6	n.d.	n.d.	n.d.
UWW after mixing with RF-USW	5.70	6.40	5,158	2,286	16,1	8,43	192	32.92	3.32

The lab anaerobic digester was operated in batch mode and in continuous mode. Obtained data elucidated that treating UWW mixed with RF-USW by using AD technology is a feasible and efficient option. Hence, the bases for a continuous operation mode were established, considering it the most economically suitable process as high amounts of USWs are produced in continuous manner. Obtained results during lab scale trials led to the design and construction of a pilot plant for further testing and demonstration at larger scale (Figures 2 and 3).

Figure 2. Hydro mechanical Unit

Figure 3. Biological Unit+Wetland

Ongoing experimentation is being performed at the pilot plant. It is focused on increasing organic load rate to achieve continuous COD removal while increasing biogas production as well as depurating wastewater. Preliminary results allow demonstrating the viability of proposed URWASTECH strategy; the organic matter from RF-USW can be valorised instead of being disposed to landfill in an environmentally friendly approach.

The technology allows the improvement of the /valorisation of organic matter in RF-USW, producing a high amount of biogas and high quality depurated water. This implies economic revenue and also a decrease of current processing costs in USW treatment.

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(15) Respirometric Evaluation of Ultrasonication Effect on the Characteristics of Domestic Sludge

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Abstract

This study investigates the potential of ultrasonication, a minimization technique for the generation of readily biodegradable substrate. Ultrasonic specific energy of 2000 to 50000 kJ/kg TS was studied with variable sonication time to obtain the optimum value for anaerobic stabilization. Specific energy input of 3700, 9500 and 23500 kJ/kg TS were selected for further respirometric analyses regarding on the soluble COD (SCOD) release, sludge dewaterability characteristics, subsequent anaerobic stabilization performance. Activated Sludge Model No.1 was used to predict the COD components in the ultrasonicated sludges. Experimental evaluation indicates that 3700, 9500 and 23500 kJ/kg TS of ultrasonic specific energy applications converted 18.4, 11, and 12% of the initial total COD in the sludge into biodegradable COD, respectively.

Keywords

Biodegradability; COD components;sludge stabilization; modelling; minimization

INTRODUCTION

A large amount of waste activated sludge (WAS) is generated in wastewater treatment plants and the cost of sludge management increases tremendously due to the expansion of population and industry. Anaerobic stabilization is known to be a conventional and economical method as it reduces the sludge volume, generates energy-rich biogas in the form of methane and produces a stabilized sludge (Eskicioglu et al., 2006). However, anaerobic stabilization has often been limited due to the longer retention time and low degradation efficiency of WAS. WAS comprises microorganisms together with various organic and inorganic matter in a matrix formed by microbial extracellular polymeric substances (EPS) (Khanal et al., 2007). Generally, the hydrolysis of EPS and microbial biomass limits the rate and extent of degradation. Pre-treatment methods disintegrate the sludge flocs to improve the biodegradability of WAS and increase the biogas production. Ultrasonic pre-treatment (sonication) disrupt the sludge flocs, lyse the cells and facilitate the release of intracellular matter (Pilli et al., 2011). COD components identifying fractions with different biodegradation rates have been a milestone in understanding and modeling the substrate utilization (Cokgor et al., 2009, Orhon and Okutman 2003). This approach recognizes biodegradable and inert fractions in the available COD and differentiates at least two or three groups of biodegradable compounds subject to different biochemical mechanisms, namely, readily biodegradable COD, S_S, rapidly hydrolysable COD, S_H and slowly biodegradable particulate COD, X_S. Respirometric measurements have been proposed and widely implemented as scientifically acceptable and technically reliable procedures for this purpose. They rely on the assessment of the oxygen uptake rate profile, (OUR), of the biomass fed with the tested wastewater/substrate/sludge at a selected food to microorganism ratio, under controlled conditions. The area under the OUR profile gives the amount of oxygen consumed, which directly relates to different substrate fractions utilized in the course of the experiment. The profile can also be interpreted by means of model simulation to evaluate stoichiometric and kinetic coefficients. The objective of this study was to evaluate the production potential of biodegradable COD components through ultrasonication of sludge.

MATERIALS AND METHODS

Sludge samples were obtained from a biological wastewater treatment plant removing nutrients located in Istanbul. Wastewater treatment plant serves 2400000 people by operating with a 400000 m^3/day of biological treatment capacity. The main units of the plant are primary sedimentation, biological treatment units, secondary sedimentation for wastewater; thickening, anaerobic digestion, dewatering and drying for sludge. Sludge samples were withdrawn from aeration tank operated with a sludge retention time of 10 days. The ultrasonic disintegration was performed with an ultrasonic homogenizer (Bandelin Sonopuls HD 2200, Berlin, Germany) equipped with a VS 70T probe. The ultrasonic unit has an operating frequency of 20 kHz and a power supply of 200 W. The amplitude of 100% was applied for a 200 mL of WAS sample which resulted in a sonication density of 1 W/mL. Ultrasonic specific energy of 2000 to 50000 kJ/kg TS was investigated with variable sonication time to obtain the optimum value for anaerobic stabilization. The solubilisation of waste activated sludge due to ultrasonic disintegration was assessed in terms soluble COD and the extent of sludge disruption was determined by the calculation of disintegration degree. The selected optimum specific energy values of 3770, 9500 and 23500 kJ/kg TS were applied for respirometric analyses. All analyses of conventional parameters were performed as defined in Standard Methods (2005) except for COD measurements (ISO6060, 1986). OUR measurements were conducted with Applitek RA-1000 continuous respirometer. The respirometric results were interpreted using Activated Sludge Model No.1 (Henze et al., 1987, Orhon and Artan, 1994, Cokgor et al., 2006). AQUASIM software is used for the parameter estimation and calculation of confidence intervals of the model parameters (Reichert et al., 1998).

RESULTS AND DISCUSSION

This study was part of a comprehensive survey conducted on the characterization and anaerobic treatability of domestic WAS using ultrasonication for pre-treatment. Total COD, suspended solids and volatile suspended solids concentrations of the WAS were around 12200, 12050 and 8000 mg/L, respectively. The raise in the specific energy input increased the COD solubilization significantly (Fig. 1). The maximum COD solubilization was observed for 50000 kJ/kg TS with a SCOD value of 4500 mg/L. However, high specific energy inputs deteriorate the sludge dewaterability and do not improve the biogas yield. Specific energy beyond 22000 kJ/kg TS and 10000 kJ/kg TS was reported to be resulting in deterioration of sludge dewaterability and biogas production, respectively (Pilli et al., 2011). In this study, the potential of ultrasonication for the generation of biodegradable substrate was also determined. Specific energy input of 3700, 9500 and 23500 kJ/kg TS were selected as the optimum values for further respirometric analyses regarding on the SCOD release, sludge dewaterability characteristics, subsequent anaerobic stabilization performance. At the end of the ultrasonication application, the contents of the samples were subjected to respirometric analysis. Respirometric methods rely on evaluating the area under the OUR curve, excluding the fraction associated with endogenous respiration and calculating its COD equivalent using the basic relationship between substrate COD utilized and oxygen consumed. The respirometric profile were used to estimate biodegradable COD fractions together with biodegradation kinetics according to Insel et al. (2003). Fig. 2 illustrates the respirometric data and the modelling results obtained after the ultrasonication application with the specific energy input of 3700 and 23500 kJ/kg TS. Interpretation of the OUR measurements for the assessment of different COD components for disintegrated sludges in accordance with Activated Sludge Model No.1 is outlined in Table 1. Experimental evaluation indicates that the ultrasonication application of 3700, 9500 and 23500 kJ/kg TS specific energy converted 18.4, 11 and 12 % of the initial total COD in the sludge into soluble biodegradable COD, respectively. Although the SCOD content of the WAS increased with rising specific energy, the biodegradable content in this SCOD decreased. In addition, it was observed that the changes in the specific energy input did not affect the maximum growth rate. The readily hydrolysable fraction of the disintegrated WAS seems to disappear with the increasing specific energy input. Moreover, the slowly hydrolysable fraction of the COD decreased as the specific energy input was increased from 3770 kJ/kg TS to 23560 kJ/kg TS.

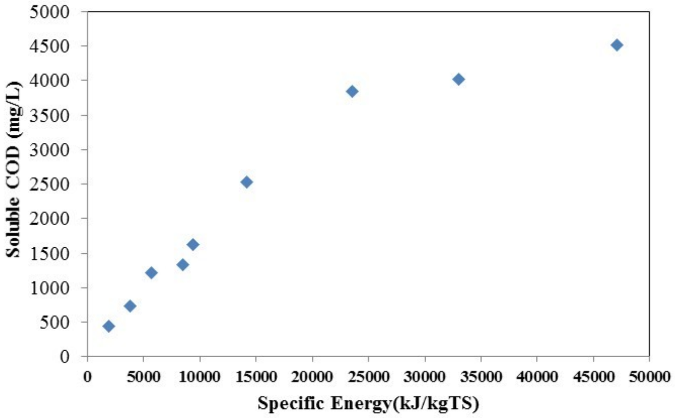
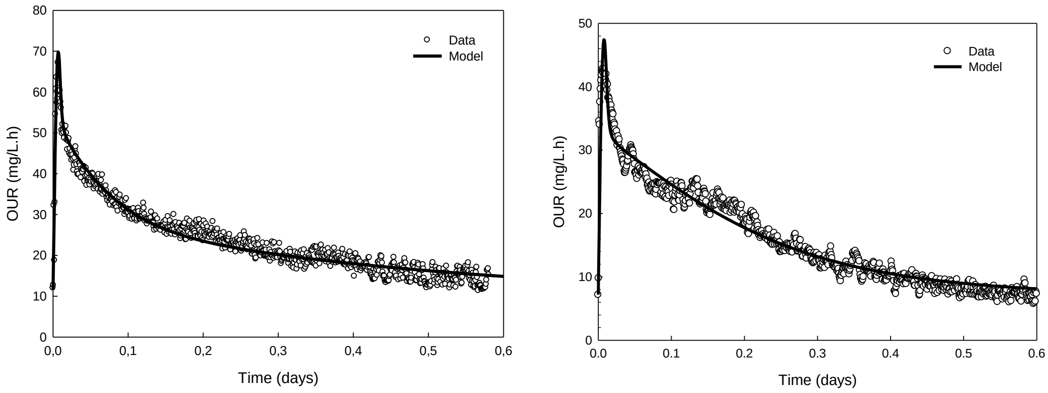


Figure 1. Soluble COD versus Specific Energy.



(a) (b)

Figure 2. OUR profiles for the ultrasonicated sludge of (a) 3700 (b) 23500 kJ/kg TS**.**

CONCLUSION

Anaerobic stabilization has often been limited due to the longer retention time and low degradation efficiency of WAS. The remaining non-digestible material in WAS is known to be inorganically bound carbon or slowly digestible organics that needs to be converted to biodegradable material for an effective stabilization. The increase in the biodegradability potential in WAS after the ultrasonication will improve the anaerobic digestion performance of the sludge. However, the level of the applied specific energy will define its efficiency in terms of the biodegradable substrate generation. Therefore, although ultrasonication seems to increase the soluble organic matter content of the sludge, the degradation potential of the produced soluble organic matter depends on the applied specific energy with ultrasonication.

Table 1. Estimated model parameters and state variables by means of model calibration.

Model Parameter & State		**Unit**	**Specific Energy Applied (kJ/kg TS)**		
			3770	**9425**	**23560**
Maximum growth rate for X_H	$\hat{\mu}_H$	1/day	5.2	5.2	5.2
Half saturation constant for growth of X_H	K_s	mg COD/L	6	6	6
Maximum hydrolysis rate for X_{S1}	k_{h1}	1/day	5.7	-	-
Hydrolysis half saturation constant for X_{S1}	K_x	g COD/g COD	0.32	-	-
Maximum hydrolysis rate for X_{S2}	k_{h2}	1/day	1.90	5.1	5.7
Hydrolysis half saturation constant for X_{S2}	K_{xx}	g COD/g COD	0.79	0.79	0.79
Endogenous decay rate for X_H	b_H	1/day	0.24	0.24	0.24
Yield coefficient for X_H	Y_H	g COD/g COD	0.58	0.58	0.58
State variables					
Initial total COD	C_{T1}	mg COD/L	2425	2425	2425
Initial soluble COD	S_{T1}	mg COD/L	146	324	770
Initial biodegradable COD	C_{S1}	mg COD/L	445	266	291
Initial biodegradable COD/Initial total COD		%	18.4	11.0	12.0
Initial readily biodegradable COD	S_{S1}	mg COD/L	4	6	6
Initial readily hydrolysable COD	X_{S1}	mg COD/L	106	-	-
Initial slowly hydrolysable COD	X_{S2}	mg COD/L	335	260	285
Total Oxygen Consumed for biodegradation	Δ_{O2}	mgO_2/L	187	113	124

$^{*}f_P$ is assumed as 0.25

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(16) Removal of sulfide and phosphorus from anaerobic fluidized bed reactor effluent by chemical coagulation

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Abstract

Recently anaerobic treatments of domestic wastewater are receiving increasing interest. In this study, applicability of chemical coagulation for the removal of sulfide and phosphorus from anaerobic fluidized bed reactor (AFBR) effluent was evaluated. Sulfide was not completely removed at the theoretical Fe^{3+}/S^{2-} ratio of 0.67, but reduced from 14.3 to 0.52 mg/L at the ratio of 1.20. Although bboth sulfide and phosphorous could be removed simultaneously by Fe^{3+} ion, removal of phosphorus rather than sulfide appeared to be a controlling factor in determining the coagulant dosage. Coagulation with Fe^{3+} ion would be a good post-treatment option for the removal of sulfide from the AFBR effluent with the additional organic removal capacity.

Keywords

Anaerobic, Fluidized reactor, Coagulation, Sulfide, Phosphorus

INTRODUCTION

Anaerobic treatment of domestic wastewater is receiving more attention in recent years as it can produce energy and reduce bio-solids production than conventional aerobic systems. However, polishing of the anaerobic reactor effluent should consider the management of hydrogen sulfide and dissolved methane together with phosphorous and nitrogen. Hydrogen sulfide may bring about several problems, such as unpleasant odor, corrosion of facility/pipes, and negative impacts on the human health, if not properly managed (Zhang et al., 2008). Recovery or removal of phosphorus is also necessary where discharge standard is strict.

Coagulation is a process that can remove organic removals as well as sulfide and phosphorus simultaneously, and thus would become a suitable for the post treatment of the anaerobic reactor effluent. This study was conducted to evaluate the characteristics of sulfide and phosphorus removal by coagulation with Fe^{3+} ion for the AFBR effluent treating domestic wastewater.

MATERIALS AND METHODS

Coagulation was applied for the pilot-scale AFBR effluent that has been operating at Bucheon wastewater treatment plant, Korea. Detailed description of the AFBR is given elsewhere (Shin et al., 2014). The AFBR, filled with GAC as fluidizing media, was fed with a settled domestic wastewater for more than 400 days of continuous operation at ambient temperatures and feed rate of 12 m^3/d, and corresponding hydraulic retention time (HRT) was 1.9 h.

Coagulation experiments were conducted with the AFBR effluent with the following procedure. First, the AFBR effluents kept under anaerobic condition or synthetic wastewater bearing sulfide were filled in 2 L jars. After addition of desired amount of coagulants together with alkalinity, if needed, the jar-tester was operated under rapid mixing in 2 min at 180 rpm. Next, slow mixing was applied for 20 min at 50 rpm, and then settled for 20 min. The supernatant samples were analysed for sulfide, T-P, pH, etc. Coagulant used was ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and coagulant aid was anionic polymer.

RESULTS AND DISCUSSION

To evaluate the coagulant dosage for the removal of sulfide, experiment was conducted using synthetic wastewater. Theoretical molar ratio of ferric ion to sulfide has been reported as 0.67 as expressed in equation (1) by Ge et al. (2012).

$2Fe^{3+} + 3HS^{-} \rightarrow 2FeS + S^{o} + 3H^{+}$ (1)

Sulfide removal from synthetic wastewater was proportional to the dosage of ferric ion at the Fe^{3+}/S^{2-} ratio below 0.67, but 10% to 25% higher than that predicted by eq. (1). At the Fe^{3+}/S^{2-} ratio of 0.67, sulfide removal was almost complete.

Sulfide and phosphorus removals for the pilot-scale AFBR effluents were evaluated at various coagulant dosages. Contrary to the synthetic wastewater, sulfide removal at the Fe^{3+}/S^{2-} ratio of 0.64 (20 mg Fe^{3+}/L), close to the theoretical value of 0.67, was only 75.2%. Up to the Fe^{3+}/S^{2-} ratio of 1.20, sulfide removal increased almost linearly, at which sulfide concentration was 0.52 mg/L, and corresponding removal efficiency was 96%. At the Fe^{3+}/S^{2-} ratio of 2.0, sulfide concentration was below 0.1 mg/L. Phosphorus concentration decreased almost linearly from 2.44 to 0.01 mg/L as the Fe^{3+}/S^{2-} ratio increased up to 2.80. This indicates that the removal of phosphorus rather than sulfide is a controlling factor in determining the coagulant dosage. At the Fe^{3+}/S^{2-} ratio of 2.0, or 50 mg/L of Fe^{3+}/L, sulfide and phosphorous concentrations were 0.07 and 0.41 mg/L, respectively. Removals of sulfide and phosphorus are not greatly affected by pH and type of coagulant aids. However, size and settleability of flocs were affected by coagulants aids, and anionic polymer yield better results than cationic and non-ionic polymers.

With the excess Fe^{3+} ion required for complete sulfide removal, partial COD removal was also achieved. For example, COD removal increased from 25% to 55% as the Fe^{3+}/S^{2-} ratio increased from 0.64 to 2.0. At the Fe^{3+}/S^{2-} ratio of 2.8 (70 mg Fe^{3+}/L), TCOD was below 76 mg/L. Although COD removal was mainly based on the removal of particulate matter, soluble COD removal at the Fe^{3+}/S^{2-} ratio of 2.0 was 28%. Yoo et al., (2013) reported that COD removal by lab-scale AFBR was 58% to 72% at an HRT of 1.0 h and temperatures between 10 to 25 ^{o}C. Considering the additional COD removal by excess coagulant required for sulfide removal, the AFBR followed by coagulation process may be appropriate technology with low cost at short retention time where high quality effluent standards are not enforced.

CONCLUSTION

Ferric chloride was effective coagulant for the removal of sulfide and phosphorous from the AFBR effluent, although the Fe^{3+}/S^{2-} ratio required to reach sulfide below 0.5 mg/L was 180% of the theoretical value. Removal of phosphorus rather than sulfide is a controlling factor in determining the coagulant dosage. Coagulation with Fe^{3+} ion would be a good post-treatment option for the removal of sulfide from the AFBR effluent with the additional organic removal capacity.

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(17) Green wastewater treatment with symbiotic microalgae-bacteria biomass

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Abstract

Algae can be integrated into activated sludge flocs and are capable to reduce energy demand and CO_2 emissions in aerobic waste water treatment plants and therefore earn high interest.. As phototrophic organisms algae consume CO_2 and deliver O_2 for the aerobic metabolism of bacteria degrading organic substances in waste water. In an initial project „ALBAQUA" treatment of paper mill effluents by mixed algae-bacteria biomass (ALBA biomass) was tested. Algae were seen to incorporate into the activated sludge flocs easily. The biocoenosis always adapts during the test period – biodiversity increased. Tests with different effluents from paper industry showed good degradation results with potential for further optimization. Pilot plant trials in a paper mill producing printing papers approved the lab test results. They also attested that algae deliver sufficient oxygenation. The effluent treatment with ALBA works very well for most of the paper mill effluents at low and medium loads. Aeration is not required. Further research and development is necessary to optimize the process and check for a suitable reactor design.

Keywords
ALBA; algae, bacteria, wastewater treatment; symbiosis; energy efficiency, greenhouse gases

Background

Paper mills are obliged to reduce emissions and improve their effluent quality due to strict EU environmental legislation. A lot of companies have already implemented biological treatment as secondary stage waste water purification process in order to improve overall efficiency and thus comply with environmental standards. Conventional aerobic treatment provides good results, however on the other hand it is quite energy demanding. For this reason innovative techniques intended to improve performance and reduce costs are constantly observed and examined. One possible way to make biological treatment more effective is introduction of microalgae into the conventional stage using activated bacterial biomass (1-3). Heterotrophic bacterial organisms decompose organic impurities in water to CO_2 and H_2O for which they need oxygen which is conventionally supplied via aeration. An alternative source of oxygen supply may be autotrophic microalgae which consume available CO_2 (provided by bacterial action) and H_2O during photosynthesis for which they use energy in the form of sunlight. Oxygen is released in the process as waste product. The latter can be conveniently used by bacteria for their heterotrophic degradation of organic impurities. Symbiotic co-existence of two types of microorganisms within the same effluent can be exploited for improved cleaning performance. Due to efficient interchange of gaseous products between algae and bacteria no external aeration should be required, because all the necessary oxygen is to be provided by algae which at the same time efficiently consume CO_2 released by bacteria (figure 1). In addition, improved cleaning efficiency is expected due to specific ability of microalgae to remove toxins, heavy metals as well as nitrogen and phosphorous compounds.

Main objective of an initial research work was to introduce and optimize this innovative technique of biological effluent treatment first on laboratory level and than transfer the obtained experience and knowledge to pilot scale in real papermaking conditions in order to evaluate its potential and efficiency as alternative, energy saving effluent treatment technique.

Research was performed within the frame of EU sponsored Cornet project "ALBAQUA" (Combined **al**gal and **ba**cterial waste water treatment for high environmental **qua**lity effluents, www.cornet-albaqua.eu).

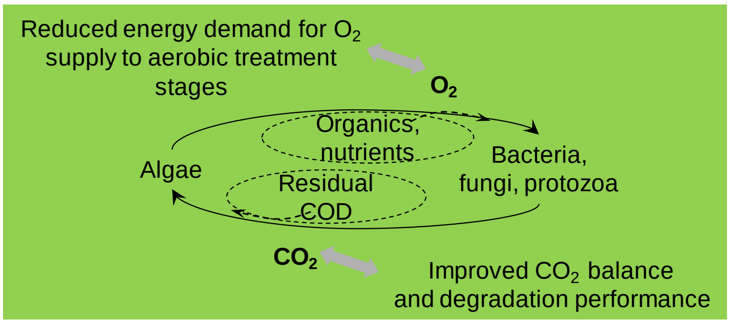

Figure 1: Combined action of bacterial biomass and algae in effluent treatment plant

Experimental work

All tests so far were performed with *Chlorella vulgaris*, a microalgae that is adapted to wastewater properties and proved to be suitable for ALBA wastewater treatment, because of its specific properties, such as relatively quick growth and good flocculation with bacterial biomass.

Effluent treatment tests with mixed algae-bacterial biomass were performed in small laboratory bioreactors after optimization of experimental parameters, such as hydraulic retention time (HRT), biomass concentration or dissolved and suspended matter (DSM), algae-bacteria proportion, nutrition load (C:N:P), sludge retention time (SRT), sedimentation time, O_2 concentration, temperature, pH and light intensity. Real effluents from several different paper production processes were used in laboratory experiments in order to determine purification performance.

Pilot tests were performed in a Slovenian paper mill using waste water from different production programs. The paper mill produces different printing paper grades from primary fibers. Experimental adjusted parameters are collected in table 1.

The efficiency of the pilot performance was determined by measuring the common waste water parameters before and after the treatment. The algae content of the biomass was characterized by spectrophotometric determination of chlorophyll concentration. Biomass condition was also observed by microscopy in order that different microorganisms within the mixture were identified and their abundance evaluated.

Table 1: Operating parameters for lab scale and pilot plant operation

Operating parameter	**Lab scale/pilot trials**
F/M	0,03–0,1 kg BOD5/(kg dsm.d)
HRT	2–5 d
DSM	0,3–2,5 g/l
Temperature/pH	T 25 – 30°C; pH 7,5-9,5
Lighting	10:14 h and 12:12 h in lab, natural daylight outdoors

Results

Due to the algae photosynthetic activity an oxygen concentration of 2 – 12 mg/l adjusted without external aeration tools in all tests. The oxygen concentration was sufficient for the bacteria even in dark periods simulating night (see Figure 2).

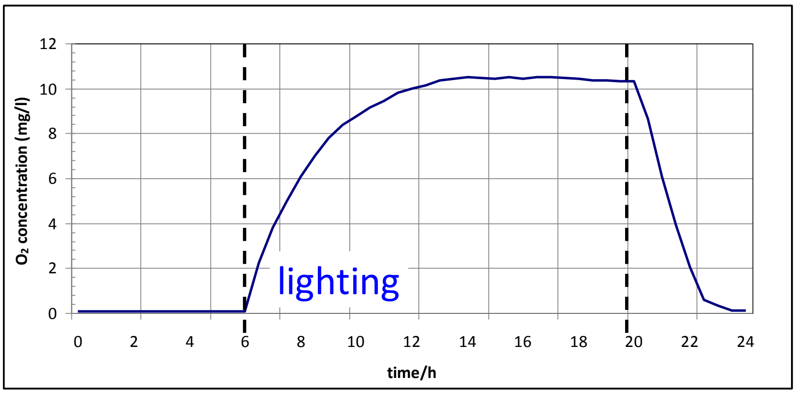

Figure 2: Course of oxygen during a daily period – trials with real paper mill effluent

Starting with *Chlorella vulgaris* species after a while an increasing biodiversity regarding algae and bacteria can be observed. Figure 3 gives an impression of the ALBA biomass composition.

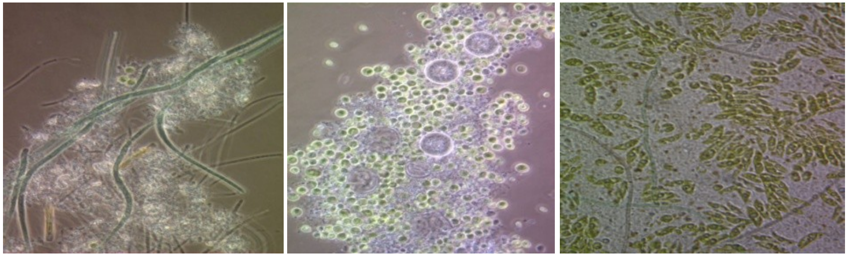

Figure 3: Biodiversity of ALBA biomass – phase contrast microscopic images, magnify. 100x left: *cyanobacteria* sp. (bluealgae) , middle: C*hlorella vulgaris* sp., right: *Scenedesmus* sp.

The performance of the tests with three different wastewaters and and adjustment of pH with different media is shown in Figure 4. Performance of ALBA treatment depends both on the effluent composition and the pH control. The results show that the best degradation efficiency can be achieved with pH adjustment by CO_2 addition and for effluents containing carbon hydrates and low molecular organic acids.

Table 2 shows the summary of results for all effluents tested. An average surplus sludge production of ~ 0.2 g TS/m^3*d was achieved, depending on the loading conditions.

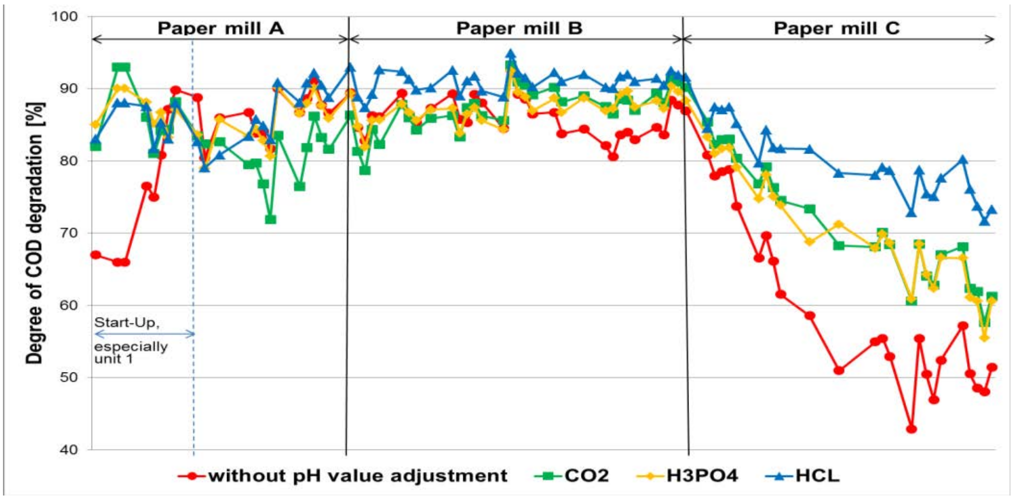

Figure 4: Course of COD degradation performance during continuous operation in lab scale – trials with 3 real paper mill effluents and adjustment of pH with different media

Table 2. Summary of results for degradation performance of various paper mill effluents

Raw material	**Products**	**Ø ⍰COD**
pulp, waste paper	printing papers	> 70 %
mech. pulp, waste paper	wood containing coated printing paper	> 65 %
waste paper	board	> 70 %
waste paper, pulp	Woodfree graphic paper	> 76 %
waste paper, mech. pulp	Newsprint	~65 %

Conclusions

Effluent treatment with mixed algae-bacteria biomass worked well for paper mill effluents at low and medium loads. External aeration was not required as sufficient oxygenation was easily achieved by algae. Light intensity proved not to be a major factor, which can be used for minimising the landuse of reactors. Further research will be needed to optimize this novel energy saving effluent treatment technology and transfer it to the industrial scale.

Acknowledgement

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(18) Ciliate diversity in the start-up of a MBBR partial nitrification process

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Abstract

The start-up of a Moving Bed Biofilm Reactor (MBBR) partial nitrification process was studied in order to determine the ciliate diversity and the distribution of the different species within the system. Up to 9 ciliate species were observed during the experimental period: 3 Colpodea (*Colpoda ecaudata*, *Colpoda colpidiopsis* and *Cyrtolophosis acuta*), 2 Hymenostomata (*Cyclidium glaucoma* and *Pseudocohnilembus pusillus*) and 4 Peritrichia (*Epistylis* cf. *rotans*, *Opercularia coarctata*, *Vorticella microstoma*-complex and *Vorticella* sp). The most abundant and frequent species were *Epistylis* cf. *rotans* and *Cyclidium glaucoma*. All ciliate species colonized biofilm (BF) and mixed liquor (ML), but the ecology of each species determined their capability to develop and remain in each subsystem. The ciliate community evolved in response to the physicochemical and operational parameters, suggesting that ciliates can be useful as bioindicators of the MBBR partial nitrification process.

Keywords
Ciliates, biofilm, *Epistylis*, MBBR, protozoa.

OBJECTIVE

The start-up of a MBBR partial nitrification process was studied in order to determine the ciliate diversity and the distribution of the different species within the system.

MATERIAL AND METHODS

Experimental set-up and analytical methods

A jacketed lab-scale MBBR (5L) filled with biofilm carriers working at 30ºC was set up to carry out this study. The reactor was equipped with pH and dissolved oxygen (DO) probes, an air supply system and a peristaltic pump that continuously added reject water from anaerobic digestion of sewage sludge collected in a municipal Wastewater Treatment Plant. The treated effluent was withdrawn of the reactor by an overflow system. Analyses of total and suspended solids (TSS), COD, NH_4^+-N, NO_2^--N and NO_3^--N were performed according to the Standard Methods (APHA, AWWA, WEF 1998).

Counts and determination of the ciliate species

Microscopic counts were carried out weekly by using a Zeiss microscope Axioskop 40. For each sampling two samples were analysed: mixed liquor (ML) and biofilm (BF; samples obtained following Canals *et al*, 2013). Counts were carried out using well-homogenised samples, and two 25 µL replicates were performed for each sample. Abundance values of both mixed liquor and biofilm species were expressed as individuals per millilitre (ind·mL^{-1}). Identification of ciliates species was carried out by using Foissner (1993) and Foissner *et al*. (1992 and 1994).

RESULTS AND DISCUSSION

During the start up of the MBBR, diluted reject water was treated (150 mg NH_4^+-N L^{-1}) and it was progressively concentrated until treating non diluted reject water (730 mg NH_4^+-N L^{-1}). Up to 9 ciliate species were determined (Table 1). The most abundant and most frequent species were *Epistylis* cf. *rotans* (78.3% of the total ciliate abundance in the BF) and *Cyclidium glaucoma* (74.5% of the total ciliate abundance in the ML).

Table 1. Mean, standard deviation (SD), maximum (Max), minimum (Min) and frequency (Freq) of total suspended solids (TSS) and ciliate species of mixed liquor (ML) and biofilm (BF).

	Mixed Liquor (ML)				Biofilm (BF)			
	Mean ± SD	Max	Min	Freq (%)	Mean ± SD	Max	Min	Freq (%)
TSS (mg·L^{-1})	142,2 ± 156,9	880,0	22,5		740,9 ± 258,4	1289,4	295,3	
CILIATES (ind·mL^{-1})	2088 ± 2347	8020	0	97	9837 ± 15282	59800	0	97
Colpodea								
Colpoda ecaudata	151,8 ± 860,3	5020	0	18	91,8 ± 514,2	3000	0	9
Colpoda colpidiopsis	52,4 ± 159,8	820	0	32	379,4 ± 1208,5	6700	0	47
Cyrtolophosis acuta	35,3 ± 116,4	440	0	9	50 ± 241,5	1400	0	9
Hymenostomata								
Cyclidium glaucoma	1557,1 ± 2368,7	8020	0	74	97,1 ± 200,7	900	0	35
Pseudocohnilembus pusillus	43,5 ± 233,1	1360	0	9	20,6 ± 120	700	0	3
Peritrichia								
Epistylis cf. *rotans*	101,4 ± 262,6	1320	0	50	7707,1 ± 15352,7	59200	0	82
Opercularia coarctata	45,9 ± 125,7	580	0	32	298,5 ± 1336	7800	0	32
Vorticella microstoma -complex	35,4 ± 99,5	480	0	26	145,6 ± 343,4	1900	0	38
Vorticella sp	33,5 ± 68	280	0	35	767,6 ± 1535,4	7200	0	41
Telotroch	31,2 ± 83,4	420	0	35	279,4 ± 484,8	2200	0	62
Other (non identified)	0,6 ± 3,4	20	0	3	0 ± 0	0	0	0

Data provided information about the ecology of the different species. Free-swimming ciliates as *Cyclidium glaucoma*, *Colpoda ecaudata* and *Pseudocohnilembus pusillus* developed mainly in the ML, while sessile ciliates as *Epistylis* cf. *rotans* presented their main population adhered to carriers. Data regarding the distribution of the other peritrich species observed (specifically *Opercularia coarctata*) may be confusing as the frequencies of these species did not differ too much between ML and BF. Nevertheless, it can be explained since *O. coarctata* and *V. microstoma*-complex are opportunistic species with a higher growth ratio than *Epistylis*. Finally, crawling species (*Colpoda colpidiopsis* and *Cyrtolophosis acuta*) were generally more associated to the BF.

During the start-up period, the ciliate community evolved in response to the physicochemical and operational parameters, suggesting that ciliates can be useful as bioindicators of the MBBR partial nitrification process.

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(19) Simultaneous Absorption, Disinfection and Coagulation of Municipal Wastewater in a Multifunctional Reactor for Unrestricted Reuse

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Abstract

A secondary settled effluent was subjected to simultaneous treatment by dosing aluminium polychloride (dose range: 0-150 µL/L, stock solution at 17.5% w/w as Al_2O_3), natural zeolites (dose range: 0-150 mg/L), sodium hypochlorite (dose range: 0-7.5 mg/L) and powder activated carbon (dose range: 0-30 mg/L). The combined process was optimized using response surface methodology and a Latin square DOE technique. Sixteen combinations of dosages were pilot tested on an 8 m^3/h multifunctional reactor fed by a secondary effluent with initial COD and total coliform concentrations of ≈ 22.4-57.1 mg/L and from 10^5-10^6 CFU/100mL. Remarkably, the combined process was able to consistently remove up to 70% of incoming COD, >5 Log of incoming total coliforms and 50% of incoming phenols (a micropollutant known to be recalcitrant to conventional wastewater treatments).

Keywords

Enhanced Coagulation, Combined Processes, Multifunctional Reactor, Wastewater Reuse

Introduction

Multifunctional reactors are not new in chemical reactor engineering (Levenspiel, 1999; Westerterp, 1992); however, only recently they have been considered for the treatment of municipal wastewater (Jian-xiao et al., 2011). When compared against conventional technologies, multifunctional reactors have the potential of accomplishing treatment at a lower capital, operational and maintenance cost and with lesser land usage. In this paper, the treatment performance of a new multifunctional reactor combining the functions of coagulation, adsorption, disinfection and particle separation for the reclamation and agricultural reuse of secondary settled municipal wastewater were investigated.

Material and Methods

A prototype multifunctional reactor (Fig.1) was fed by secondary settled municipal wastewater which was treated at different flowrate and with different combinations and concentrations of the selected chemicals. A statistical technique known as Latin square was used to design the testing points associated with pilot plant experiment (Table 1).

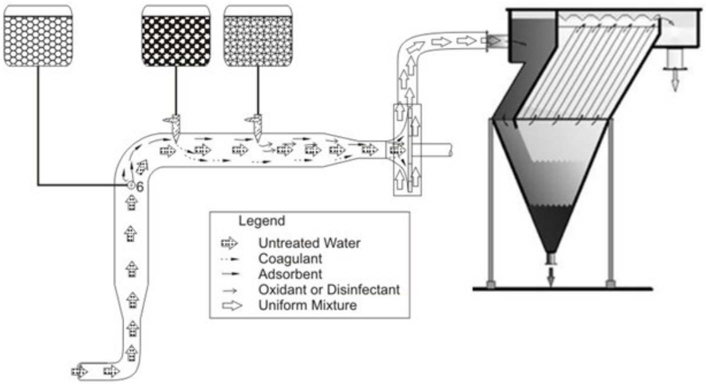

Figure 1. Schematic of the multifunctional reactor (mixing-pump and lamella clarifier)

Such sampling strategy was selected to minimize the disturbance of nuisance factors, an issue often encountered in experimental conditions dominated by uncontrolled variables (Montgomery, 2012).

Results and Conclusions

For each of the sixteen conditions, COD and total coliform removal efficiency is reported together with the associated sludge production and treatment cost (Table 1).

Table 1. Pilot plant investigation: design of experiments and results (AP=Aluminum polychloride, PAC= Powder Activated Carbon, SH= Sodium Hypochlorite, Z=Natural Zeolite)

Experiment [#]	**COD Removal [%]**	**Log N_0/N [-]**	**Sludge Volume [mL/L]**	**Cost [€/m^3]**	**Experiment [#]**	**COD Removal [%]**	**Log N_0/N [-]**	**Sludge Volume [L/m^3]**	**Cost [€/m^3]**
1	0.12±0.04	0.14±0.83	0.1±0.1	0.031	**9**	0.28±0.25	4.67±0.51	0.2±0.1	0.039
2	0.39±0.27	1.04±2.43	5.0±1.0	0.076	**10**	0.53±0.15	4.68±0.39	3.4±1.4	0.084
3	0.52±0.12	5.05±0.59	27.7±10.8	0.080	**11**	0.21±0.18	4.63±0.35	0.5±0.0	0.097
4	0.42±0.09	4.94±0.37	42.7±8.7	0.094	**12**	0.58±0.14	4.90±0.63	5.5±4.3	0.111
5	0.24±0.14	4.56±0.69	0.1±0.1	0.033	**13**	0.64±0.10	4.93±0.43	24.3±1.2	0.123
6	0.52±0.21	4.41±0.57	4.0±0.0	0.047	**14**	0.67±0.09	4.70±0.12	28.7±5.5	0.168
7	0.57±0.19	4.80±0.27	10.7±3.5	0.129	**15**	0.38±0.14	4.17±0.19	31.0±3.6	0.149
8	0.50±0.16	4.80±0.53	25.3±6.8	0.143	**16**	0.38±0.05	4.14±0.52	26.3±1.2	0.104

Pilot results were fitted using a radial-basis function (RBF) in order to identify the surface response and optimize the combined process carried out in the multifunctional reactor (Fig.2). It can be observed that an optimal combination of treating agents for maximizing both processes should follow in the ranges of AP=84-106 µL/L, PAC=5 mg/L, Z=34-70 mg/L and SH=3.4-5.6 mg/L. The treatment conditions and the agents associated with optimal COD removal performance were tested for long term, uninterrupted operations to evaluate the removal of micropollutants potentially recalcitrant to conventional treatment such as phenols. Notably, excellent removal performance for total phenols was also revealed over the entire duration of the pilot trials, as confirmed in Fig.3.

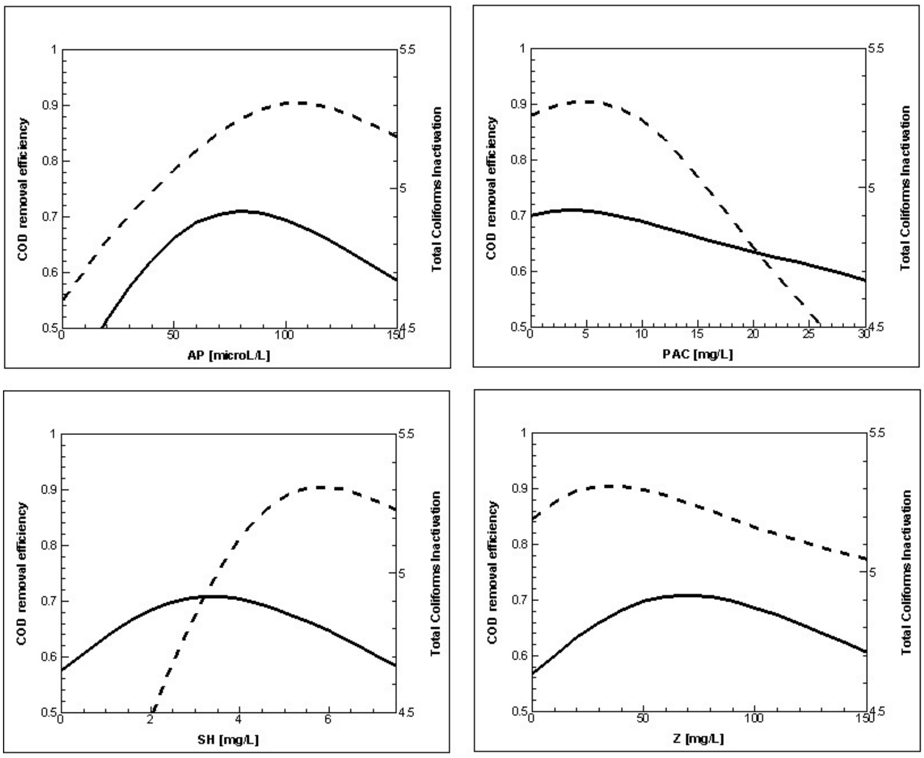

Figure 2. Response Surface for COD removal efficiency (solid line) and Log inactivation (dotted line).

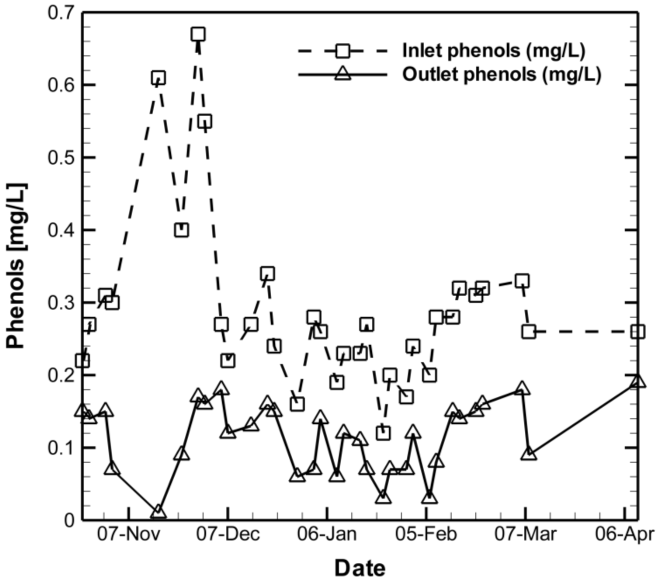

Figure 3. Phenols concentration as observed for the inlet and outlet of the multifunctional reactor.

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(20) Nitrogen removal of sewage sludge anaerobic digestion supernatant by partial nitritation/Anammox

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Abstract

A two-step process of partial nitritation (PN) and Anammox was started-up to treat the supernatant of anaerobic digestion (600-760 mg NH_4^+-N L^{-1}) from a wastewater treatment plant (WWTP). PN was carried out in a granular sequencing batch reactor (GSBR) treating nitrogen loading rates up to 3.1kg N m^{-3} d^{-1}. The effluent from the PN process, consisting in 50%NH_4^+-N and 50% NO_2^--N, was fed to theAnammoxGSBR which was observed to be very sensitive to changes in influent concentration. Therefore,it was diluted based on the efficiency of NH_4^+–N removal and thespecificAnammox activity (SAA)tests. Globally, up to88% of theNH_4^+–N present in the supernatant was successfully removed. However, the stoichiometry observed did not exactly fit with the theoretical Anammox stoichiometry, which leads to consider the presence of heterotrophic denitrifiers.

Keywords

Partial nitritation; Anammox; Biological nitrogen removal; Granulation

INTRODUCTION

The partial nitritation (PN)/Anammox process has become an interesting system for the treatment of wastewaters with a low carbon to nitrogen ratio and high ammonia concentrations. Compared to the conventional nitrification/denitrification process, the PN/Anammox system has the advantage to reduce the oxygen required in the nitrification step, and to avoidanyorganic carbon source in the denitrification step. Hence, over a 65% of the oxygen supply is saved and lower amount of sludge is produced(Fernándezet al., 2012). The aim of this work is to test the two-step PN/Anammox process to treat anaerobic digestion supernatant in two granular sequencing batch reactors (GSBR).

MATERIALS AND METHODS

The PN was carried out in a lab-scale SBR at 30ºC, with a cycle length of 4h and an exchange volume ratio of 50% per cycle. During each operating cycle, pH, dissolved oxygen (DO) and ORP were monitored. The Anammox lab-scale reactor was also operated as an SBR at 35ºC, in cycles of 6h. The AnammoxSBR was inoculated with granular Anammox biomass from a Dutch pilot plant. The anaerobic digestion supernatant was collected in a wastewater treatment plant located near Barcelona. Analysis of solids, chemical oxygen demand (COD) and nitrogen compounds were performed according to the Standard Methodsfor the Examination of Water and Wastewater.

RESULTS AND DISCUSSION

In the PN reactor, 600-760 mg NH_4^+-N L^{-1} were partially oxidized to nitrite by means of aerobic granules (Feret Diameter of 5.8 mm and roundness 0.76). Further oxidation to nitrate was prevented by keeping high levels of free ammonia in the reactor which inhibited nitrite oxidizing bacteria (NOB). Since the influent had an average molarratio NH_4^+-N/alkalinity of 1.03, only 50% of NH_4^+-N was oxidized. The cycle length was fixed at 4h, corresponding to a hydraulic retention time (HRT) of 8h that is long enough to assure the required effluent conditions. A maximum nitrogen loading rate of 3.1kg Nm^{-3} d^{-1} was successfully treated. FISH analyses revealed the presence of ammonium oxidizing bacteria (AOB) of the genera Nitrosomona,whereas NOB was not detected.

The effluent from the PNstep was fed the AnammoxGSBR. Figure 1 shows theNH_4^+-N, NO_2^--N and NO_3^--N concentration profiles in the influent and effluent of the Anammoxprocess. The AnammoxGSBR was started up with diluted effluent from the PN. Biomass was slowly adapted to treat increasing nitrogen loading rates that were adjusted once a week according to the results of ammonium and nitrite removal and theSAAtests. After 100 days of operation, the PN effluent was directly fed, after pH adjustment, to the Anammoxstep and the observed Anammoxstoichiometry was 1:1.17:0.21 (NH_4^+:NO_2^-:NO_3^-) which slightly differs from the theoretical relation, namely 1:1.32:0.26 (Van Dongenet al., 2001). Since the partially oxidizedeffluent fed to the Anammox reactor contained 480-530 mg COD L^{-1}, it was considered that heterotrophic denitrifying bacteria was present in the reactor which could coexist with Anammox bacteria. During more than 120 days of operation, up to 88%of the total NH_4^+-N was removed in the completelyautotrophicPN/Anammox system.

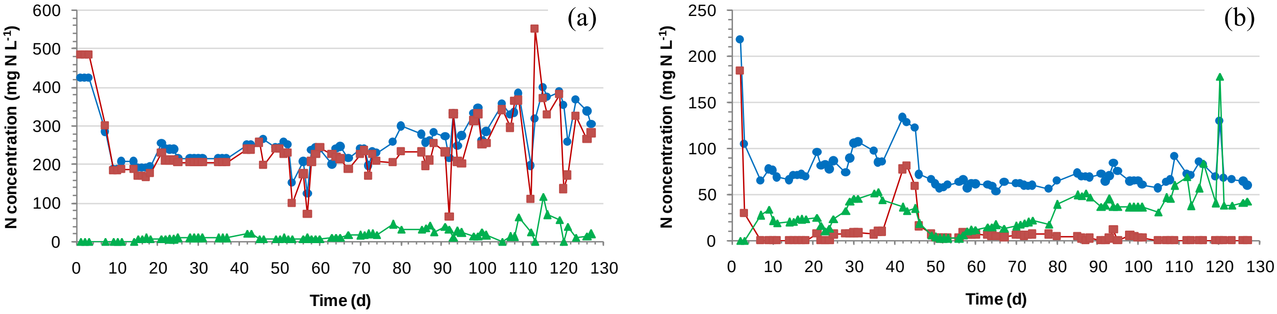

Figure 1. Concentration profiles in theAnammox step(a) influent and (b) effluent of (●) NH_4^+-N, (■) NO_2^--N and (▲) NO_3^--N

CONCLUSIONS

In this study, the PN/Anammox process was assessed to treat anaerobic digestion supernatant from a WWTP, obtaining NH_4^+-N removal efficiencies up to 88%.The PN process was carried out in a GSBR operated at fixed conditions assuring the required effluent conditions treating up to 3.1kg N m^{-3} d^{-1}. The Anammoxstep was set up as a GSBR and it was operated treating the effluent of the PN reactor. It was observed that it is a very sensitive system that requires a very long acclimation time. The obtained stoichiometry wasslightly different from the theoretical one, which lead to considerthat heterotrophicdenitifying biomass could coexist with Anammox bacteria, as a consequence of organic matter present en the PN effluent.

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(21) Constructed wetlands for micropollutants removal and biodiversity conservation

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Abstract

The implementation of constructed wetlands at the outlet of wastewater treatment plants (WWTP) is growing in order to better protect receiving aquatic ecosystems. Similarly to natural wetlands, constructed wetlands can serve a variety of hydrological, purification, landscape and biodiversity purposes. The aim of the research project ZHART (2012- 2015) is to convert basic constructed wetlands at the WWTP outlet into an integrated solution giving a full set of ecosystem services. Several case studies are focused on the evaluation of the secondary effluent treatment performances on micropollutant, nutrients (C, N, P) and pathogens. The first results are encouraging with removal rates over 70% of micropollutants for more than half of the quantified substances. The on-site biodiversity, and its relation and integration within the local landscape are also investigated, as well as the social valorisation. An increase of biodiversity (fauna and flora) was observed in some constructed wetlands.

Keywords

Abstract; constructed wetlands, full-scale, micropollutants, biodiversity, ecosystem services, wastewater treatment

INTRODUCTION

In order to improve the status of our water bodies according to the Water Framework Directive, the implementation of buffer spaces, diffusion zones, or constructed wetlands (CW) at the outlet of wastewater treatment plants (WWTP), has been growing (Matamoros, 2012; Dordio, 2013).

The functions of natural wetland systems are well known to provide a diversity of social benefits as sustainable alternatives for the integrated management of a range of water-related issues (Everard et al, 2012). For a long time, wetlands have suffered destruction driven by population growth, increasing infrastructure and other problems such as eutrophication and pollution (Millenium Ecosystem Assessment, 2005). Similarly to wetlands, CW could serve a variety of hydrological, purification, landscape and biodiversity purposes. In this context, the aim of the project ZHART is to convert basic constructed wetlands at WWTP outlet into an integrated solution giving a full set of ecosystem services.

Several full-scale case studies were carried out for the evaluation of the secondary effluent treatment performance for the removal of micropollutants, but also nutrients (C, N, P) and pathogens. The on-site biodiversity, landscape integration and social acceptance were also studied.

MATERIAL AND METHODS

Five constructed wetlands fed with secondary urban effluents are investigated, four of them in spring and/or summer. The selected sites, all located in France, are different in terms of morphologies, design and territorial context, as summarized in Table 1. The fifth one, namely the "Zone Libellule©" of Saint Just, was specifically designed to promote micropollutant removal and biodiversity growth (Figure 1). Its monitoring was enforced, with data available for two years.

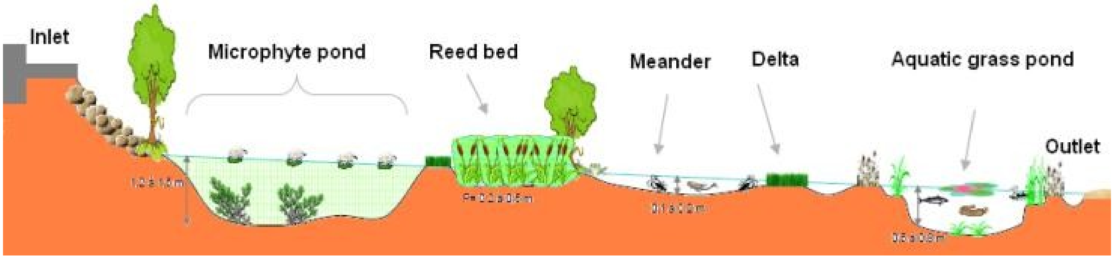

Figure 24. Scheme of the "Zone Libellule®" of Saint Just.

Water quality monitoring was carried out at the inlet and at the outlet of each CW. Analytical parameters are summarized in Table 2. In addition, the behaviour of micropollutants in CW was investigated by monitoring of micropollutants in soil and plant matrices. The biodiversity of each site, their territorial integration (landscape integration and social acceptance) were also studied (Table 2). Moreover, this study has led to the creation of a model able to predict the evolution of the constructed wetland biodiversity.

In addition, experiments in microcosms were carried out in semi-controlled conditions (in greenhouse) to measure the kinetics of micropollutants removal and to highlight and quantify the micropollutants transfer to soil and preselected aquatic plants commonly presents in CW, such as common reeds (Phragmites australis) and Broadleaf cattail (Typha latifolia).

Table 13 Main characteristics of the selected sites (configuration, size, context).

Site	Zone Libellule®	A	B	C	D
Description	Microphytes pond, reed bed, aquatic grass pond and meander	Tree planted ditches and two ponds in series	Three ponds in series	Microphytes and macrophytes ponds + ditch + reed bed	Natural reed bed
Size	1.5 ha	0.5 ha	22 ha	0.3 ha	10 ha
Hydraulic residence time	15-20 days	4 -5 days	30- 60 days	6 - 7 days	40 - 50 days
Date of creation	2009	2009	1997	2012	2009
Climate	Mediterranean	Atlantic	Mediterranean	Continental	Mediterranean
Territorial issues	Agriculture	Tourism, agriculture	Seaside resort, hunters	Agriculture	Small seaside resort, hunters
WWTP	Activated Sludge	Activated Slugde	Activated Sludge	Rhizopur® (biofilter + planted filter)	Several ponds in series
	5 000 p.e.	5 000 p.e.	90 000 p.e.	600 p.e.	30 000 p.e.

Table 14. Analytical parameters and/or methods used in this study and classified by main research area

Water quality	Micropollutants: 33 organic and inorganic compounds	Pharmaceutics and pesticides (LC/MSMS) Alkylphenols, HAP and Musk (GC/MS and LC/MSMS) Metals (ICP/MS)
	Organic matter and nutrients (C/N/P)	Suspended solids, COD, BOD5, NH4, NO3, NO2, NTK, Ptotal
	Bacteriology	E. Coli and Enterococcus
Biodiversity	Flora	Inventories of aquatic and terrestrial species
	Fauna	Inventories of aquatic and terrestrial species (macrobenthos, odonates, batrachians, reptiles and birds)
Territorial integration	Context definition	Maps, general plan, administrative documents, statistic data (demography, economics, agriculture, industries)
	Social acceptation	Stakeholder interviews (elected members, technicians, users, administrators), on-site observations
	Landscape integration	Aerial and satellite imagery, connectivity indexes, on-site observations

RESULTS AND CONCLUSIONS

The applied methodology enabled to evaluate the efficiency of the Saint Just CW, with the following major findings:

- Reduction in the volume of water and thus in the load released into the surface water.
- Reduction of the micropollutant concentrations of more than 70% for more than half the quantified substances (Figure 2). When one considers the flow of micropollutants discharged into the surface ecosystem, the ”Zone Libellule®” enables the micropollutants discharged quantities to be reduced by at least 80%.
- Removal of fecal contamination, on average 3.5 log removal for E.coli and 2.6 log removal for intestinal enterococci, with potential seasonal impacts on the local fauna.

The inventory of biodiversity on Saint Just site shows more than a hundred plant species. Six times more species were observed on the Saint Just CW by comparison with the diversity observed on a control plot (dry prairie) representative of the state of the land before the wetland construction.

Each site was evaluated through several aspects (spatial, social, environmental, institutional and technical), in order to study their diversity and highlight positive and negative factors for constructed wetlands integration and acceptance.

Critical factors explaining the efficiency of different design and operating conditions with respect to expected ecosystem services will be presented and discussed.

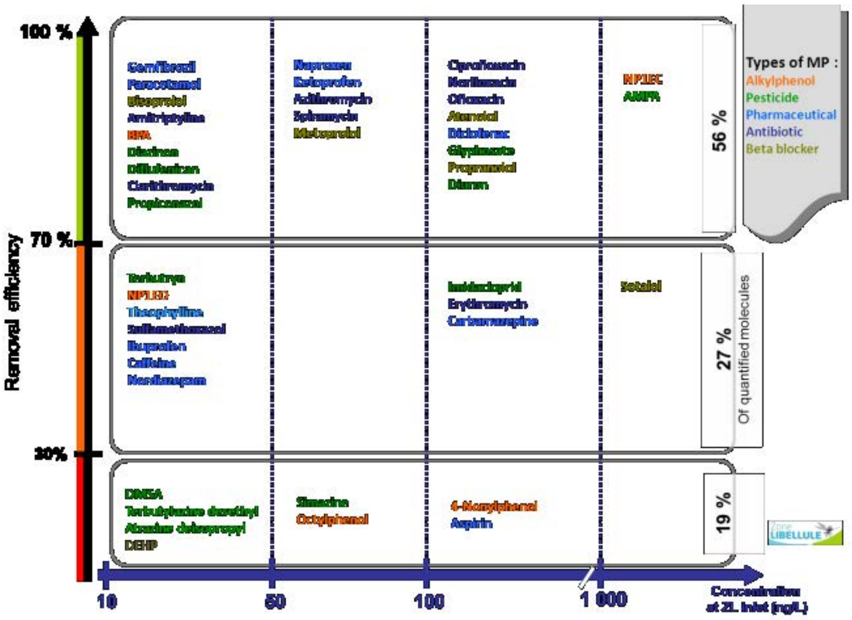

Figure 25. Micropollutants removal efficiency of Saint Just constructed wetland

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(22) Biological groundwater treatment for hexavalent chromium removal under low hydraulic residence times

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Abstract

Removal of hexavalent chromium from groundwater can be achieved by both physicochemical and biological treatment methods. The objective of the present study is to evaluate the effectiveness of anaerobic biological treatment systems to provide for appreciable hexavalent chromium reduction from groundwater. Furthermore the effect of the hydraulic residence time on process performance was assessed through the operation of a series of anaerobic sequential batch reactors at different hydraulic residence times. According to the results it is anticipated that hexavalent chromium at concentrations to the order of 200 μg/L can be completely removed biologically from water under anaerobic conditions, provided that an external substrate would be added to the water in order to support microbial growth. More specifically an anaerobic sequential batch reactor treating groundwater with hexavalent chromium concentrations as high as 200 μg/L, can achieve complete hexavalent chromium removal when operating at a hydraulic residence time of 0.9 d at a sludge age of 6.5 d. Complete hexavalent chromium removal can also be achieved for a hydraulic residence time of 0.6 d at a sludge age of 10 d for temperatures greater than 20^{o}C or at a sludge age of 20 d for temperatures less than 20^{o}C.

Keywords

Biological groundwater treatment; hexavalent chromium reduction; hydraulic residence time; sequential batch reactors

INTRODUCTION

The natural reducing capacity of aquifers to facilitate hexavalent chromium (Cr(VI)) reduction and detoxification to trivalent chromium (Cr(III)) is very often exceeded by the amount of Cr(VI) present in contaminated groundwater. In order to tackle the problem of high Cr(VI) concentrations in groundwater several treatment technologies have been developed. The most often used methods are physicochemical techniques and most specifically: a) chemical oxidation (Barrera-Diaz et al., 2012), b) ion exchange (Ren et al., 2012), c) adsorption through activated carbon (Babel et al., 2003) and d) membrane separation (Bodzek et al., 2011). Furthermore additional physicochemical methods have also be developed for chromium removal from water such as electrocoagulation (Parga et al., 2005), electrodissolution of iron (Martinez et al., 2000) and photocatalytic reduction (Rivero-Huguet et al., 2009). All these methods present several disadvantages such as high capital and operational cost, production of chemical sludge, sludge disposal problems, etc. In recent years, interest has been developed in pursuing biologically-mediated Cr(VI) reduction by enhancing microbial activity. The reduction of Cr(VI) to Cr(III) was shown to be possible, using pure and mixed cultures enriched from soil sources, under either aerobic or anaerobic conditions (Lovley and Phillips, 1994). Despite the extensive literature regarding the physicochemical methods for Cr(VI) removal from water, there is essentially very limited literature on the biological treatment of groundwater for Cr(VI) removal. On the other hand the microbial reduction of Cr(VI) to Cr(III) has been extensively reported in the literature for the treatment of liquid wastes under both aerobic and anaerobic conditions (Stasinakis et al., 2004). Many bacterial genera have been reported to reduce Cr(VI) to Cr(III) including *Bacillus, Pseudomonas, Escherichia, Arthrobacter, Ochrobactrum, Brevibacterium, Shewanella*, *Rhodococcus, Shigella, Brevibacterium, Pannonibacter, Sphaerotilus* (Caravelli et al., 2008; Contreras et al., 2011). Recently Mamais et al., (2013) demonstrated that effective biological treatment of highly polluted groundwater for hexavalent chromium reduction can be achieved under anaerobic conditions. The authors report that treatment of groundwater in an anaerobic sequential batch reactor (SBR) operating at a sludge age of 10 d and a hydraulic residence time around 1.7 d can provide for a complete hexavalent chromium reduction to trivalent chromium for groundwater with hexavalent chromium concentrations as high as 200 μg/L.

In view of the above the objective of this work was to evaluate the ability of anaerobic SBR systems to perform appreciable hexavalent chromium reduction under lower hydraulic residence times.

MATERIALS AND METHODS

In order to evaluate the effect of hydraulic residence time (HRT) on the biological removal of hexavalent chromium under anaerobic conditions three bench scale units were employed. All experimental units were operated as SBR systems. All systems were operated as pure anaerobic systems and were fed with tap water which was supplemented with a mixture of milk and sugar as the external substrate at a total COD concentration of 200 mg/L and a mixture of nutrients to support microbial growth. The concentration of Cr(VI) in the influent water, was equal to 200 μg/L and was achieved through hexavalent chromium addition in the form of $K_2Cr_2O_7$ solution. One system (System F1) was fed with influent water once a day, while systems F2 and F3 were fed with the same water twice and three times daily respectively. The nominal hydraulic residence time of the three systems were equal to 1.75 d (System F1), 0.9 d (System F2) and 0.6 d (System F3), while sludge age was equal to 10 d for system F1 and 6.5 d for system F2. System F3 was operated under different operating conditions in three phases. Sludge age of system F3 was equal to 10 d for the first two phases (phase A and B) and increased to 20 d at the third phase of operation (phase C). Furthermore average temperature of mixed liquor for system F3 was equal to 24^oC, 19^oC and 20^oC for the three phases of operation. Accordingly average mixed liquor temperature of systems F1 and F2 was greater than 23^oC.

The performance of the bench scale units was assessed by routine measurements of temperature, total and soluble COD, TSS, VSS, NH_4-N, NO_3-N, redox, pH, DO, total and hexavalent chromium throughout the experimental period. All analyses were done in accordance with *Standard Methods* (APHA, 2005).

RESULTS AND DISCUSSION

A series of bench scale anaerobic SBRs were operated in order to evaluate the effect of HRT on process performance and more specifically on the ability of the systems to perform appreciable hexavalent chromium reduction. The results from the operation of the three units are summarized in Table 1. Based on the results it seems that both systems F1 and F2 (even at a sludge age of 6.5 d) exhibited complete hexavalent chromium removal along with an appreciable COD removal. On the other hand the results of system F3 are rather controversial. More specifically during phase A the system was operated very satisfactorily with complete hexavalent chromium removal. However, following the decrease of mixed liquor temperature from 24^oC (phase A) to values below 20^oC (phase B), system's efficiency to provide for a satisfactory hexavalent chromium removal decreased gradually. Evidently hexavalent chromium concentrations in the treated water increased from values below the limit of detection during phase A to values higher than 80 μg/L at the end of phase B (Figure 1). The decrease of system's ability to achieve satisfactory hexavalent chromium removal was accompanied by a parallel decrease in COD removal (effluent soluble COD concentrations even above 150 mg/L). The decrease of temperature resulted in a drop of system's pH from values around 7 in phase A to values less than 6.4 in phase B. The decrease of pH is an indication of the prevalence of acidified conditions in the anaerobic reactors. According to measurements, VFA concentrations in phase B were equal to 54-64 mg/L with acetic acid being the dominant VFA with concentrations to the order of 50-60 mg/L.

Table 1. Results from the operation of the three experimental units

Parameter	System F1	System F2	System F3 – Phase A	System F3 – Phase B	System F3 – Phase C
MLSS (mg/L)	570	390	736	957	1016
MLVSS/MLSS (%)	90	86	90.8	98	87
$CODsol_{eff}$ (mg/L)	25	25	50	113	42
TSS_{eff} (mg/L)	25	37	40	26	46
$CODsol_{rem}$ (%)	87.5	87.5	75	43.5	79
$Cr(VI)_{eff}$ (μg/L)	< LOD*	< LOD	< LOD	59	3.1
$Cr(VI)_{rem}$ (%)	>99	>99	>99	70	98.5
$Tot\text{-}Cr_{eff}$ (μg/L)	73	84	104	120	92

*: LOD = 2.5 μg/L

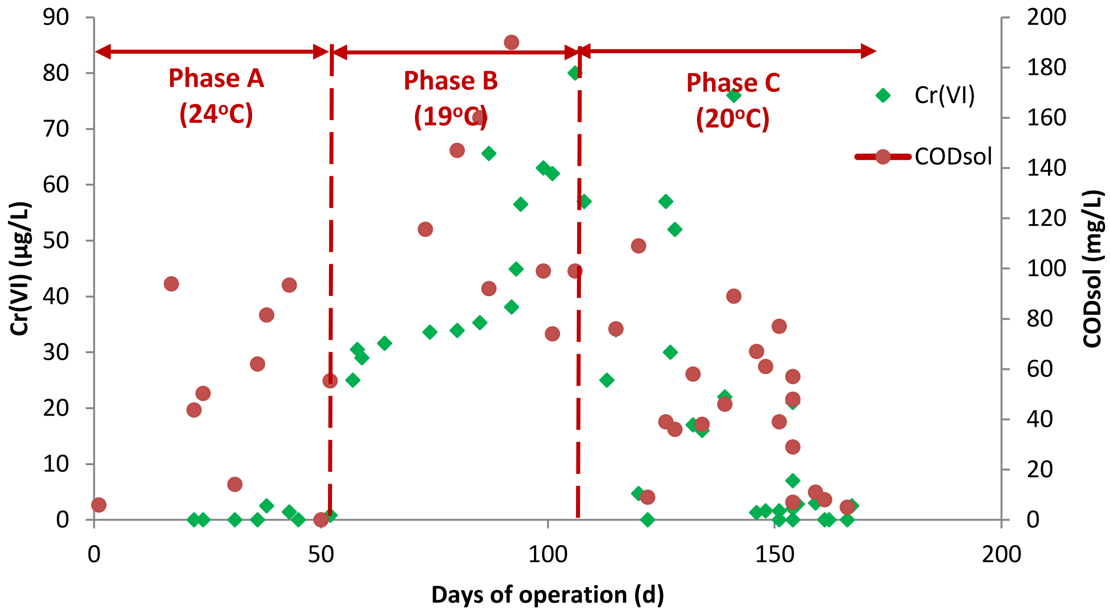

Figure 1. Variation of hexavalent chromium and soluble COD concentrations in treated water for experimental system F3.

In order to increase system's performance sludge age was increased from 10 d to 20 d. As a result system's F3 operation was gradually improved and after a period of approximately two sludge ages (40 d) the system exhibited almost complete hexavalent chromium removal, appreciable COD removal while at the same period (phase C) system's pH increased at values around 7 and VFA concentrations ranged between 10-18 mg/L. Finally, as can be seen from Table 1, effluent total chromium concentrations to the order of 70-100 μg/L were recorded for all experimental systems. Based on the fact than in all bench scale units almost complete hexavalent chromium removal was achieved, effluent chromium is trivalent chromium mostly in a colloidal and particulate form which can easily be removed from treated water in a post-treatment stage (e.g. in a sand filter) as postulated from Mamais et al., (2013).

CONCLUSIONS

The objective of this study was to evaluate the effect of HRT on the ability of anaerobic SBR systems to perform biological hexavalent chromium removal. Based on the results it is postulated that an anaerobic SBR system treating groundwater with hexavalent chromium concentrations as high as 200 μg/L, can provide for complete hexavalent chromium removal when operating at a HRT of 0.9 d at a sludge age of 6.5 d. The same results can be achieved for a HRT of 0.6 d at a sludge age of 10 d for temperatures greater than 20^{o}C or at a sludge age of 20 d for temperatures less than 20^{o}C.

AKNOWLEDGMENTS

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(23) Anaerobic co-digestion of the OFMSW in mixture with the sludge from septic tanks for CH_4 production

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Abstract

Semi-dry thermophilic anaerobic co-digestion of the OFMSW (90% w.w.b.) in mixture with the sludge from septic tanks (10% w.w.b.) for CH_4 production was carried out at lab-scale. Three one-stage completely mixed batch reactors (R1, R2 and R3) with a working volume of 3 L were loaded with the aim to assess the influence of type and concentration of the inoculum sludge on process performance: R1 was inoculated with a sludge coming from a wet mesophilic full-scale facility; R2 was inoculated with the same mesophilic inoculum sludge which was subjected to a centrifugation treatment in order to increase the biomass content inside the reaction chamber and for the R3 reactor a sludge coming from a wet thermophilic plant was used. As regards process stability, all the experimental trials showed good results, no significant differences were detected between the R1 and R2 reactors and the R3 reactor showed the best performance as regards cumulative biogas and CH_4 production (68.08 and 22.08 NL, respectively), average biogas and CH_4 production rate (1.24 and 0.40 NL/d, respectively, respectively) specific biogas and CH_4 production (407.80 and 132.24 $NL/kg_{VSremoved}$, respectively), VS removal efficiency (31.13%) and CH4 content in biogas (65% vol.).

Keywords
Anaerobic co-digestion; Biogas; Methane production; Organic Fraction of Municipal Solid Waste

INTRODUCTION

This study has to be contextualized within a larger research project which aims to advance environmental sustainable technologies and green economy development within the Green District of the Province of Prato (Tuscany, Italy), in order to mitigate the environmental impacts of the activities related to the waste management. Several experimental trials were planned moving from the suggestions of the Preliminary Environmental Study (A.S.M.&G.I.D.A., 2010) of the anaerobic full-scale facility which will be realized in the next future within the district itself. A great amount of the main municipal organic waste streams generated within the district (Mechanically-sorted Organic Fraction of Municipal Solid Waste (OFMSW); Source-sorted OFMSW and Green garden waste from cuttings and prunings) will be treated by means of a semi-dry thermophilic process in plug-flow anaerobic reactors; the sludge from septic tanks will be used as co-substrate for the biological process.

MATERIALS AND METHODS

Several experimental trials on the semi-dry thermophilic anaerobic co-digestion of the OFMSW in mixture with the sludge from septic tanks for CH_4 production at lab-scale were carried out by means of an experimental apparatus composed of one-stage completely-mixed batch reactors (Fig. 1). All the experimental trials were run until the end of biogas production.

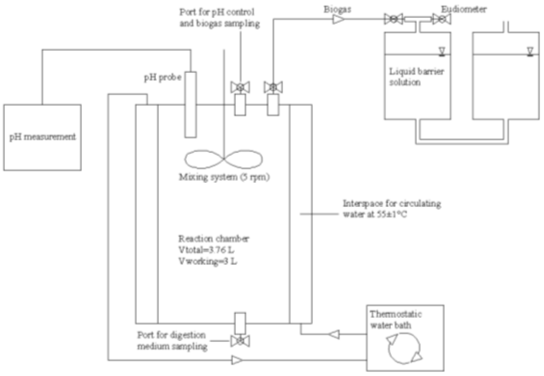

Figure 1. Experimental set-up.

The OFMSW (85% w.w.b. Kitchen waste an paper; 3% Mater-Bi; 12% w.w.b. Green garden waste) was prepared in laboratory on the basis of seasonal analysis performed on samples from the door-to-door collection system of the Prato district and it was stored at -20°C until subsequent use. The sludge from septic tanks was collected at the liquid wastes treatment plant of Calice (Prato, Tuscany, Italy) immediately after the centrifugation step and it was frozen at -20°C until subsequent use. Two different types of inoculum (mesophilic and thermophilic sludge) were sampled from full-scale anaerobic digesters for starting up the experimental trials; the inoculum samples were stored at room temperature. On the basis of the suggestions coming from the Preliminary Environmental Study (A.S.M.&G.I.D.A., 2010) of the anaerobic full-scale facility which will be realized in the next future within the Prato district, a fed-in mixture made of 90% w.w.b. OFMSW and 10% w.w.b. sludge from septic tanks was prepared to load three different batch reactors (R1, R2 and R3). R1 and R2 were inoculated by means of the mesophilic inoculum (which was centrifugated for the R2 reactor in order to increase the amount of biomass inside the reaction chamber), while for R3 the thermophilic inoculum was used. The amount of inoculum sludge to be added was evaluated taking into account the need to dilute the fed-in mixture up to a TS content of around 20% w.w.b., in order to perform a semi-dry anaerobic co-digestion process.

Table 1. Characterization of the fed-in mixtures.

	R1	R2	R3
pH	6.20	6.43	7.20
TS [% w.w.b.]	19.46	20.48	19.09
VS [% ST]	84.75	83.91	84.12
COD_{total} [g/kg_{VS}]	1352.79	1417.91	1572.25
$COD_{soluble}$ [g/L]	55.09	48.93	56.17
N_{tot} [g/L]	2.16	1.19	4.75
$N\text{-}NH_4^+$ [g/L]	0.80	0.67	0.41
P_{tot} [g/L]	0.40	0.64	0.45
C/N [% d.w.b.]	21.91	24.51	18.20

Analytical determinations

Reference methods for compost were applied (ANPA, 2001) for samples with a high TS content; methods for water and waste-water were followed (APAT, 2003) for liquid samples. The COD_{total} for solid sample was determined by following the suggestions of Raposo et al. (2008). N_{tot}, $N\text{-}NH_4^+$ and P_{tot} were evaluated through a flow injection analysis equipment (Lachat QuikChem 8500). VFA_s concentrations in the digestion medium were determined by means of the static head space technique (Agilent Technologies 7890A GC and Agilent Technologies 5975C mass spectrometer). Biogas samples were periodically withdrawn from the headspace of each reactor by means of Tedlar bags and analyzed through a Varian Chrompack CP-3800 GC equipped with a FID.

Table 2. Analytical determinations.

		Analytical determinations
Characterization of substrates	OFMSW, Septic tanks, Inoculum	pH, TS, VS, COD, N_{tot}, P_{tot}
	Fed-in mixture	pH, TS, VS, $COD_{total/soluble}$, N_{tot}, N-NH_4+, P_{tot}, C/N
	Digestion medium	Alkalinity, $COD_{soluble}$, VFA_s (C2, C3, C4, C5)
	Digestate	pH, ST, SV, $COD_{total/soluble}$, N_{tot}, N-NH_4^+, P_{tot}
Treatment process performance		pH, Process and room T, Biogas production and composition

RESULTS AND DISCUSSION

As reported by Liu et al. (2008), the methanogenic bacteria activity is carried out in optimal conditions if the pH is within the 6.5-7.5 range, although the optimal value varies with the substrate and digestion techniques. NaOH addition to the digestion medium was necessary for all the experimental trials in order to avoid the acidification of the system and the inhibition of the methanogenic activity especially during the hydrolytic and acidogenic phase, which occurred in the first two weeks of the treatment process, when no CH_4 production was detected (Fig. 4). The R3 reactor showed an increase in pH up to 8.0 in the last phase of the treatment process (Fig. 2); even if this value resulted to be higher with respect to the above-mentioned optimal range for the methanogenic bacteria activity, no inhibition phenomena were observed for this reactor, since, during this phase, an higher $COD_{soluble}$ and VFA_s degradation (Fig. 3) and biogas and CH_4 production (Fig. 4) was detected with respect to the initial phase of the treatment. VFA_s concentration (mainly acetic and butyric acid, Fig. 3) showed a sharp increase during the hydrolytic and acidogenic phase; these values resulted to greatly exceed the highest concentrations reported as by other authors (Capela et al., 2008), otherwise, especially for the R3 reactor, no inhibition phenomena seemed to occur, since after two weeks of treatment a significant decrease in VFA_s concentration was detected, consistently with the decrease of $COD_{soluble}$ and with the increase of CH_4 content in the biogas up to 65% vol. The R3 reactor showed the best performance as regards cumulative and specific biogas production (68.08 and 407.80 NL/$kg_{VSremoved}$, respectively), cumulative and specific CH_4 production (22.08 NL and 132.24 NL/$kg_{VSremoved}$, respectively), average biogas and CH_4 production rate (1.24 and 0.40 NL/d, respectively) and VS removal efficiency (31.13%) with respect to the other experimental trials. The presence of an higher amount of biomass didn't seem to affect the CH_4 production, which was more or less five times higher for the R3 reactor with respect to the reactors inoculated with the mesophilic sludge (3.89 for reactor R1 and 4.77 for reactor R2).

CONCLUSIONS

Lab-scale experimental trials on the anaerobic co-digestion of the OFMSW in mixture with the sludge from septic tanks were carried out; different types and concentrations of sludge were tested to inoculate the fed-in mixtures with the aim to assess the influence on process performance. The mixture which was subjected to treatment seemed to be a suitable substrate for this type of biological process, since all the trials were characterized by a certain amount of organic matter degradation and CH_4 production. The presence of an higher amount of inoculum didn't seem to affect process efficiency, since the R1 (mesophilic inoculum sludge) and R2 (mesophilic centrifugated inoculum sludge) reactor showed similar performance. The R3 reactor (thermophilic inoculum sludge), showed the best performance in terms of cumulative biogas (68.08 NL) and CH_4 (22.08 NL) production, specific biogas and CH_4 production (407.80 and 132.24 NL/$kg_{VSremoved}$, respectively) and organic matter removal efficiency. Furthermore, in this reactor, an higher amount of intermediate compounds was degraded during the process and, as a consequence, an higher amount of CH_4 was generated with respect to the other reactors, where the VFA_s concentrations remained more or less constant during the process, indicating an hypothetical accumulation of these intermediate compounds.

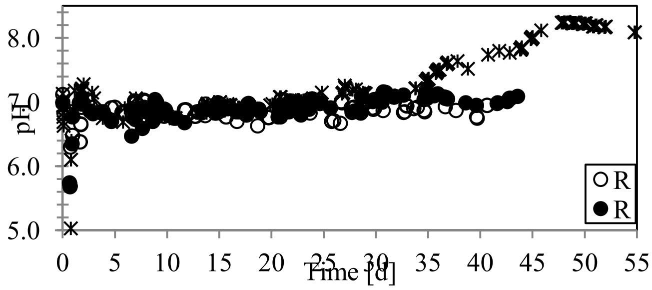

Figure 2. pH of the digestion medium during the anaerobic co-digestion treatment process.

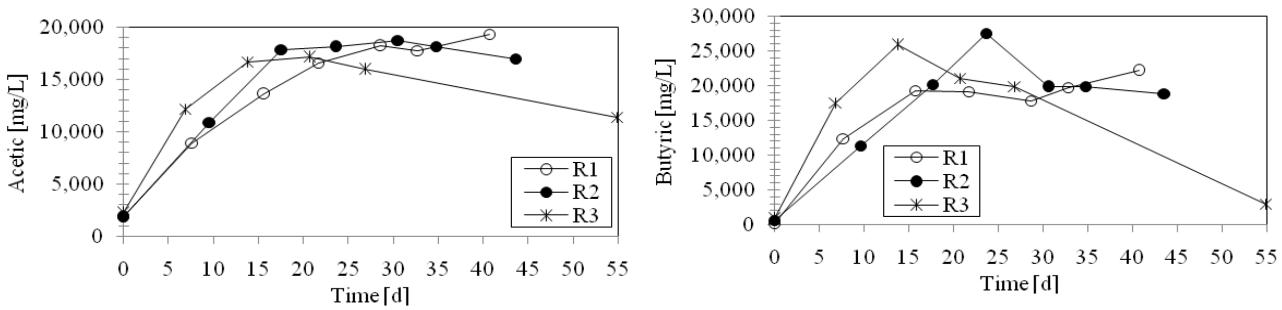

Figure 3. Acetic and butyric acid concentrations in the digestion mediums.

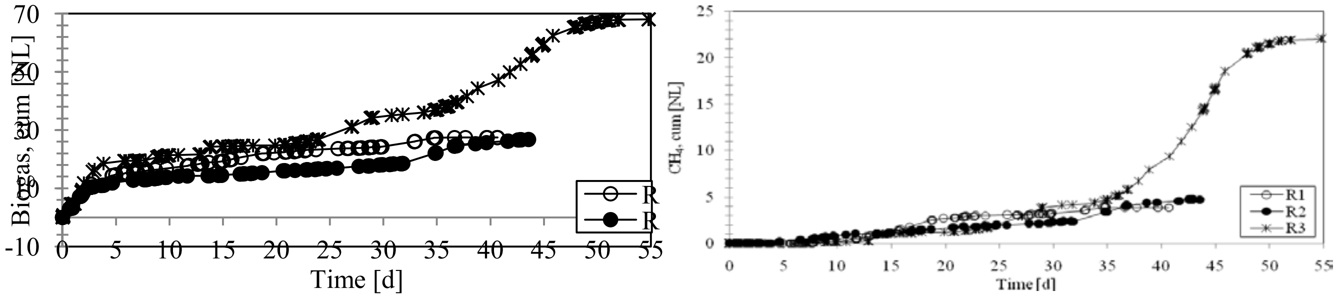

Figure 4. Biogas and CH_4 cumulative production.

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(24) Effects of seawater intrusion in sewage transport and treatment infrastructures: monitoring, diagnosis and solutions

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Keywords
Wastewater, seawater intrusion, sewer system, biological WWTP, sulphate reduction

Extended Abstract

Sewage seashore urban networks frequently have problems related with seawater intrusion. This leads to negative effects on wastewater transport and treatment infrastructures, mainly because of concrete and equipment corrosion (Lens and Pol, 2000) as well as deflocculation of biomass in the Wastewater Treatment Plants (WWTP). On the other hand, there is also an increase in hydrogen sulphide product, which raises concerns about worker health and safety conditions (Tchobanoglous *et al.*, 2003). Problems related to seawater intrusion tend to become more severe with the aging of the sewer systems, due to lack or poor maintenance. The magnitude of this type of problem is often unknown, although it is often correlated with storm discharger's malfunction.

Águas do Algarve, S.A. (AdA) is responsible for the management and operation of the Water and Wastewater Treatment Multimunicipal System that serves Algarve, the south region of Portugal. Production of water, in quality and quantity, for domestic consumption and wastewater according the effluent discharge standards have been its main core businesses. AdA operates 63 WWTP, 165 sewage pumping stations and 456 km of sewers network. Seawater intrusion occurs in several seashore sewer systems, making it a relevant issue in the operation and maintenance of sewage transport and treatment systems.

The present communication describes the methodology applied in the detection and diagnosis of the seawater intrusion in the sewers network system, as well as the main findings and the measures which were adopted to minimize this problem. It also describes the effect of seawater in the treatment process, in what concerns foam/scum production, sludge deflocculation and settling deterioration, sulphide production in anaerobic digesters and anaerobic ponds.

First, chloride and electrical conductivity (EC) parameters were measured in the raw wastewater, by collecting 24h grab samples. This procedure enabled the identification of the systems with seawater intrusion as well as to determine the salinity values in effluents without this problem (Table 1).

Table 1 – Average salinity values for wastewater in Algarve in the absence of seawater intrusion and seawater average salinity values (Kennish, 1989)

Parameter	Unit	Average salinity values for waste water with no seawater intrusion in Algarve region	Seawater average salinity values (Kennish, 1989)
Electrical conductivity	mS/cm	1,4	53
Chloride	mg/l	167	19.800
Salinity	-	0,7	3,5

EC probes were then used for continuously salinity measurement. This approach allowed the identification of the critical points of seawater entrance into the sewer systems. Also the tidal influence of seawater intrusion was evaluated. For instance, wastewater from Frito Velho pumping system had a maximum EC value of 50,9 mS/cm (Figure 1). Through the application of this methodology the main critical point was identified. In this case, a sewer valve was corrected and the maximum electrical value decreased to less than one quarter (9,9 mS/cm) of the initial value.

Nevertheless, salinity concentration is still very high and sewer repair work has to keep going. Most likely, repair all the salt water intrusion points will be very difficult and expensive. Furthermore, with the global warming and, subsequently, the increase of the sea level, the problem might persist or even become worst. Since sulphate concentration is quite high in wastewater with seawater intrusion (about 300-500 mg/l SO_4^{2-}) a possible wastewater treatment solution is to use the sulphate reduction coupled with autotrophic denitrification, like SANI® process (Lau *et al.*, 2006; Lu *et al.*, 2012). It might be a very promising treatment technology also for sewage with seawater intrusion and it is our intention to evaluate it according our real wastewater conditions.

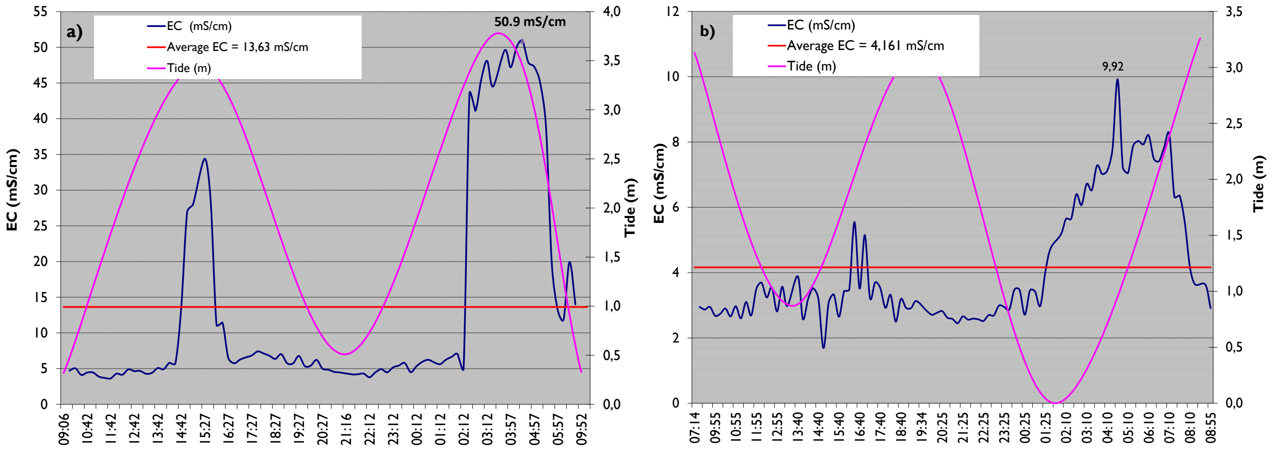

Figure 1. Relation between tidal variation and EC measurements in wastewater Frito Velho pumping station (Companheira sewer system): a) before the monitoring campaign (12 January 2009); b) after the monitoring campaign and the intervention in the sewer valve (6 May 2013).

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(25) Thermal Hydrolysis System Optimization of Sewage Sludge Reduction & Reuse

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This study provides the results of research on discovering optimal reduction of sewage sludge by utilizing thermal hydrolysis reaction. There is an important correlation among temperature, pressure, and reaction time for destroying the cell wall of microorganisms of sewage sludge by thermal hydrolysis. This study has measured the capillary suction time by sampling based on a specified time interval from among the reaction times whereby thermal hydrolysis is achieved. Also the study has evaluated the level of sludge reduction by dehydrating the final sludge with membrane filter press. As a result of the experiment, it has been recognized that the effect of increasing the percentage of dehydration according to the thermal hydrolysis effect of sewage sludge is feasible after sixty minutes of reaction above the temperature of 180oC and above the pressure of 18bar. It appears that such a result will provide much information for the development and administration of the engineering method for the reduction of sewage sludge.

Keywords
Sludge reduction, Organic sludge, Thermal Hydrolysis, Sludge reuse

INTRODUCTION

Recently for Korea, much attention has been shown to the method of treating sludge after the London Convention has prohibited the dumping of sludge onto the ocean. Korea has achieved rapid economic development over the past sixty years, moving from 109th with respect to its GDP in 1953 to 13th this year. The country's rate of sewage provision and technology for related fields likewise achieved rapid progress. As a result, 470 sewage disposal facilities for above 500ton/d are operating presently countrywide with the number continuously increasing. For the same reason, the amount of sewage sludge created is also increasing rapidly.[1]

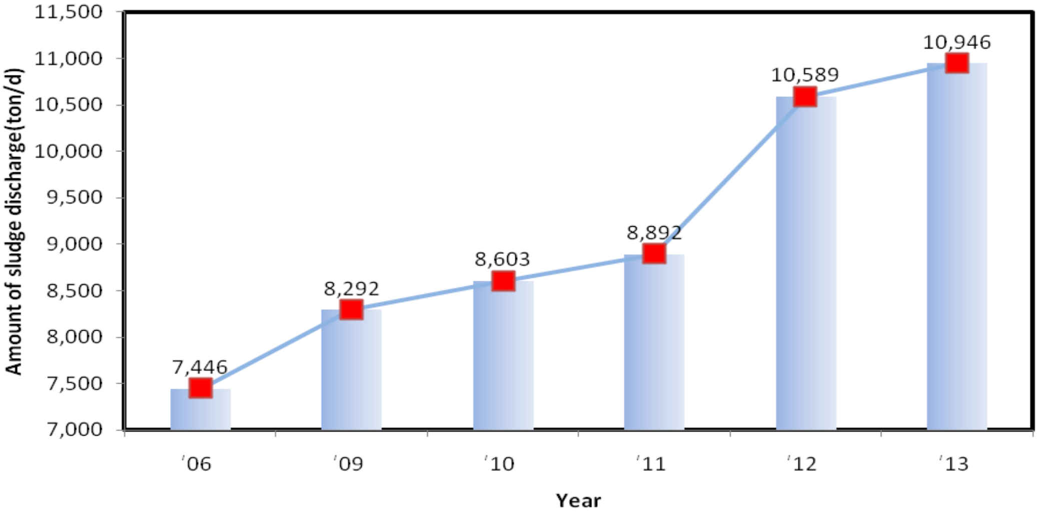

Figure 1. Present condition of sludge discharge at 2011[1]

As Figure 2 shows, much of Korea's sludge was dumped out onto the ocean until 2011 when maritime disposal of sewage sludge was possible. Yet as this was prohibited from 2012, the expenditure associated with processing sludge has increased two to three times over the past two years owing to the absence of an appropriate method. It is expected that the expenditure will continue to increase for the future.

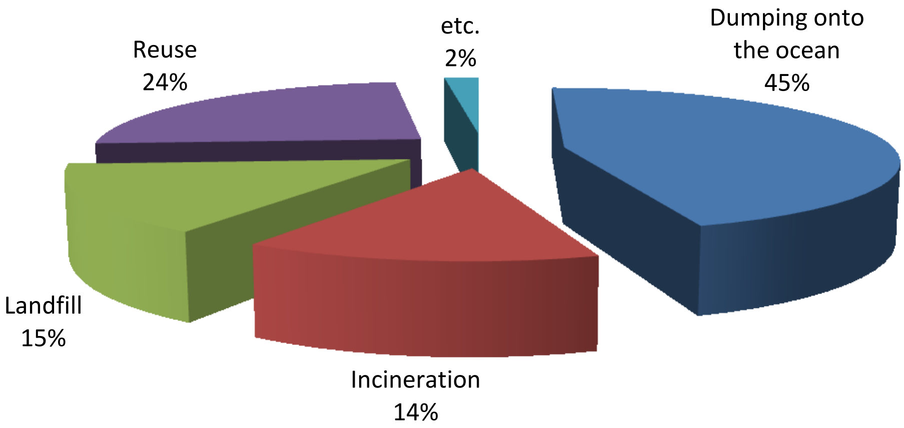

Figure 2. Sludge processing in Korea / 2011

Thermal hydrolysis has been researched for many years as a preprocessing of anaerobic digestion. It has been shown that the elevated temperature and pressure of thermal hydrolysis increases the dehydration efficiency of effluent as they dissolve the cell wall of sludge as well as increases the effect of sludge reduction. Therefore recently, people have called attention to sewage sludge reduction which utilizes thermal hydrolysis. Still there have been very few studies on the influence of thermal hydrolysis on the icon change and reduction percentage of sewage sludge according to time, temperature, and pressure. This article seeks to find optimal operating requirements while monitoring the sludge icon change according to temperature, pressure, and reaction time.

EXPERIMENTAL

Lab scale

This study increased temperature and pressure by introducing steam to 20L thermal hydrolysis reactor for ninety minutes. The temperature was increase by 10℃ and gradually up to 200℃, and then we observed the capillary suction time change and icon change of sewage sludge per hour. Haug has provided a result which shows that the dehydration effect increases after thirty minutes of heat processing of sludge when the temperature ranged from 171℃ to 218℃.[2] Likewise based on the result of an experiment on sewage sludge for 165℃ to 180℃, Brooks[3] has shown that the heat dissolving influence is limited from ten to thirty minutes. Both Haug and Brooks' experiment considered T_0 as the time which commenced after attaining to a specified temperature. Based on this, we executed sampling every fifteen minutes after thirty minutes elapsed from initial reaction as shown by Figure 2. To verify the reduction rate of the final stage slurry, we executed dehydration by utilizing the membrane filter press of 7bar.

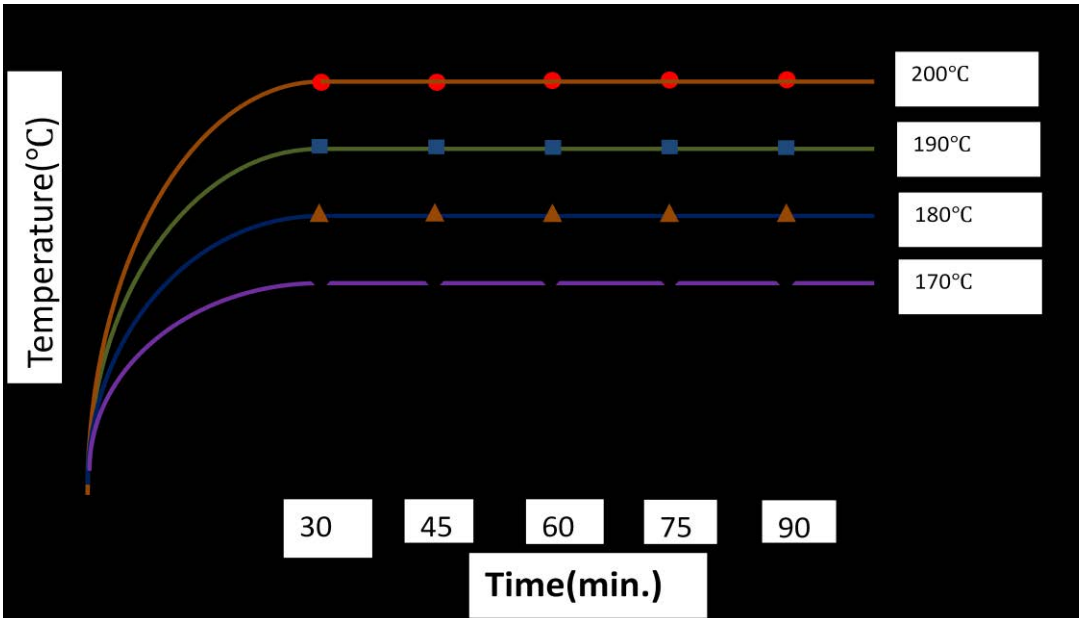

Figure 3. Sampling time per reaction temperature

Figure 4 is a graph which shows the icon change of Capillary Suction Time per hour of thermal hydrolysis. This study has found that the capillary suction time decreased suddenly as the temperature increased and that CST decreased uniquely and gradually when the temperature was 170℃.

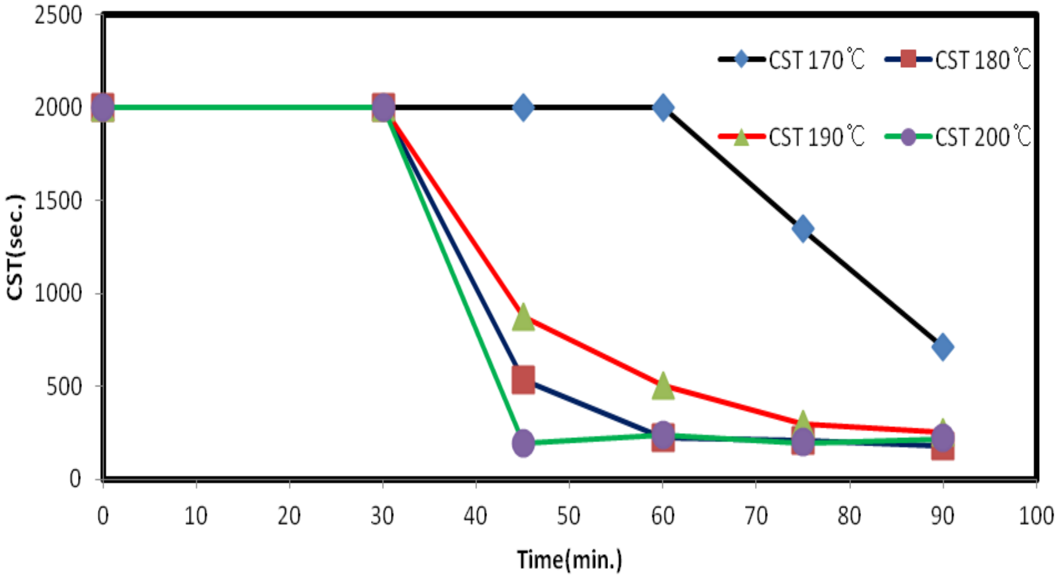

Figure 4. Correlation of time per temperature with CST

Last by dehydrating the slurry which has been reacted by thermal hydrolysis for ninety minutes, this study has shown a hydration percentage of over 60% reduction for the slurry which has been reacted with temperatures ranging from 180℃ to 200℃. Such a result is a phenomenon originating from an increased concentration of extra cellular polymers or ECPs which form the key components of cell wall during the process where sludge organisms dissolve, and Choi has shown that he verified the cause of decreased dehydration capacity based on an analysis of protein and viscosity representative of ECPs.[6] This study has obtained results similar to Choi's study because dehydration was not actually realized for the reaction interval of 170℃.

Conclusion

This experiment has established that the increased efficiency of dissolution and dehydration of the cell wall of sewage sludge from thermal hydrolysis correlates with temperature, pressure, and time. We have obtained the result that the optimal reaction requirements of TH for the reduction of sewage sludge is approximately over one hour of reaction time with a temperature of over 180℃ along with over 18bar. It can be concluded that such a result can be utilized valuably for determining the time and scale of the reactor when developing the thermal hydrolysis process.

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(26) Electrochemical water treatment system in the dairy industry with hydrogen recovery

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Abstract
The current paper demonstrates the viability of a new electro-coagulation (EC) system for a partial dairy effluent treatment with the simultaneous hydrogen recovery. This technology is integrated within a whole eco-efficient treatment strategy for dairy effluent treatment based on the coupling of several advanced electrochemical technologies for the c, enabling water reuse and valorisation of some by-products. Research is being carried out under the European project called REWAGEN (FP7-ENV-2011-ECO-INNOVATION-TwoStage).

Keywords
Dairy treatment; electro-coagulation; hydrogen recovery; REWAGEN project; whey; wastewater.

INTRODUCTION

REWAGEN is an EU project that aims to research on an eco-efficient strategy for dairy effluent treatment based on advanced electrochemical technologies for the abatement of contaminants, enabling water reuse and valorisation of some by-products, including residual hydrogen.
The process includes a pre-treatment, an electrocoagulation and electrooxidation step and a final conductivity reduction process. The energy needed for the treatment will be partially recovered from the valorisation of hydrogen produced during the electrochemical treatments.
Moreover it is consider the separation of metals from the electrocoagulation sludge so that the final separated organic sludge can be valorised for energetic or fertiliser purposes.

The current paper is focused on one of the advanced electrochemical technologies investigated during REWAGEN project: the electro-coagulation (EC) process.

OBJECTIVES

The main objective is the research on a new EC design and performance that allow not only the achievement of a suitable technology for the simultaneous abatement of (i) turbidity, organic matter, nitrogen and phosphorous content of the dairy effluents, and (ii) recovery and valorisation of hydrogen; but also that could be integrated to other electrochemical technologies for a sustainable and costly efficient dairy effluent treatment.

SYSTEM DESIGN

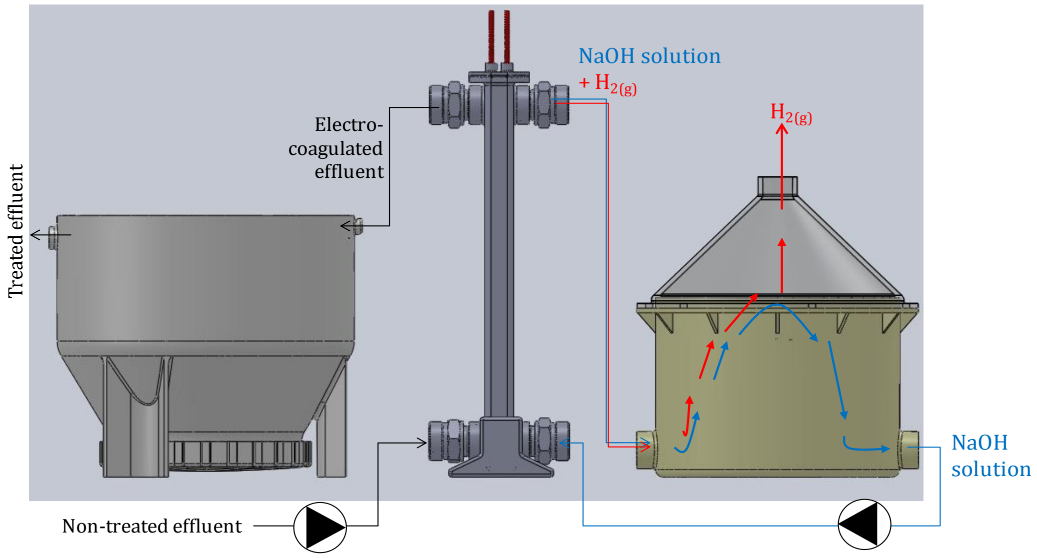

Figure 26. 2D view of bench scale EC unit.

REWAGEN EC system operating at continuous mode is composed by the following three modules:

- An electrochemical bi-compartment cell, where hydrogen is recovered from cathode compartment and dairy effluent is treated in anode compartment. The electrochemical cell can be also operated as a mono-compartment cell.
- A sealed tank for hydrogen recovery and catholyte recirculation.
- An opened tank where electro-generated coagulants will be removed from the treated effluent.

Figure 26 shows a 2D view of continuous EC system at bench scale used in REWAGEN project.

RESULTS

Results based on the performance of the REWAGEN EC continuous system (working with the mono-compartment electrochemical cell) show that turbidity removal is higher than 97% in all experiments (

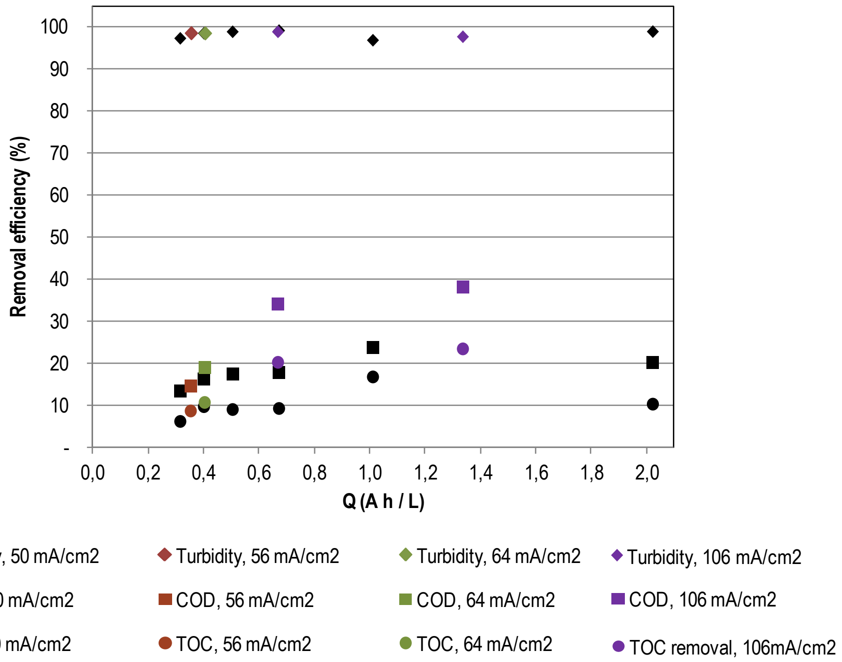

Figure **27**). An increase on applied charge (A L /h) for a same applied current density (i.e.,50 mA/cm^2) brings to a slightly increase on TOC and COD removal; as well as an increase on current density for a same applied charge gives to higher TOC and COD removals.

Focusing on an applied charge of 0.67 A L/h, 20% and 34% of TOC and COD removal, respectively, are achieved working at 106 mA/cm^2, being these last results better than these ones obtained at batch mode, under the same applied charge (data non shown).

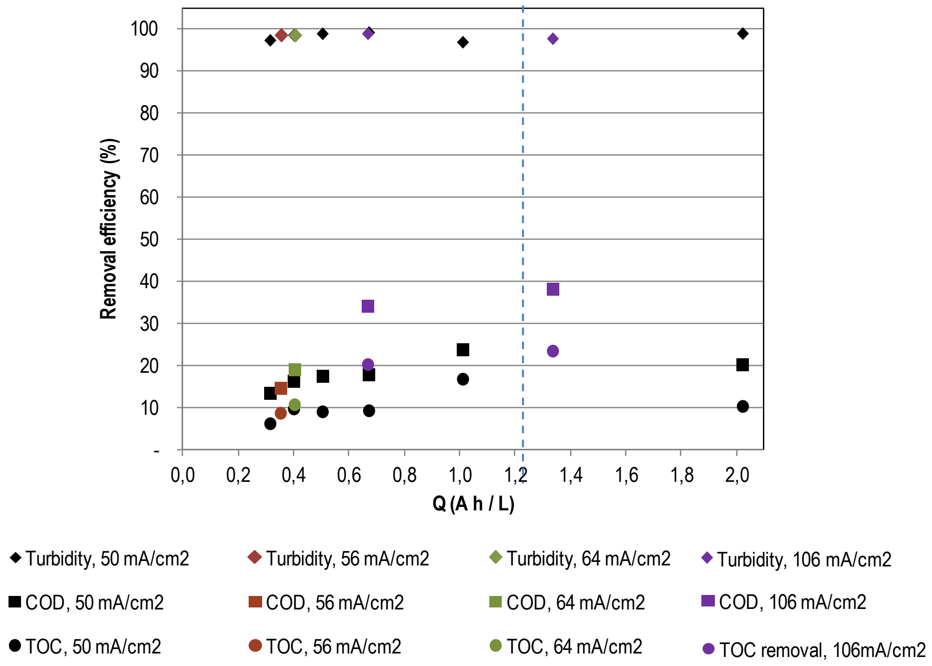

Figure 27. Removal efficiency for dairy effluent treatment by EC system at continuous mode, under several current densities and flow rates, using aluminium anode.

The fact of reducing both (i) current density and (ii) time during EC process brings to the reduction on electrical consumption. Consequently, 0.67AL/h and 106mA/cm^2 has been proposed as the most appropriated operational conditions for EC system since abatement of contaminants is achieved with low electrical costs.

EC continuous experiments with the bi-compartment cell and simultaneous hydrogen recovery are being carried out, showing promising results.

ACKNOWLEDGEMENTS

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(27) Hydroxyapatite precipitation from a highly concentrated phosphate solution

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Abstract

Depletion of world phosphorus reserves is driving research into options to recover and recycle this essential, non-renewable resource, furthermore phosphate removal from water is of great concern sinceit causes eutrophication. To achieve this objective, phosphate recovery is proposed to be accomplished inwastewater treatment plants (WWTPs). Nowadays, phosphate is mainly removed from water in the form of biomass or precipitated or-coprecipitated with Fe and Al hydroxides. However, efforts to recover phosphate from the WWTP streams after the biological carbon removal by sorption and ion-exchange are under development. Elution of the loaded ion exchangers and sorbents will produce rich phosphate solution (from 1 to 3 g/l).Efforts then are directed to recover phosphates as marketable fertilizers like hydroxyapatite (Hap)(Ca/P 1.67).Phosphate recoveryby chemical precipitation from aqueous solutions using high concentrations of calcium and phosphate in a batch reactor was studied. These calcium concentrations simulate those that can be obtained in reverse osmosis/nanofiltrationbrines (e.g. sea water desalination) and sorption/ion exchange effluents as sources of calcium and phosphate, respectively. The chemical precipitation of phosphate in a batch reactor wascarried outin order to evaluate several conditions, such as pH, calcium flow rate, phosphate initial concentration and then,the solid precipitatedwere characterized by XRD, IR, SEM/EDAX.... etc.

Keywords
Phosphate;calcium from reverse osmosis brines;hydroxyapatite; batch reactor;chemical precipitation

INTRODUCTION

Wastewatertreatmentplantsmustremovephosphorusand nitrogencompoundsfromthewastewaterbeforeitsfinal disposalinordertopreventeutrophication [1,2].
Several physical, biological and chemical processes have beeninvestigated for the removal of dissolved phosphates in water andwastewaters. These processes include adsorption/ion exchange,chemical precipitation/coagulation, crystallization and membranefiltration/reverse osmosis. Adsorption/ion exchange technologies are promising, because they aresimple and economical, result in less sludge production andtherefore experience minimal disposal problems [3].
Incorporation of water recycling into conventional wastewater treatment plants normally involves the addition of a dual membrane process consisting of ultrafiltration or microfiltrationfollowed by reverse osmosis. However, the recent growth in membrane based water recycling projects, where reverseosmosis is used to produce high quality water has resulted in the production of liquid waste streams that could be used to recover the residual phosphate content by using sorption and in-exchange concentration processes.
The application of reverse osmosismembranes produces a nutrient rich concentrate stream containing phosphorus levels four to six times higher [4] than theinfluent wastewaterwhich is currently either discharged aswaste or further treated. However the subsequent application of an ion exchange or sorption process could increase the concentration factor au to a factor of 100-200 folds, and then rich phosphate streams (1-5 g/l) could be obtained. Additionally, reverse osmosis treatment of many industrial effluents produces high calcium andmagnesium brines that could be used as source of calcium and magnesium to precipitate phosphate hydroxyapatite (Hap) or struvite fertilizer.

Hap has been extensively used in bone replacement applications due to its biocompatibility, bioactivity, and osteoconductivity. Inthiscontext, it is desirable that Hapcrystals meet specific requirements, such as high specific surface area (favoured by small crystalsize), narrow size distribution, and high purity, in order to optimize bone related cell growth around them.

Moreover, researcher shave demonstrated that batch reactors (BRs) have the advantage of providing extreme flexibility in operation and at the same time being physically simple, since all the treatment activity (i.e. flow equalisation, biological reactions and biomass settling) takes place in one single tank. The simple physical structure of the BR systems also means less cost for maintenance.

The main objective of this study was to apply (BR) for the precipitation of hydroxyapatite (Hap)under several operation conditions(pH, phosphate concentration...etc) in order to optimize the phosphate recovery as Hap in a stirred tank batch reactor.

MATERIAL AND METHODS

Experimental set-up and analytical methods

The precipitation of Hap was performed in a (BR) made of glass with 2L of volume. The phosphate ($NaH_2PO_4.H_2O$) and calcium ($CaCl_2.2H_2O$) were mixed at room temperature in order to reach a suitable molar ratio Ca/P of 1,67. The concentration of calcium and phosphate were determined by Ion Chromatography System (ICS-1000). pH was measured with a pH glass electrode Mettler Toledo (HA405-DPA-SC-S8/225).

Chemical and physical characterization of Ca/P precipitates.

Samples were withdrawn at the batch reactor and then filtrated and dried at T=50°C during 24h. Solid precipitated werethencharacterizedbyX-raydiffraction,Fouriertransforminfraredspectroscopy (FTIR),andscanningelectronmicroscopy(SEM /EDAX).

Experimentaldesign.

The MEDUSA/HYDROCHEMICAL equilibrium calculation numerical code was used to theoretically predict the effect of pH on Ca-PO4 precipitation reactions.

RESULTS AND DISCUSSION

The most important factor concerning calcium phosphate precipitation is the pH.As it could be seen in Figure1, at slightly alkaline pH (7.0 to 8.5) the decreaseof phosphorus from phosphate rich solutions is inversely proportional to the increase in pH value and for pH up to 7 the stable mineral phase present is the Hap ($Ca_5(PO_4)_3OH(s)$).

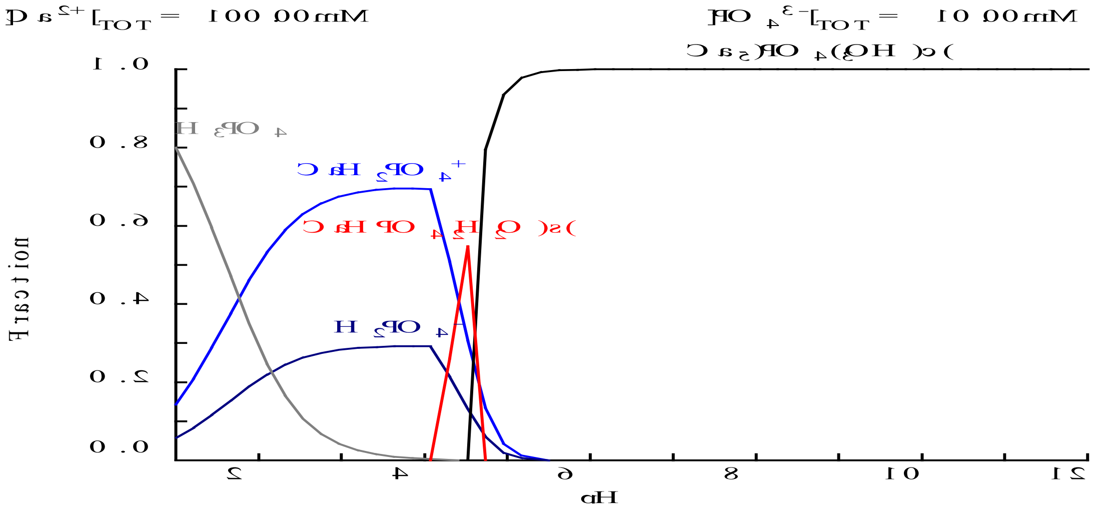

Fig.1.Variation of phosphate and calcium concentrations with the pH and precipitation of Hap using the

hydro chemical HYDRA/MEDUSA equilibrium calculation code.

Effect of pH control in Hap precipitation

A batch reactor tests were performed without and with pH control in the range of basic level. The results showed that the maximum removal of phosphate were obtained with pH control for this reason keeping pH constant along the whole experiment represents the favourable condition from the point of view of the phosphate precipitation (table 1.).

Tab1. Hap recovery with and without pH control

	Initial pH	*Final pH*	*% PO4 removal*	*Ca/P*
Without control pH	10,5-11	5,46	50	1,60
With control pH	8 10 11,5	8 10 11,5	96 93 95	- - -

Influence of Initial phosphate concentration

The evolution of phosphate profiles in the supernatant in fourexperiments carried out with pH control at different initial phosphate concentration is shown in Fig.2. The initial phosphate concentrations ranged between 250 and 1000 ppm. As it could be observed phosphate concentration decreased along the experiment reaching a final concentration below 0.1 mg/l (limit of quantification for phosphate in this study). It should be pointing out that the all experiments were carried out following a Ca/P ratio of 1.67 and once this ratio was reached not additional calcium was added into the reactor leaving some amount of phosphate available in solution.

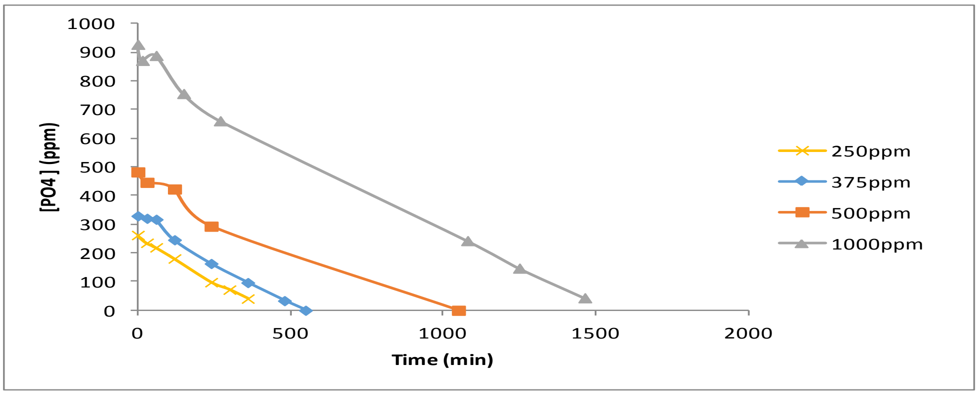

Fig.2. The influence of the initial phosphate concentration onto the Hap precipitation in a BR

The influence of the stirring speed and the calcium flow rate addition to reactor were also studied. The results indicated that the kinetic behaviour and the recovery percentage it is always the same and around more than 80% under the different agitation rates used (50, 100, 150 and 250rpm). Also for maximum calcium addition flow-rate (Q= 0,3ml/min) the removal of phosphate is quantitative (>99%) and the precipitation rate is higher.

Conclusions

Hap precipitation from rich phosphate effluents was studied as a solution to recover phosphate as a Ca-

P fertilizer from wastewater treatment plant effluents and using Ca brines as precipitant. This potential Ca-P precipitation scheme considers the use of higher concentration of calcium (rejected reverse osmosis/nanofiltration effluents) and also of phosphate (sorption/ion exchange pre-concentration effluents).The results showed that the most important parameter is the pH control, since it should be maintained constant along the experiment, thus ensuing higher levels of phosphate removal. The Ca/P ratio appeared also as a critical parameter at higher phosphate concentrations.Theparticlesize ofprecipitantappearstobeincreasedbytheseparateand combinedeffectsoflimitingsupersaturatingandgoodmixing. Moreover, the phosphate can be stripped from waste water at room temperature, and recovered by precipitation with calcium and then crystalized for fertilizer production.

Acknowledgments

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(28) Mixed culture PHA production with alternating feedstocks: process robustness and population dynamics

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Abstract

Polyhydroxyalkanoates (PHA) are a sustainable alternative to conventional plastics that can be obtained from industrial wastes/by-products using mixed microbial cultures (MMC).MMC PHA production is commonly carried out in a 3-stage process consisting ofan acidogenicstage,a PHA producing culture selection stage, and a PHA production phase. This workinvestigatedthe performance robustness and microbial population dynamics of a PHA producing MMC when subjected toa feedstock shift, mimicking a seasonal feedstock scenario, from cheese whey to sugar cane molasses. Research was focused on the possibility of tailoring PHA throughthe selection of feedstock: either using feedstocks with different compositions or mixing two or more fermented substrates with different organic acidprofiles. This knowledge is expected to contribute to the extended application of this promising process for resource recovery from industrial wastes.

Keywords

resource recovery; polyhydroxyalkanoates; industrialwastewater;mixed microbial cultures

Introduction

PHA are a bio-based and biodegradable alternative to plastic-based polymers. PHAs implementation has been limited by high production costscompared with conventional plastics. Low cost processes for PHA production, such as the use of MMCs which do not require sterile conditions and usecheap substrates, like industrial wastes/by-products, have been recently developed (Reis *et al.* 2011). MMC PHA production commonly involvesa 3-stage process: (1) acidogenic fermentation of the organic carbon to produce mixtures of organic acids, which are PHA precursors; (2) culture selection stage, where a MMC issubjected to a high selective pressure for PHA storage through the use of alternate feast and famine regime; and (3) PHA production stage where the selected MMCis fed with the organic acidsproduced in the acidogenic fermentation in conditions to promote PHA storage up to the culture's maximum capacity.The PHA monomers composition, which determines the physical and mechanical properties of the final polymer, depends on the percentage of each organic acid in the fermented feedstock. The use of wastes/wastewaters or industrial by-products as feedstock is the most promising strategy to reduce the cost of biopolymers produced by microbial processes, given their availability, large diversity, lack of valuable alternative utilisations, and low cost (Jiang *et al.*, 2012; Chakravarty*et al.*, 2012; Albuquerque *et al.,* 2012; Beccari*et al*., 2009). However, many of the industrial wastes/by-products are seasonal, so PHA producing processes will have to comply with this seasonal availability. Therefore, this study investigated the process robustness and microbial population dynamics when subjectedto alternate operation with different available feedstocks throughout the year. A shift in the feedstock will also likely affect the composition of the fermentation product, and thus the final polymer composition.Therefore, the results of this study can also be used to manipulate the obtained PHA by alternating of mixing feedstocks with different compositions.

Material and Methods

The feedstock acidogenic fermentation (stage1) was carried out in an anaerobic membrane bioreactor (AnMBR). The permeated fermented feedstock obtained, rich in organic acids, was used as influent for the subsequent stages:the culture selection stage and the PHA accumulation stage. Enrichment of a PHA-storing culture (stage2) was carried out in a sequencing batch reactor (SBR) subjected to feast and famine conditions. PHA production (stage3) was conducted in a batch reactor using sludge collected from the culture enrichment SBR and pulse-fed with the clarified fermented feedstock produced in stage1. Two feedstocks were investigated in this study: cheese whey (CW) and sugarcane molasses (SCM). In terms of carbon source, CW is mainly composed of lactose and proteins, and SCM is mainly constituted by sugars.Samples from the influent feeds, reactor biomass, and effluents of each reactor were frequently analysed.Microbial community analysis of both the acidogenic MBR and the PHA-storing MMC were followed by high throughput amplicon sequencing of the16S rRNA gene using IlluminaMiSeqtechnology. Moreover, the dynamics of the MMC was quantitatively monitored throughfluorescence *in* situ hybridisation (FISH) quantification, using probes for previously described PHA producing organisms (see Albuquerque et al., 2013).

Results and Conclusions

The fermentation products obtained with the two studied substrates had substantially different profiles (Figure 1), where a higher abundance of acetate was obtained with CW and higher fractions of propionate and valerate were observed for SCM. Interestingly, almost the exact same profile was obtained with CW once it was restored as feedstock after a period using SCM, showing the reproducibility and robustness of the process.

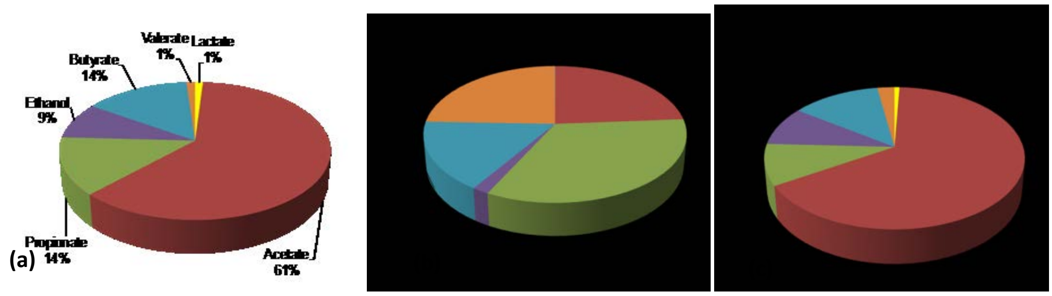

Figure 1. Fermentation products obtained in the acidogenic fermentation statefed with alternating feedstocks: (a & c) CW and (b) SCM.

The monomer composition of the biopolymer in the PHA accumulating stage was linearly correlated to the concentration of precursors obtained in the acidogenic stage for production of hydroxy-butyrate (HB) - acetate and butyrate - and hydroxy-valerate (HV) - propionate and valerate. Thus, alternating seasonal feedstocks with different compositions will lead to the seasonal variation of the polymer composition, which is not compatible with the market requirements. This situation may be overcome through mixing two fermented feedstocks to continuously produce a polymer with a defined composition (Figure 2). In practice, this may be achieved by having two acidogenic fermentation reactors fed with two different raw feedstocks (available during the same season) to produce different organic acids profiles, which can then be mixed in variable volume proportions according to the target polymer composition. Moreover, using this approach,it is possible to fine-tunethe polymer composition.

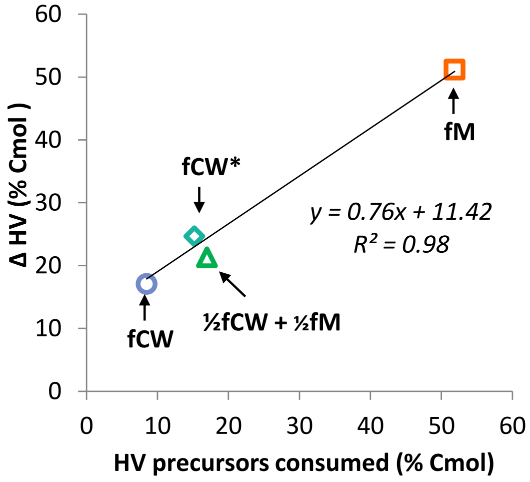

Figure 2.HVproduced (*ΔHV*)during fed-batch PHA accumulation assays as a function of the consumed precursors in fermented SCM (□)and fermented CW (○&◇), and in the fermented feedstocks mixture(△).

High throughput sequencing was performed to follow the changes in microbial populations in the acidogenic fermentation reactor and in the PHA culture selection reactorobserved upon the shift in feedstock from SCM to CW. In the acidogenic reactor, a clear change in ecology accompanied the substrate shift. During the SCM phase, the *Actinomycetaceae* family constituted 75-93% of the total ampliconreads, whereas a more dynamic population was detected during the CW phase. The *Streptococcaceae* family dominated during the first 18 days of this phase, followed by *Lactobacillus delbrueckii*–related species 42 days after the introduction of CW.In the selection SBR, quantitative FISH showed a decrease in the *Azoarcus* and *Thauera* populations with the introduction of fermented CW(Figure 3). The sum of *Thauera*, *Azoarcus* and *Paracoccus*biovolume of the bacterial population was less than 50% throughout the CW phase, whereas these three groups covered most of the population when fed with fermented SCM. However, both systems had high PHA storage capacity (55% for SCM and up to 65% for CW), suggesting that the remaining population also contained high abundance of other organisms with PHA-storing capacity.

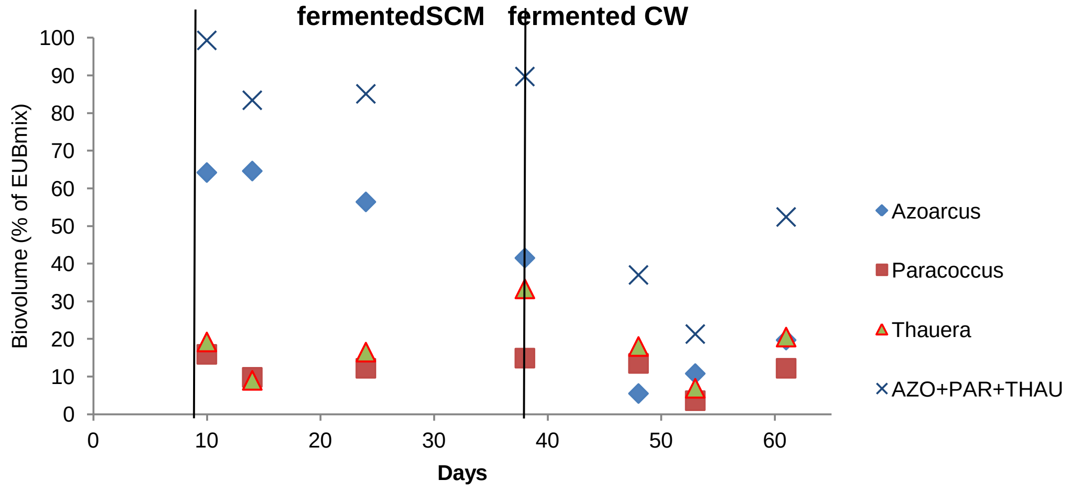

Figure 3. Populationdynamics of the selection SBR fed with fermented sugar molasses (SCM) and fermented cheese whey (CW), determined through quantitative FISH using specific probes (AZO644 for *Azoarcus*, THAU832 for *Thauera*, PAR651 for *Paracoccus*) as a percent of all the bacterial population, determined with the EUB mix probe.

In fact, when the feedstock shifted to CW, the resulting organic acids composition increased in propionate and valerate in detriment of acetate (Figure 1), which resulted in a dramatic change in the SBR population composition. High throughputsequencing results showed a very dynamic community, indicating temporary presence of other organisms with PHA-storing potential, including some members of the Bacillales order such as *Clostridium* and *Paenibacillus*.These results indicate that the feedstock has a high impact on the PHA MMCstructure, and that certain feedstocks may be more prone to develop more diverse microbial populations, contributing to a higher level of functional redundancy.

Acknowledgements

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(29) Optimization and impact of sludge alkaline fermentation on nutrient removal from sewage

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Abstract

The use of sludge fermentation liquids to enhance denitrification and biological phosphorus removal from wastewater is becoming more attractive, following the growing concern on sustainability and greenhouse gas emissions. This work investigated the pilot scale production of the best mixture of short chain fatty acids (SCFAs) in terms of the subsequent biological valorization. Three major aspects are hereby presented and discussed: the alkaline fermentation of sewage sludge; the membrane filterability of the fermentation effluent; the impact of the fermentation liquid on nutrients removal.

Keywords
sludge alkaline fermentation; short chain fatty acids membrane separation; minerals

1. INTRODUCTION

Wastewater facilities are increasingly being asked to implement treatment process improvements to meet stricter discharge limits with respect to nutrients. Recoveringshort chain fatty acids (SCFAs) from sewage sludge is a challenge to optimize the operation of WWTPs. Fermenting sludge to generate SCFAs seems to be a sustainable process to produce external carbon source to be used in the subsequent biological nutrient removal (BNR) process.Recent research is focusing on the investigation of sludge alkalinefermentation (SAF) to produce a valuable external carbon source (Tong and Chen, 2007).It is still not well documented how key parameters can affect SCFA production. Furthermore, most applications ofwaste-derived SCFAs still remain in laboratory scale (Lee et al., 2014). To ascertain the transferability of the process from the laboratory to the market,pilot scale studies are required. The pH is an important factor that controls the hydrolysis and acidification during sewage sludge fermentation. Alkaline conditions are expected to lead to more soluble protein and carbohydrate generation. Recent studies have demonstrated enhanced SCFAs production under alkaline conditions sincethe inhibition of methanogenic activity resulted in less SCFAs consumption. The optimum pH range was 9-11 and was reached using chemicals (Wu et al., 2010; Su et al., 2013).The effective separation of fermentation liquid from the fermented sludge can enhance the sustainability and can lead to reduced production of wet sludge. Previous studies showed that the sludge dewatering ability was negatively affected by the use of caustic soda due to Na^+release (Su et al., 2013).Separation may not be effective and the deteriorated filterability of sludge makes conventional dewatering methods unpractical (Tong and Chen, 2007). The application of an efficient separation method based on membrane filtration is examined. The use of a suitable mineralto enhance the fermentation process and the subsequent separation stage is also investigated.Finally, the producedSFL was tested for BNRfrom wastewater.

2. MATERIAL AND METHODS

The sewage sludge used for the fermentation experiments was collected from themunicipal WWTPof Carbonera (Veneto Region,Italy). It consisted of mixed primary and secondary sludge.A pilot scale SAF unit was set up and was operated in the Carbonera WWTP. It was composed of the sewage SAF unit (reaction volume 500 L) and an ultrafiltration (UF) membrane filtration skid (MO P13U 1m, Berghof, Germany) for the solid/liquid separation of the fermentation effluent (Fig 1). Sludge screening through 50 mm was sufficient to prevent membrane clogging.

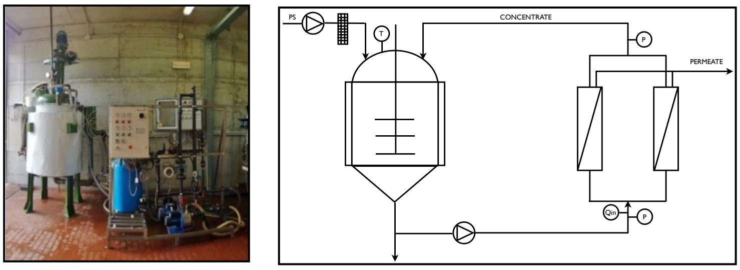

Fig 1 Integrated pilot scale SAF and membrane separation system

The impact of pH (8.0, 9.0, 10.0) and temperature (35,40^{o}C) on the production of SCFAs was investigated in the SAF pilot (Fig. 1). The temperature was maintained by electric water heater andcaustic soda was used to buffer the pH. The use of wollastonitewas examined to increase pH without chemicals andenhance the dewatering characteristics of fermented sludge. Wollastonite was the mineral that was employed to control the pH and to improve the sludge dewatering characteristics. The mineral was supplied by Sigma Aldrichand was used in its natural form. Five batch reactors (1 L) were operated as follow: 1 batch reactor as blank and 4 having different wollastonite concentrations(1, 10, 20, 40 g/L).The temperature was maintained at 37^{o}C.In the pH and mineral experiments SCFAs, pH, total and volatile suspended solids (TSS, VSS), ammonium and phosphorous release were measured daily in the SFL. Capillary suction time (CST), time to filter (TTF) and step-flux tests were carried out at the end of every fermentation test to evaluate the sludge filterability and the critical flux.Batch experiments were also conducted to investigate the effect of the produced SCFAs on the specific nitrite and phosphate uptake rate (i.e. sNUR and sPUR) and on the specific phosphorus release rate (sPRR). The tests were carried out as reported by Alvarino et al. (2014)and Janssen et al. (2002).The pH, TSS, VSS, COD, soluble COD (sCOD), ammonium, CST, TTF were determined by standard methods (APHA, AWWA, WEF, 1998). NO_2-N, NO_3-N and PO_4-P were determined by ion chromatography (Dionex ICS-90 with AG14 and AS14 columns). SCFAs were analyzed by gas chromatography (Column: Nukol 15 m, 0.53 ID; temperature 85-125°C, 30°C min^{-1}; carrier: N_2, 5 mL·min^{-1})

3. RESULTS AND DISCUSSION

3.1 Sewage sludge characteristics

The main sludge characteristics of the sewage sludge used as raw material in the fermentation process are presented in Table 1.

Table 1 Sewage sludge characteristics.

Parameter	Average ± standard deviation	Parameter	Average ± standard deviation
TSS (g/L)	19.1 ± 1.5	pH	6.4± 0.3
VSS (g/L)	15.6 ± 1.6	SCFAs (mg/L)	235± 142
sCOD(mg/L)	274 ± 56	NH_4-N (mg/L)	46.1 ± 13
Total COD (mg/gSS)	954.04 ± 45	PO_4-P (mg/L)	12.6± 2.7

3.1. Determination of the optimum sludge fermentation conditions

The highest production of SCFAs was obtained at pH=10, T=40°C at the 5th day of operation. The maximal conversionof VSS to SCFAs rate was 220mgCOD/gVSS. The yield of SCFAs production was linearly dependentonthe change of pH and T:

$$\Delta \mathrm{Y}\left(\frac{\mathrm{mgSCFAs}}{\mathrm{gVSS}}\right) = (21\Delta\mathrm{pH} + 2.4\Delta\mathrm{T})$$

When 20 g/L (pH 7.0) and 40 g/L (pH 8.0) of wollastonite were applied at37°C, high production of SCFAs was obtained: 301 and 314mgCOD/gVSS respectively. Wollastonite may optimize the economical and environmental sustainability of the fermentation, together with the solid-liquid separation properties of the fermented sludge.

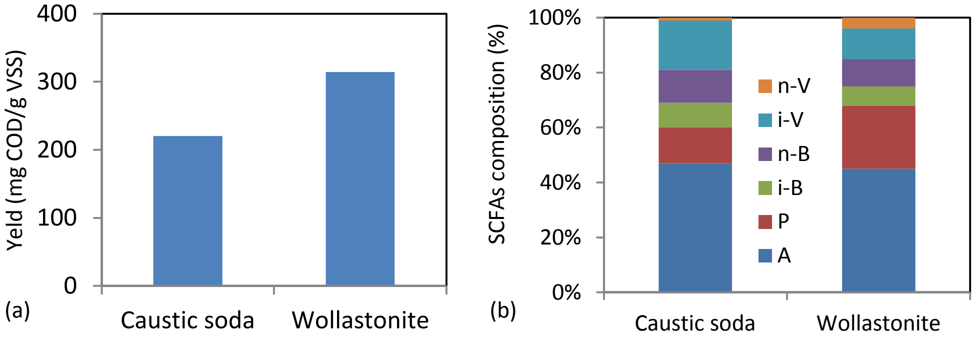

Fig 2 Comparison between caustic soda (pH 10.0 / 40°C) and wollastonite (40 g/L/ 37°C) fermentation experiment: (a) SCFA production; (b) SCFA composition.

Acetic, propionic and butyric acids are the compounds of major interest as they enhance BNR(Frison et al., 2013).Acetic acid was the most prevalent acid andpropionic acid the second one (13-23%). The use of wollastonite not only led to higher production of SCFAs, but also increased the percentage of propionic acid in SCFAs.Similar nutrient release was foundwhen pH was controlled using caustic soda, the maximum release was at pH 10 and 40°C (521.0 mgN/L and 81.2 mgP/L). The effect of temperatureon nutrients release diminished as the pH increased.

3.2 Filterability and membrane separation

The solid-liquid separation of the fermentation effluent is often a bottleneck. The membrane process was employed as a sustainable option for the solid/liquid separation. The UF membrane module allows the complete retention of suspended solids within the reactor. However, the filtration performance decreased with time due to the deposition of soluble and particulate matter on the membrane.The temperature of the SFL was high (~35^{o}C), fact that is expected to benefit the filtration process.

The filterability of the caustic soda fermentation effluent was evaluated by the step-flux filtration test (Fig3a).The increase of TMP caused an increase of the permeate flux. However, beyond a certain TMP the flux decreased. This indicates that there is an optimum operating TMP. Moreover, the increase of pH negatively affected the permeate flux probably due to the release of Na^{+}. The sludge dewatering characteristics and the separation process can be adversely affected from the use of caustic soda(Su et al., 2013). Furthermore, caustic soda reduced the efficiency of the separation process. In this study wollastonite was added to increase the pH without chemical use, and to favor the dewatering characteristics of the sludge and maximize the separation performance.In light of that high-energy demand, better dewatering characteristics need to be investigated in order to reduce energy consumption.Significantly lower NH_4 and PO_4 release occurred when wollastonite was added, (Fig 3b). The addition of 40 g/L of wollastonite decreased the CST and TTF (37% and 60% respectively) resulting I more favorable dewatering characteristics (Fig 3c).Compared to the use of soda, the alkali silicates may optimize the economical and environmental sustainability of the fermentation process, together with the solid-liquid separation properties of the fermented sludge.

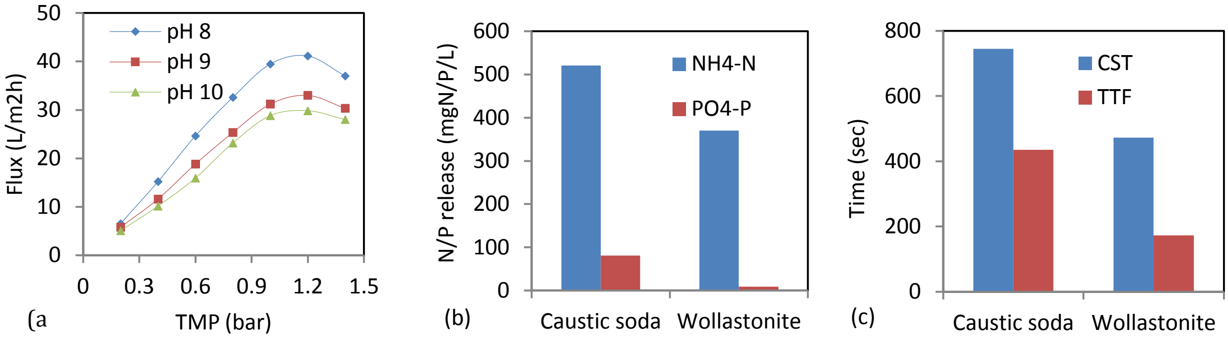

Fig 3 (a) Effect of pH and TMP on flux (20°C); (b) CST and TFF (dilution 1:5) of SFL for caustic soda (pH 10.0, 40°C) and wollastonite (40 g/L, 37 °C) addition; (c) ammonium and phosphate release for caustic soda (pH 10.0, 40°C) and wollastonite (40 g/L, 37°C)

3.4 Impact of sewage sludge fermentation liquid on nutrient removal

The use of SFLusing caustic soda for pH buffering enhancedthe sNURby 26% by and the sPUR by53%compared to the rates obtained with the use of acetic acid.Wollastonite addition changed the quantity and composition of the SLF, as it increased the content of propionic acid. Therefore, improved nutrient kinetics are expected; kinetic batch tests are planned to take place at February-May 2014. The full presentation of this work will include mass balances considering the full scale plant of Carbonera and cost comparison to evaluate the economic feasibility of the process.

Table 2 Comparing nutrient uptake in municipal wastewater for different carbon sources

External carbon source	sNUR mgN/(gVSS·h)	sPRR mgP/(gVSS·h)	sPUR mgP/(gVSS·h)
Wastewater	2.3	n.a.	n.a.
Acetic acid	4.6	1.9	2.1
Fermentation liquid using caustic soda	5.8	3.0	3.2
Fermentation liquid using wollastonite	Test ongoing	Test ongoing	Test ongoing

CONCLUSIONS

The use of SFL using caustic soda for pH buffering enhanced the sNUR by 26% by and the sPUR 53% compared to the rates obtained with the use of acetic acid. The use of wollastonite (20 g/L and 40 g/L) was beneficial as it maintained the pH at 7.0 and 8.0 respectively, increased the SCFAs production, enhanced filterability and limited the release of ammonium and phosphate in the SFL.

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(30) Reuse of wastewater: a feasible option, or not? A Decision Support System can solve the doubt

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Abstract

A wide debate on wastewater reuse has been turning on within the scientific community (and also at the legislative level) for several years. Beyond the undeniable advantages linked to the recovery of a material resource, the typical question plaguing water managers sounds like: "Is this practice feasible, in terms of both technical suitability and economic sustainability?". To answer their query, we have developed an innovative tool that rates the three actors of the reclamation process (the wastewater treatment plant WWTP, the hydraulic system and the final user) by means of a waterfall-framework based on: i) the definition of meaningful Indicators, ii) the calculation of robust Indices, and iii) the synthesis process up to a Final Evaluation (numerical values). The model has been successfully applied to real case studies, where the reuse is either already practiced or under study, in order to identify opportunities and threats. In summary, as a general implication, this tool represents a useful technical support for decision-makers, to be applied whenever a judgment on reuse feasibility is required.

Keywords

Decision Support Systems; experimental validation; indicators; wastewater reuse; water availability

INTRODUCTION

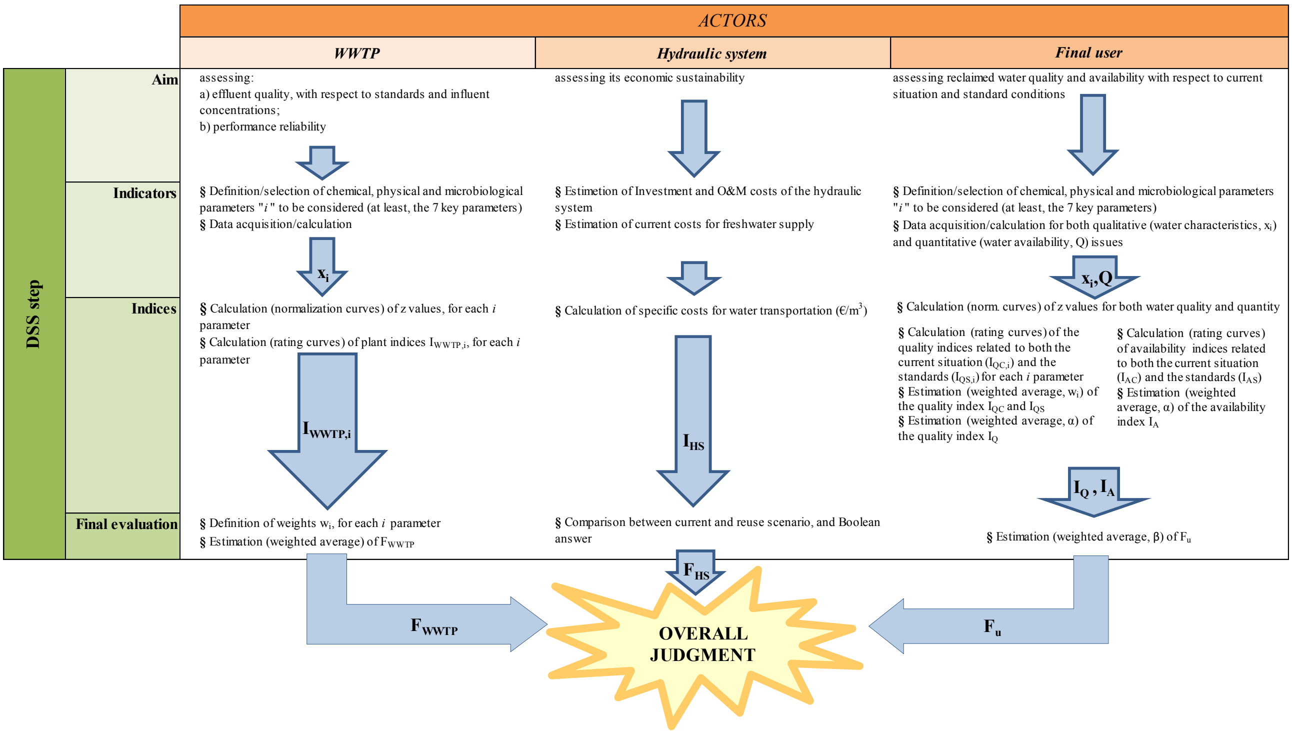
Water resources are currently subject to strong pressures, and water scarcity is threatening increasingly more Europe, and mainly the Mediterranean basin (Barbagallo *et al.*, 2012). Thus, legal and operational instruments must be developed to face these challenges: the possibility to save freshwater and increase water supply by using treated wastewater can help in this direction. Widely diffused reuse practices are well documented in scientific literature (Norton-Brandão *et al.*, 2013); nevertheless, a full development of reuse is actually hampered by 2 factors: i) on the technical side, finishing treatments are necessary to satisfy water quality criteria; ii) on the economic side, an increase of the costs (either for plant upgrade, water distribution system and the monitoring of the whole reuse system) cannot be avoided.

For these reasons, wastewater reuse feasibility can be fully assessed only by means of a technical-economic tool. Several works have been developed for its assessment (among others, Iglesias *et al.*, 2011, and Verlicchi *et al.*, 2011), showing how multi-criteria analyses are extremely appropriate, producing results as much accurate as higher the number of inputs.

Following these research lines, we have developed a Decision Support System (DSS) for the evaluation of wastewater reuse feasibility in the *status quo* (i.e. the current situation); technical-economic indicators have been built for each "actor" of the reclamation process: 1) the wastewater treatment plant (WWTP); 2) the hydraulic system, required to transport water from the plant to the user; 3) the final user (e.g., crops irrigation). This work first describes the definition procedures; next, it validates the proposed DSS by the application to several case studies.

MATERIALS AND METHODS

The proposed DSS is aimed at calculating a synthetic index (namely "final evaluation") which is a unitless number representing the suitability of the studied situation to implement reuse. As starting point, an aggregate set of measured technical and economic parameters (namely "indicators"), describing the actors of the process, is defined (Figure 1).



DSS step	ACTORS: *WWTP*	ACTORS: *Hydraulic system*	ACTORS: *Final user*
Aim	assessing: a) effluent quality, with respect to standards and influent concentrations; b) performance reliability	assessing its economic sustainability	assessing reclaimed water quality and availability with respect to current situation and standard conditions
Indicators	§ Definition/selection of chemical, physical and microbiological parameters "*i*" to be considered (at least, the 7 key parameters) § Data acquisition/calculation	§ Estimetion of Investment and O&M costs of the hydraulic system § Estimation of current costs for freshwater supply	§ Definition/selection of chemical, physical and microbiological parameters "*i*" to be considered (at least, the 7 key parameters) § Data acquisition/calculation for both qualitative (water characteristics, x_i) and quantitative (water availability, Q) issues
Indices	§ Calculation (normalization curves) of z values, for each *i* parameter § Calculation (rating curves) of plant indices $I_{WWTP,i}$, for each *i* parameter	§ Calculation of specific costs for water transportation (€/m^3)	§ Calculation (norm. curves) of z values for both water quality and quantity § Calculation (rating curves) of the quality indices related to both the current situation ($I_{QC,i}$) and the standards ($I_{QS,i}$) for each *i* parameter § Estimation (weighted average, w_i) of the quality index I_{QC} and I_{QS} § Estimation (weighted average, α) of the quality index I_Q § Calculation (rating curves) of availability indices related to both the current situation (I_{AC}) and the standards (I_{AS}) § Estimation (weighted average, α) of the availability index I_A
Final evaluation	§ Definition of weights w_i, for each *i* parameter § Estimation (weighted average) of F_{WWTP}	§ Comparison between current and reuse scenario, and Boolean answer	§ Estimation (weighted average, β) of F_u

Figure 1. DSS conceptual framework: flow-sheet diagram summarizing main steps and outcomes.

The Indicators

For the WWTP, attention is focused on wastewater quality, and chemical, physical and microbiological parameters to be chosen depend on the final destination of reused wastewater. For the hydraulic system, chosen indicators are investment and operation and maintenance (O&M) costs for water conveying. For the final user, water quality and availability are the crucial factors for this stage.

The Indices

The indicators are then transformed in comparable indices with uniform variability ranges, by means of appropriate normalization (z) and rating (I) curves:

1) actual conditions (e.g. WWTP effluent concentration of a given parameter) are compared with standard reference values, e.g. limits for reuse (normalization step);
2) the more the system is far from neutral conditions (e.g. WWTP effluent concentration equal to the standard to be complied with), the stronger is the positivity/negativity of judgment, I (rating step): calculated score varies from +1 (best case) to −1 (worst case), and a positive ranking denotes a favorable situation.

The Final Evaluation

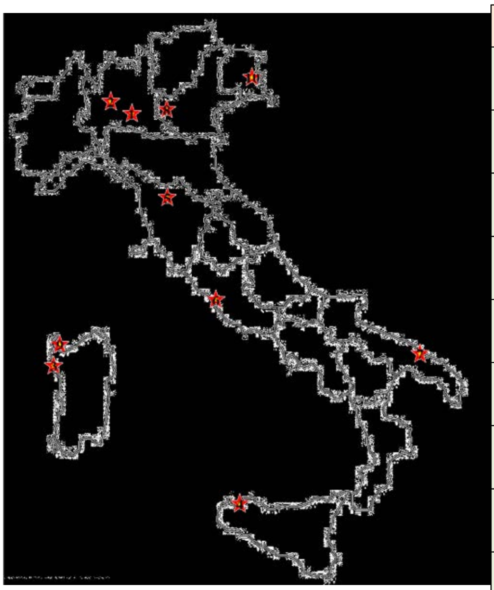
The final evaluation *F* is a synthetic numerical value that is determined by a weighted average of all indices I contributing to the assessment of the specific actor: then F varies from +1 (best performance) to −1 (worst performance). In this way, the overall judgment on the feasibility of reuse can be finally drawn as the average of the single ratings calculated for each actor (F_{WWTP}, F_{HS} and F_u): therefore, values greater than zero indicate the suitability of such a practice, even if an adverse assessment can arise also if at least one of the three actors expresses some critical issues (F < 0).

RESULTS AND DISCUSSION

The proposed model was validated through the application to several case studies. Ten plants were investigated, differing in terms of:

- reuse status: already practiced *vs* under study;
- WWTP characteristics: size, polishing treatments and reused/reusable flow-rate;
- current water availability;
- reuse scenario (either agricultural or industrial applications);
- geographical location.

Figure 2 reports the main DSS findings (numerical final evaluations and the overall judgment), and the resuming radar charts in Figure 3 clearly allow to rank assessed case studies and to identify main strengths and weaknesses: as results, the most suitable scenario for reuse was #1 WWTP, characterized by a crucial increase in water availability for the final user.



Analyzed WWTP	Reuse status	Polishing Treatments	Q_{reuse} [m^3/d]	Water availability	Reuse scenario	INDICES			Overall judgement
						WWTP F_{WWTP}	Hydr. Syst. F_{HS}	Final F_u	
# 1	Practiced	filtration + disinfection (UV)	25,000	scarce	Agricultural	✓ **+0.52**	✓ **+1**	✓ **+0.69**	↑
# 2	Under study	filtration + disinfection (O_3)	30,000	good (surface)	Agricultural	! **+0.19**	✓ **+1**	! **+0.14**	→
# 3	Practiced	filtration + disinfection (UV)	20,000	scarce	Agricultural	✓ **+0.5**	✓ **+1**	! **+0.09**	↑
# 4	Under study	coagulation/flocculation + filtration + disinfection	30,000	scarce	Agricultural	✓ **+0.42**	✗ **-1**	! **+0.27**	↓
# 5	Practiced	filtration + disinfection (O3)	6,000	scarce	Industrial	✓ **+0.41**	✓ **+1**	! **+0.21**	↑
# 6	Under study	filtration + disinfection (UV)	30,000	good (surface)	Agricultural	✓ **+0.36**	✓ **+1**	! **+0.02**	→
# 7	Practiced	physical-chemical + biological	5,000	scarce	Agricultural	✓ **+0.51**	✓ **+1**	✓ **+0.5**	↑
# 8	Under study	filtration + disinfection (UV)	120,000	good (surface)	Agricultural	✓ **+0.38**	✓ **+1**	! **+0.22**	↑
# 9	Practiced	coagulation/flocculation + filtration + disinfection	5,000	scarce	Industrial	✓ **+0.48**	✓ **+1**	✓ **+0.49**	↑
# 10	Under study	Absent	35,000	scarce	Agricultural	✓ **+0.55**	✗ **-1**	! **+0.16**	↓

Figure 2. Map of investigated WWTPs, together with main characteristics and outcomes of DSS application.

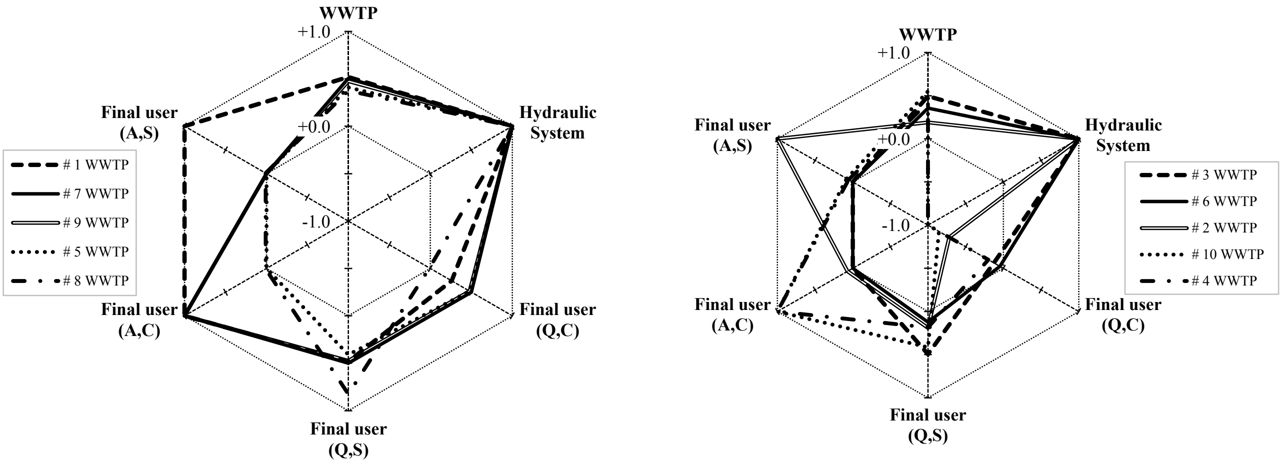


Figure 3. Radar charts summarizing strengths and weaknesses of the reclamation process actors (Q=quality; A=availability; C=current situation; S=standard condition).

CONCLUSIONS

In this work, an innovative DSS (Decision Support System) was built up as a tool to judge wastewater reuse feasibility, taking into account the three actors of the process: the WWTP, the hydraulic conveying system and the final user. If, from one hand, synthetic numerical values can darken detailed information about single issues, a final score, on the contrary, can provide to water managers quick and unbiased answers, an effective help in decision-making processes. A further strength lies in flexibility of proposed DSS: it is, indeed, capable to easily change the weight of parameters and/or add others, according to site-specific conditions / requirements (e.g. new regulatory references).

The application to real case studies revealed, indeed, model ability to assess complex situations, where several factors have to be simultaneously considered, and to achieve synthetic but comprehensive judgments, for a fast identification of main strengths and weaknesses of assessed scenario.

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(31) Applying the autotrophic nitrogen removal process for the treatment of anaerobic pig slurry

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Abstract

The completely autotrophic nitrogen removal process was applied in order to remove nitrogen from anaerobically digested pig slurry having a high content of organics. The presence of high content of biodegradable organic matter due to the uncontrolled anaerobic digestion resulted in a significant drop of the specific anammox activity (sAA) to 2.2 mgN $gVSS^{-1}h^{-1}$ from 14-15 mgN $gVSS^{-1}h^{-1}$. The use of synthetic wastewater without any carbon source resulted only in a partial recovery of sAA (56%). The high dissolved oxygen (DO≈5-6 mg L^{-1}) that was accidentally introduced was detrimental to anammox biomass resulting in irreversible decrease in sAA. The anammox activity was recovered following some inoculation.

Keywords

Anammox; anaerobic pig slurry; organic content; sequencing batch reactor

INTRODUCTION

The completely autotrophic nitrogen removal (ANR) is a promising process with attractive application prospects for the treatment of nitrogen-rich effluents. It is based on the combination of partial nitrification (PN) and anoxic ammonium oxidation (anammox) to remove nitrogen. It has been demonstrated that by coupling the removal of nitrogen from concentrated streams by ANR process with its industrial recovery by the Haber-Bosh process, less energy is required compared to the on site stripping and recovery of nitrogen (Maurer et al., 2003). The application of the anaerobic digestion followed by the ANR has already been suggested as a sustainable technological solution for the treatment of livestock manure, considering energy and economic data (Karakashev et al., 2006). This practice can be adopted in local agricultural facilities that cannot receive as fertilizer all the digestate produced due to the limitations imposed to the application rates of manure by the EU Council Directive 91/676/EEC. ANR can be considered more competitive than alternative processes for the treatment of digester supernatant for ammonium concentrations up to 2 kg m^{-3}. However, the demonstration of a full-scale treatment system running continuously for the treatment of anaerobic pig manure still remains pending (Magrí et al., 2013). The anammox process is adversely affected by the high organic content (OC) of the effluents, since denitrifiers are much more competitive than anammox bacteria at high OC/N ratios (Jin et al., 2012; Zhang et al., 2012). The current study investigates the feasibility of the anammox process in a short-cut sequencing batch reactor (scSBR) for the treatment of anaerobic supernatant originating from the uncontrolled psychrophilic anaerobic digestion of piggery wastewater.

MATERIAL AND METHODS

A scSBR (working volume: 26 L), was inoculated with anammox biomass, which was treating anaerobic supernatant from sewage sludge. The length of the SBR cycle was 8 h having the following sequence: 6 h of aerated feeding (DO = 0.2-0.3 mg L^{-1}), 0.5 h of anoxic phase, 1.5 h of settling and 0.5 h of discharge. The reactor was fed with real anaerobic supernatant originating from the uncontrolled psychrophilic anaerobic digestion (ambient temperature without agitation) of pig slurry. This stream was characterized by high total nitrogen concentration (TN = 1.22 gN L^{-1}, where 83% was ammonium) and high organic content (chemical oxygen demand COD = 2.61 gCOD L^{-1}). Although the C/N ratio of the influent was low (~2.1), the soluble COD (sCOD) represented 45% of total COD and around 50% of it was biodegradable. The electrical conductivity was 13.8 mS cm^{-1}. During the experimental period 1, the scSBR was fed with real anaerobic supernatant that was diluted with tap water by a dilution factor of 3. Then, ammonium and phosphate were added manually (using NH_4HCO_3 and K_2HPO_4 respectively) in order to reach the initial concentrations contained in the pig slurry. The aim was to investigate the influence of organic matter on anammox activity. In period 2, the real pig slurry supernatant was replaced with a synthetic solution with the same concentrations of ammonium and phosphate, but without any addition of organic carbon. The hydraulic retention time (HRT) and the volumetric nitrogen loading rate (vNLR) ranged from 1.24-1.97 d and vNLR=0.52-0.90 kgN $m^{-3}d^{-1}$ during the operation of the scSBR (i.e. both periods). The volumetric organic loading rate (vOLR) was 0.14 kgCOD $m^{-3}d^{-1}$ in period 1 and 0 in period 2. During the system's operation, the specific anammox activity (sAA) was determined in batch tests according to the method reported by Dapena-Mora et al. (2007). Ammonium nitrogen (NH_4-N), total Kjeldahl nitrogen (TKN) and P were determined according to standard methods (APHA, AWWA, WEF, 1998). Phosphate (PO_4-P), nitrite (NO_2-N) and nitrate (NO_3-N) and the SCFAs were determined by ion chromatography (Dionex ICS -900 and Dionex ICS-1100).

RESULTS AND DISCUSSIONS

During the first 10 days high sAA was obtained (14.3-14.4 mgNg$VSS^{-1}h^{-1}$) in combination with an efficient nitritation rate (13.0 ± 2.7 mgNg$VSS^{-1}h^{-1}$), resulting in a low concentration of ammonium (17.7±17.2 mgNL^{-1}) and nitrite (1.1 ± 0.9 mgNL^{-1}) and in the accumulation of nitrate (up to 135.5mgN L^{-1} at day 7) in the treated effluent (Figure 1). The nitrogen removal efficiency was 90.7%. Afterwards (i.e. days 15-40) a drop of sAA was observed below 4 mgN g$VSS^{-1}h^{-1}$ (days 28-40). As a result, the nitrate concentration in the treated effluent sharply decreased with the simultaneous increase of ammonium. The presence of abundant organic carbon and nitrite promoted the growth of heterotrophic denitrifies and resulted in the decrease of sAA; in that period the specific nitrite uptake rate (sNUR) was 30.6 mgNg$VSS^{-1}h^{-1}$.

In period 2, the use of synthetic effluent without any organic carbon resulted in the partial recovery of sAA up to the value of 8.1 mgN g$VSS^{-1}h^{-1}$ (day 62). However, this sAA was only 56% of the maximum sAA obtained during the first 10 days of operation. The increase of sAA resulted in an increase of the nitrate concentration of the treated effluent to the levels of 149-257 mgN $L^{-1}$and a decrease of the nitrite to 0.4-8.2 mgN L^{-1} (days 42-64). At days 66-67 a problem in the control of the aeration resulted in an uncontrolled increase of the DO in the reactor above 5 mg L^{-1} for 48 hours. As a result, the anammox activity dropped immediately to 1.66 gNkg $VSS^{-1}h^{-1}$ and it remained quite stable. The ammonium concentration increased up to 490.87 mgN L^{-1}. Jina et al. (2012) reported that DO levels above 0.3 mg L^{-1} can cause inhibition of anammox bacteria that may also be irreversible when the oxygen saturation is higher than 18%. For that reason, in the remaining days of period 2 the reactor was partially (by 50%) inoculated with original anammox biomass in order to restore the initial performance of the process. As expected, the activity increased and was stabilized at 6.4±1.5 mgN g$VSS^{-1}h^{-1}$.

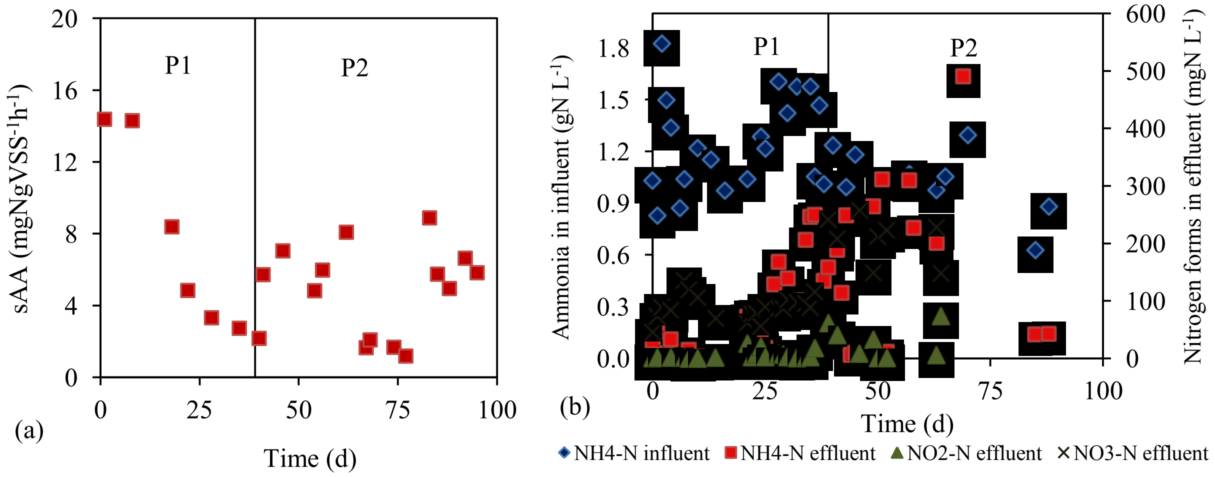

Figure 1 (a) Specific anammox activities and (b) influent ammonium and treated effluent ammonium, nitrite and nitrate concentrations during the SBR operation for the treatment of pig slurry supernatant

CONCLUSION

The anaerobic pig slurry from piggery wastewater originating from a psycrophilic anaerobic digestion (without agitation) contained high content of biodegradable organic carbon. Thus, the nitrogen removal from this particular stream by applying the ANR process in a single-stage SBR resulted in significant reduction of the anammox activity. Within 40 days of the SBR operation, the activity of biomass decreased by 85% due to the simultaneous growth of the heterotrophic denitrifiers. Anammox activity was only partially recovered (56%) when the real anaerobic supernatant was replaced by synthetic anaerobic supernatant without any addition of organic matter. Finally, it was found that high DO levels (>4 mg L^{-1}) resulted in irreversible inhibition of the anammox activity; thus the system required an efficient system to control the aeration.

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(32) Two phase anaerobic codigestion of organic waste and activated sludge: bench study and implementation potential in energy and material (VFA) recovery

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Abstract

The following study dealt with the application of the anaerobic co-digestion process for production of biohythane and volatile fatty acids (VFA).

The aim of the paper is to investigate performances in a two-phase thermophilic anaerobic co-digestion process applied on waste activated sludge and biowaste. Hydrogen and methane production reached values of 29 l/kgTVS and 287 l CH_4/kgTVS respectively when operating with a total hydraulic retention time of 19d (3d in the first phase and 16d in the second phase) and organic loading rates of 16 and 3 kg TVS/m^3d, respectively. At the same time, RBCOD production was also investigated in order to consider an integrated approach on waste and wastewater cycles. Specific VFA production of 426 gVFA/$kgTVS_{BIOWASTE}$ was obtained from the first phase of the process. An overall assessment coming from the implementation of the approach on a 70.000 AE basin was also presented, based on pilot scale results obtained.

Keywords
Anaerobic digestion; biohythane; biological nutrient removal; codigestion; denitrification; hydrogen; methane;

INTRODUCTION

Anaerobic codigestion is a well known process used to stabilize activated sludge and converting the putrescible matter of organic substrates into methane and carbon dioxide. The two-phase anaerobic digestion approach physically divides the biochemical step named hydrolysis-acidogenesis in the first phase (dark fermentation) and the second step named acetogenesis-methanogenesis process in the second phase. This phase separation meets the optimal growth rates and pH requirements for acidogenic (between 5.5 and 6.5) and methanogenic microorganisms (around pH 7), and thus different requirements regarding reactor conditions (De la Rubia et al., 2009). The separate phase approach has been settled to the production of hydrogen (H_2) in the first phase reactor, while methane (CH_4) in the second phase reactor, with the final aim of mixing the two gasses to achieve bio-Hythane (50-55% CH_4, 5-10% H_2 and 35-40% CO_2). Biohythane allows a better combustion with reduced greenhouse gasses emissions compared with fossil fuels (Cavinato et al., 2011).

Past results have shown that the recirculation of the liquid effluent from the methanogenic reactor acted as a buffer system, in the dark fermentation stage, is a good strategy to maximize the hydrogen production (HP) (Cavinato et al., 2011). However, to keep the process simple, pH in the first reactor can be controlled by different means: an interesting option is the co-digestion of biowaste together with waste activated sludge (WAS) so to maintain the pH at the desired level through the buffer capacity exerted by sludge addition. This in order to integrate waste and wastewater cycles: in this field, another important effect of this process adoption came from the possibility to produce, at the same time, a low chain carbon rich stream to enhance denitrification kinetics in WWTP. This advantage allows to use a zero-cost stream instead of an external chemical, such as methanol or acetic acid, which obviously give additional costs and sludge production (Estimated cost per kg COD added: 0.79-0.90 EUR/kgAceticAcid

80%) (Frison et al., 2013). Other advantage of co-digestion comprise: valorized balance of nutrients, synergistic effect of microorganisms, enhanced load of biodegradable organic matter and higher biogas yield.

Purpose of this research is also to verify the effectiveness of the buffer system ammonia-carbonates, to keep the pH at suitable levels for the production of hydrogen. The effectiveness of this system would ensure a more affordable process, and at the same time a robust approach to integrated cycles approach. Results are used to evaluate the benefits coming from the implementation of this technology in a full scale WWTP, using as model a real plant located in north Italy (70.000 AE basin).

MATERIAL AND METHODS

Two laboratory-scale continuously stirred tank reactors were exploited. The first reactor, dedicated to the HP (first phase, dark fermentation), had a 3.5 l working volume, while the second reactor (second phase) dedicated to the methane production (MP) phase had a 18.5 l working volume, both heated by hot water recirculation system and maintained in thermophilic condition (55°C). The system was fed semi-continuously, once per day, and the organic loading rate (OLR) in the first and second phase was 16 kg TVS/m^3d and 3 kg TVS/m^3d, respectively, while the corresponding HRT were 3 and 16 d for the first and second phase reactors, respectively. The whole experiment length was 70 d. Start-up period (0-40 d), steady state period (41-70 d).

The wastes used to feed the first reactor were collected in the Waste Water Treatment Plant (WWTP) located in Treviso (northern Italy). The substrate employed in this study was a mix of BIOWASTE and WAS. The volume ratio BIOWASTE:WAS was 1:5 v/v, calculated in order to have an OLR of 6 and 10 kg TVS/m^3d in the first phase reactor for WAS and BIOWASTE respectively. The BIOWASTE was reduced in size using a grinder and mixed with WAS, simulating the same treatment used in full-scale application. The feedstock was daily prepared and no pre-treatment was considered (i.e. chemical reagent or thermal treatment). The reactor effluents were monitored 3 times per week in terms of TS, TVS, COD, TKN and TP. The process stability parameters, namely pH, volatile fatty acid (VFA) content and distribution, total and partial alkalinity and ammonia ($NH_4^+ - N$), were checked daily. All the analyses performed according to APHA (1995).

RESULTS AND DISCUSSION

Process performances and yields

The overall performances of the two-phase thermophilic anaerobic co-digestion process are summarized in Table 2.

Table 2. Characterization of reactors effluents

Parameters	Units	First phase	Second phase
TS	g/kg	48±5	25±4
TVS	g/kg	37±4	16±2
COD	g/kg TS	40±3	19±2
TKN	g/kg TS	34±1	35±1
Ptot	g/kg TS	11±0	19±1
pH		5.09±0.08	7.97±0.26
Partial Alkalinity (pH = 5.7)	mg$CaCO_3$/l	NP	3328±165
Total Alkalinity (pH = 4.3)	mg$CaCO_3$/l	1210±180	4409±16
$NH_4^+ - N$	mg$N-NH_4^+$/l	268±48	949±48
Tot VFA	gCOD/l	15.8±1.4	0.5±0.5
Yields			
SHP	l H_2/kg TVS	29±5	np
SMP	l CH_4/kg TVS	np	287±36

During the experiment the low HRT applied and the high OLR used lead to a pH value of 5.1 in dark fermentation (DF) phase, caused by the high VFA production (426 gVFA/kgTVS), with an average value of 15.8 g COD/l. The pH value addressed the best pH conditions for HP that is around 5.5 (Valdez-Vazquez et al., 2009). The low average concentration of N-NH_4^+ (268 mg/l was not sufficient to buffer the VFA increasing, with a progressive reduction of alkalinity and subsequent pH falling. Therefore to maintain steady state condition in a long term for producing Hydrogen from the first phase, the adoption of recirculation flow rate from the second phase (total alkalinity of 4400 mg$CaCO_3$/l) is required. In the first phase, the biogas produced was composed of H_2 and CO_2, no CH_4 being detected during all study. In terms of yields, biohydrogen concentration in the biogas from first reactor was 36±8 %, a value in line with those reported in literature, typically in the range 35–40% (Cavinato et al., 2011). The second phase operated with an HRT of 16 d and an OLR of 3 kg TVS/m^3d. pH reached a constant value of 8.0, this was the optimal pH for enhanced acetogenic and methanogenic activity (De la Rubia et al., 2009). The SMP 287 l CH_4/kgTVS found was similar to that obtained for the co-digestion of WAS and biowaste in previous studies of the authors (Bolzonella et al., 2006).

With specific reference to process yields, the hydrogen production was 29 l H_2/kgTVS, after approximately a period of 10 HRTs, became stable and the SHP start growing. On the contrary, the second reactor reached maintained stable conditions in a relatively short period of time.

rbCOD recovery for biological nutrient removal

The global strategy applied in the so called AF-BNR-SCP process was firstly proposed in Cecchi et al. (1994) and then followed by a few-years pilot scale experimentation (Pavan et al., 2000). In this process, located in Treviso, the biowaste is anaerobically fermented (AF) and the carbon rich liquid phase is added to the BNR plant wastewater inflow to enhance the biological nitrogen and phosphorus removal.

In previous studies (Bolzonella et al., 2006), a value of 5.5 kgN/kgMLVSS h was found when using fermentate obtained applying this approach. Same values were confirmed by the present study. Using these information, a simulation of the whole approach was done, considering the typical specific production on COD and N (110 gCOD/PE d and a COD:TKN ratio of 11) and assuming that, as a quite normal situation in several part of Italy, the RBCOD content in the inlet is quite low, precisely 10% of the total COD. In this way, the RBCOD needed to the N removal is given by the cycle integration, and the complete mass balance of the whole approach is given in figure 1.

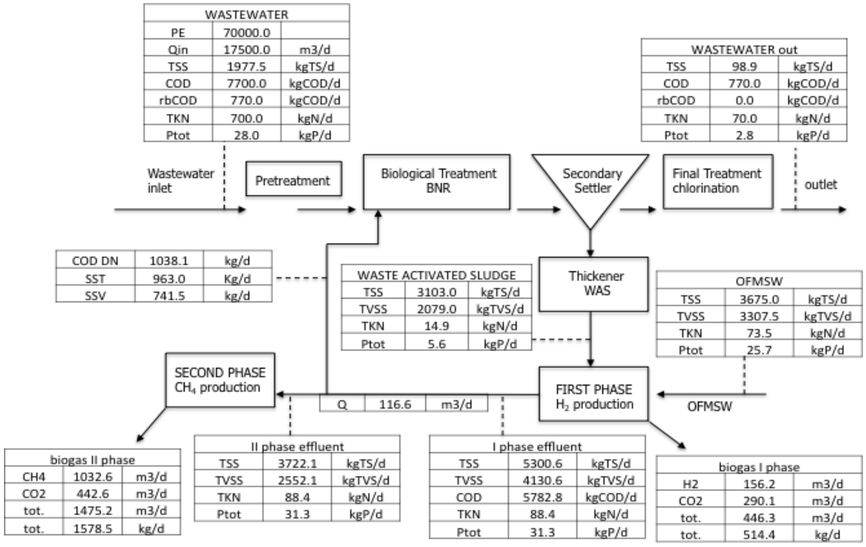

Figure 1. Full-scale cycles integration balances.

The biowaste flow rate is calculated as 13.1 t/d on the first phase and WAS flow rate is 103.4 t/d, w/w, giving a total HRT on the first phase of 72 hours. Thus the corresponding needed volume for the first phase reactor is only 349.7 m^3. The hydrogen production through the first stage is evaluated as 156.2

m^3/d. Whereas part of the effluent of the first phase, with a VFA concentration of 15.8 gCOD/l, goes to the BNR, where the COD required to denitrify the water entering in the plant is 1038 kg/d. This considering a ratio rbCOD / N for nitrates reduction of 2.87 (Beck et al., 2007). Thus, 62 m^3/d of first phase effluent flow rate, Q_{BNR} will be sent directly to wastewater treatment. This computation is precautionary indeed the rbCOD effluent was calculated as solely VFA concentration, instead of considering the whole COD in solution, which concentration is about 15% higher than the rbCOD (Bolzonella et al., 2006). The rest of the first phase effluent, with a flow rate of 864 m^3, is channeled to the second phase reactor, adopting an HRT of 16 days, as the experimentation above. The digester has a specific methane production of 1032.6 m^3. Thus, as can be seen, considering a 70.000 AE basin, the system is able to support a complete denitrification in WWTP using less than the 15.2 % of the total carbon which is produced by the first phase reactor. Considering this, a reduction of 15 % in terms of second phase gas will be produced, leading to the production of 1921 m^3/d of Biohythane with an average composition of 54/8/38 as $CH_4/H_2/CO_2$ respectively.

CONCLUSIONS

The experiment carried out show interesting results coming from the application of the integrated waste/wastewater treatment approach considering a two phase (DF+methanisation) AD process. The approach allows to obtain the production of a high value upgradable biogas, with an average composition of 54:8:38 ($CH_4/H_2/CO_2$), based on a stable and robust process, managed through the control of stability parameters using an internal recirculation flow. On a 70.000 PE basis a biohydrogen production of 156.2 m^3/d and biomethane of 1032.6 m^3/d can be achieved, when at the same time a total wastewater denitrification is reached. This last result can be obtained thanks to a specific production of 426 gVFA/kgTVS, which lead to a specific denitrification rate of 5.5 kgN/kgMLVSS h. Thus, it can be said that the integrated approach considered give considerable advantages, which lead this option in the field of the ‘smart’ opportunities for the urban services management. Important environmental and economic savings can be obtained, linked to energy production and to the avoided addition of external chemicals to support denitrification step in BNR treatment.

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(33) Impact Of External Carbon Source In Via Nitrite Treatment Of The Sludge Anaerobic Supernatant

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Abstract

Biological nutrient removal via nitrite was investigated in a short-cut sequencing batch reactor (scSBR) treating highly nitrogenous anaerobic supernatant, under a volumetric nitrogen loading rate of 0.45 and 0.53 $kgNm^{-3}d^{-1}$. Propionic acid (period 1) and a fermentation liquid derived from sewage sludge (SFL, Period 2) rich in short chain fatty acids were used as external carbon sources. Although the nitritation was quite constant during the SBR operation (11.47 and 9.10 $mgNgVSS^{-1}h^{-1}$ for period 1 and 2), the type of carbon source affected the denitritation and P removal. Propionic acid exhibited a lower denitritation rate (7.80 $mgNgVSS^{-1}h^{-1}$) compared to the SFL (22.39 $mgNgVSS^{-1}h^{-1}$), while P uptake rates were higher when SFL was used. The higher accumulation rate of the nitrite in the 1st period adversely affected the efficiency of the P removal, which was 32% compared to 58% of period 2. In periods 1 and 2 the majority of P was removed due to heterotrophic growth (89% and 67%).

Keywords

Nutrient removal via nitrite, SBR, anaerobic supernatant, external carbon source

INTRODUCTION

In the municipal wastewater treatment plants (WWTPs), the usual practice is to return the anaerobic supernatant of sewage sludge to the inlet of the wastewater treatment line. This liquid stream significantly increases the nitrogen (N) and phosphorus (P) load (15-25%), but it contains a low content of biodegradable organic matter (COD/TN ~1) that does not favour heterotrophic denitrification. Nowadays, the via nitrite nutrient removal processes are recognized to be a good alternative to treat high strength nitrogenous effluents, such as the anaerobic supernatant from digested sludge (Frison et al., 2012). Among them, the anammox process is energy-saving because it accomplishes the nitrogen removal without addition of external carbon source. However, it presents some drawbacks, such as high sensitivity to the environmental and operational conditions (Malamis et al., 2013), while enhanced biological phosphorus removal (EBPR) cannot be achieved in anammox systems. The development and reliable application of bioprocesses could be a sustainable option to enhance phosphorous bioaccumulation. The denitrifying via nitrite biological phosphorus removal (DNBPR) process offers the possibility to integrate P and N removal in a single robust process with the advantages of lower sludge production and reduced use of chemicals and plays an increasingly important role in controlling eutrophication around the world (Oehmen et al., 2007). It has been demonstrated that propionic acid (HPr) leads to the accumulation of polyhydroxyalkanoates (PHA) (up to 10-15%TVS) in sludge, which allows the simultaneous denitritation and phosphorus removal in the presence of nitrites (Carvalho et al., 2007). However, the addition of chemically synthesized short-chain fatty acids(SCFAs)increases the operating cost of the process, as the price of the commonly used synthetic carbon sources increased drastically over the last decade. The use of non-renewable petrochemicals as raw materials and the increasing price of oil have renewed the interest in biological routes of SCFAs production. In this work, the effect of two different external carbon sources (HPr and sewage sludge fermentation liquid - SFL) on biological nutrient removal via-nitrite was examined by employing a short-cut sequencing batch reactor (scSBR) scheme for the treatment of anaerobic supernatant from sewage sludge.

MATERIAL AND METHODS

The pilot scSBR was inoculated with thickened waste activated sludge (WAS) originating from the municipal WWTP of the Carbonera municipality (Veneto Region, North of Italy). The pilot scSBR in Verona had a working volume of 26 L, treating up to 24 L d^{-1} of synthetic anaerobic supernatant. The main characteristics of the influent are presented in Table 1.

Table 1 Physicochemical characteristics ofanaerobic supernatant

Parameter	Period 1	Period 2
	Average (min-max)	Average (min-max)
COD ($mgCODL^{-1}$)	406 (47-509)	418 (156-478)
TKN ($mgNL^{-1}$)	539.7 (364.0-639.7)	604.6 (454.0-807.8)
NH_4-N ($mgNL^{-1}$)	499.8 (263.0-616.2)	568.2 (427.0-748.0)
P ($mgPL^{-1}$)	20.6 (15.8-24.4)	18.3 (12.2-24.1)
PO_4-P ($mgPL^{-1}$)	19.2 (14.8-19.2)	17.0 (11.3-22.5)
pH	8.1 (7.8-8.5)	8.1 (7.9-8.4)
Total alkalinity ($mgCaCO_3\,L^{-1}$)	2051 (1284-2608)	2051 (1284-2608)

The supernatant was pumped automatically by a peristaltic pump from a storage tank into the reactor. The scSBR was equipped with two other peristaltic pumps, which allowed, when it was necessary, the dosage of NaOH (30%) to adjust the pH (during aerobic conditions) and external carbon sources (added only in the anoxic phase). The aeration was provided with the use of three blowers that were automatically switched on/off in order to maintain an aerobic DO concentration of 1.5 mg L^{-1}. The scSBR operation was controlled by a programmable logic controller (PLC, National Instruments – Compact Field Point AI-100). On-line submerged probes (Hach-Lange) of DO, pH, oxidation reduction potential (ORP) and conductivity were used to monitor the process. Two experimental periods were carried out on the basis of the external carbon source that was applied. The operating conditions of the scSBR were similar in both periods: after the start-up period (Frison et al., 2012) the volumetric nitrogen loading rate (vNLR) was 0.45 and 0.53 kgN $m^{-3}d^{-1}$ during period 1 (days 0 to 70) and period 2 (days 71 to 118) respectively.

The volumetric phosphorus loading rate (vPLR) was 16.9 gP$m^{-3}d^{-1}$in period 1 and 15.4 gP $m^{-3}d^{-1}$in period 2. The sludge retention time (SRT) was 12 d and it was kept stable during the scSBR operation. Two types of external carbon source were applied; pure HPr in period 1 and fermentation liquid originating from the sewage sludge fermentation of the Carbonera WWTP (mixed primary and secondary sludge) in period 2. The carbon sources were added during the first 1-2 min of the anoxic phase in order to obtain an initial concentration of 330 mgCOD L^{-1}. The concentration of SCFAs in the SFL was 12.8 gCOD L^{-1}, with the following composition: acetic acid 57%, propionic acid 7%, butyric acid 33% and pentanoic acid less than 3%. The anaerobic fermentation process was carried out in a batch reactor, at controlled conditions (40-45°C, HRT = 6 days). Both external carbon sources were automatically dosed at the beginning of the anoxic phase. During the scSBR cycle, in situ biomass activity tests were conducted to evaluate the rate of nutrient removal. The specific ammonium uptake rate (sAUR) was determined under aerobic conditions, while the specific nitrogen utilization rate (sNUR) under anoxic conditions. The specific P uptake rate was evaluated under aerobic and anoxic conditions (i.e. $sPUR_{aerobic}$ and $sPUR_{anoxic}$). In the activity tests the time profile of the nitrogen species (ammonium, nitrite and nitrate) and the phosphate (PO_4-P) was monitored in the mixed liquor. At the end of the anoxic phase, the biomass was sampled and analyzed for total and volatile suspended solids (TSS and VSS) and for the content of nitrogen and phosphorus (in the dried biomass) in order to investigate the presence of poly-P. Ammonium nitrogen (NH_4-N), total Kjeldahl nitrogen (TKN), alkalinity, TSS, VSS and P were measured according to standard methods (APHA, 1998). Phosphate (PO_4-P), nitrite (NO_2-N), nitrate (NO_3-N) and the SCFAs were determined by ion chromatography (Dionex ICS -900 and Dionex ICS-1100).

RESULTS AND DISCUSSION

Nutrient removal rates

The type and composition of carbon source impacted the sNUR and sPUR. As seen in Table 2, the use of SFL resulted in significantly higher denitritation rates than the one achieved by HPr. The latter is in agreement with previous research works, which have shown that carbon sources that contain a mixture of SCFAs can improve DBPRN (Frison et al., 2013; Ji and Chen, 2010).

Table 2 Nutrient removal kinetics obtained during the in situ biomass activity tests

Parameter	Period 1 (HPr)	Period 2 (SFL)
	Average (Min-Max)	Average (Min-Max)
sAUR (mgN gVSS^{-1}h^{-1})	11.47 (1.52-24.34)	9.10 (8.01-11.20)
sNUR (mgN gVSS^{-1}h^{-1})	7.80 (-)	22.39 (21.63-23.15)
sPUR$_{anoxic}$ (mgP gVSS^{-1}h^{-1})	1.09 (-)	3.41 (2.19-4.62)

Nitrogen removal via the nitrite pathway

The evaluation of the applied process was carried out based on mass balances and nutrient removal efficiencies (Table 3). During the start-up of the scSBR, the sAUR reached a high value, up to 24.34 mgNgVSS^{-1}h^{-1}, while after the addition of the HPr the sAUR stabilized at 11.47 mgNgVSS^{-1}h^{-1} due to the growth of heterotrophic bacteria. In the second period, the sAUR dropped to 9.10 mgNgVSS^{-1}h^{-1} (8.01-11.20), but without compromising the effluent quality. In both periods the nitrification efficiency was >96% and the average ammonia concentration in the effluent was 15.71 and 9.46 mgNH_4-N L^{-1}, for period 1 and 2, respectively (Table 4). However, in the first period the denitritation was not very effective, since the sNUR obtained was 7.80 mgNgVSS^{-1}h^{-1}, and did not allow complete removal of nitrite during the anoxic phase. The average nitrite concentration in the effluent was 132.9±40.8 mgNO_2-N L^{-1} and the denitritation efficiency was 67%. The composition of the carbon source affected the sNUR, which increased up to an average value of 22.39 mgN gVSS^{-1}h^{-1} when SFL was applied to the system, leading to higher nitrite removal compared to period 1 (use of HPr): the denitritation efficiency was 90% and the average nitrite concentration was 11.6 mgNO_2-N L^{-1}. The high nitrite level in the effluent at day 113 (135 mgNO_2-N L^{-1}) (Figure 1) may be attributed to the higher NH_4-N concentration in the anaerobic supernatant.

Mechanisms of phosphorus removal via nitrite

The presence of nitrite in the mixed liquor could inhibit the sPUR, while it has been found that the exposure of denitrifying PAOs to high nitrite concentrations can inhibit their activity (Saito et al., 2004; Peng et al., 2011).The high level of nitrite during period 1 (Figure 1) resulted in low sPUR under anoxic conditions (1.09 mgPgVSS^{-1}h^{-1}). In the same period, the average P removal efficiency was 32%, while 89% of P was removed due to the growth of the biomass (based on stoichiometric calculations); thus only 11% of the P removed was taken up by PAOs. The P concentration in the sludge was 20 gP kgSS^{-1}. In period 2 (SFL) the anoxic sPUR increased up to 4.62 mgPgVSS^{-1}h^{-1}, while the average anoxic sPUR was 3.41 mgP gVSS^{-1}h^{-1}. The use of SFL containing a mixture of SCFAs was beneficial for the efficiency and the rate of P removal. The average P removal increased to 58% from 32%. Also, in period 2 a maximum P removal of 95% was obtained (day 92), resulting in P concentration in the effluent of 1.1 mgP L^{-1}. Due to the high nitrite level in the effluent at day 113, the P removal efficiency decreased to a minimum of 37%. The average P removal in period 2 was 58% out of which 67% was attributed to the growth of biomass, which is lower than the respective one observed in period 1. The P content in the cell increased to 28 mgP $gVSS^{-1}$.

Table 3 Nitrogen mass balances

Parameter	Period 1	Period 2
vNLR applied (kgN $m^{-3}d^{-1}$)	0.45	0.53
vNH_4-N effluent (kgN $m^{-3}d^{-1}$)	0.01	0.01
vNO_x-N effluent (kgN $m^{-3}d^{-1}$)	0.11	0.01
vNLR effluent (kgN $m^{-3}d^{-1}$)	0.13	0.02
vNLR waste (kgN $m^{-3}d^{-1}$)	0.02	0.03
Nitrogen removal (%)	72	96
Nitritation (%)	97	98
Denitritation (%)	67	90

Table 4 Phosphorus mass balances

Parameter	Period 1	Period 2
vPLR applied (gP $m^{-3}d^{-1}$)	16.93	15.43
vPLR waste (gP $m^{-3}d^{-1}$)	4.73	8.72
vPLR effluent (gP $m^{-3}d^{-1}$)	11.48	6.51
P removal (%)	32	58
vPLR waste (gP $m^{-3}d^{-1}$) (through stoichiometric calculation)[a]	4.20	5.87
P removed by growth (%)[b]	89	67

[a] Estimated considering the biomass stoicheometric formula $CH_{1.8}O_{0.5}N_{0.2}P_{0.015}$; [b] Percent is out ofthe total P removed

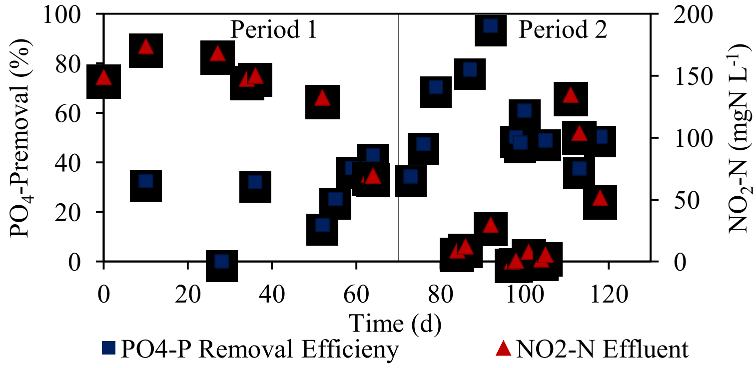

Figure 1 Nitrite concentration in the effluent and the PO_4-P removal efficiency during the periods

CONCLUSION

The present study demonstrated that treating anaerobic supernatant via nitrite led to significant phosphorus removal (average of 58%) even when the activity of PAOs was low. The growth of biomass was the most important phosphorus uptake mechanism, contributing more than 65% to the total P removal. Nitrite played an important role on the performance of P removal; high NO_2-N levels (> 100 mg L^{-1}) decreased P uptake rate more than 65%. The application of SFL containing a mixture of SCFAs enhanced the efficiency and the rate of denitrification and P removal.

ACKOWLEDMENTS

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(34) Physico-chemical treatment of vinasse aiming their use for the cultivation of microalgae *Chlorella vulgaris*

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Abstract

This paper shows the results of a study carried out to verify the potentiality of using pre-treated vinasse (from an ethanol industry) as a microalgae culture medium. Coagulation, flocculation and sedimentation techniques were used as the pre-treatment of the raw vinasse. The best results regarding color and turbidity removal (until 76% and 96% respectively) were obtained using a cationic polymer at dosage of only 20 mg.L^{-1}, which can be considered low for vinasse coagulation and flocculation. The treated vinasse, with and without dilution, was tested for *Chlorella vulgaris* microalgae cultivation. Although presenting growth rates lower than that observed in the traditional WC culture medium, the medium constituted of pre-treated vinasse (even when the vinasse concentration reached 90%) have provided the growth of *Chlorella vulgaris*, suggesting its potential use as a cultivation medium for this specie of microalgae, aiming to obtain biomass for biodiesel production.

Keywords
Vinasse reuse; physicochemical treatment; microalgae cultivation

INTRODUCTION

The vinasse is a byproduct generated in large amounts by the sugar and ethanol agroindustry – ranging from 9 to 15 m^3 for each m^3 of produced ethanol – whose main use has been in the fertirrigation of sugarcane crops. Due to its high potassium and organic matter concentrations, the vinasse has a high pollution potential when incorrectly discharged in soils and water bodies. A promising alternative is the vinasse utilization as culture medium in microalgal biomass production (BONINI, 2012; LIANG et al., 2009), which can produce lipids convertibles to biodiesel. For this purpose, their suitability for this type of cultivation is required, mainly through concentration reduction of particles causing turbidity and color (SATYAWALI; BALAKRISHNAN, 2008), providing improvement of light input in photobioreactors that could be used for biomass production. The purpose of this work was to investigate the utilization of coagulation, flocculation and sedimentation techniques for the clarification of vinasse aiming its use, with or without dilution, as a cultivation medium for the production of *Chlorella vulgaris* biomass.

METHODS

The raw vinasse samples (30°C) were submitted to coagulation, flocculation and sedimentation in a jar test equipment. A set of tests were performed to investigate the best polymer and respective dosage for the vinasse clarification. The mixture parameters adopted were: 900 s^{-1} of mean velocity gradient (G) during the 15 s of rapid mix time; a G of 60 s^{-1} during the 5 min of slow mixing period; sedimentation velocity of 1 cm.min^{-1}. The pH was not controlled (around 4,7). Aiming to evaluate the potential of using the vinasse as a culture medium for *Chlorella vulgaris*, a second experimental phase was performed. In this phase, the pre-treated vinasse was used to compose different culture media for the microalgae *Chlorella vulgaris*, obeying the following proportions: V_1 (90% treated vinasse / 10% inoculum), V_2 (45% treated vinasse / 45% deionized water / 10% inoculum), V_3 (5% treated vinasse / 85% deionized water / 10% inoculum). A standard WC culture medium was used to compare with the others. The growth was measured by optical density in 550 and 750 nm wavelengths and the counting of algae cells was made in Fuchs-Rosenthal chamber. The counting results were used to estimate the cell density (D_{cell}) in the culture mediums, and the specific growth rate (μ).

RESULTS AND DISCUSSION

The results obtained in the coagulation, flocculation and sedimentation tests of the vinasse indicated that the best cationic polymer dosage was 20 mg.L^{-1} (96% turbidity and 76% color removals). This treatment process for vinasse clarification improved the light input in photobioreactors to microalgae culture, thus increasing vinasse reuse feasibility and contributing to large scale biomass production. As can be seeing in the Figures 1 to 4, the results of the cultivation essays showed that it is possible to obtain growth of *Chlorella vulgaris* in a culture medium consisting of vinasse (pre-treated as described early), even when the highest value of vinasse concentration was used as culture medium (90% vinasse and 10% inoculum).

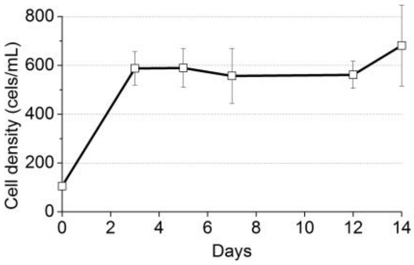

Figure 1. Cell density (cels/mL) in culture medium V_1.

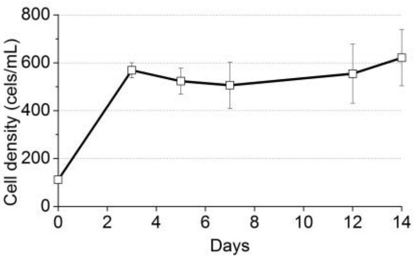

Figure 2. Cell density (cels/mL) in culture medium V_2.

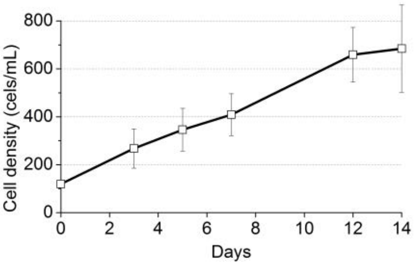

Figure 3. Cell density (cels/mL) in culture medium V_3.

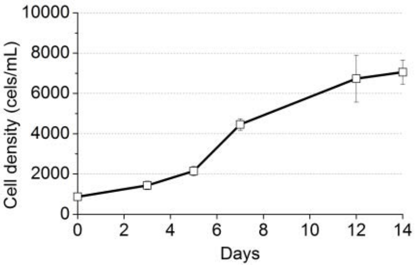

Figure 4. Cell density (cels/mL) in culture medium WC.

CONCLUSIONS

The culture medium consisted of pre-treated vinasse allowed the growth of *Chlorella vulgaris* microalgae, thus indicating the potentiality of using vinasse for the obtainment of algal biomass. New cultivation essays will be performed, in order to get better acclimatization of the *Chlorella vulgaris* in vinasse and, consequently, to get better growth rates and higher biomass productivity.

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(35) Characteristics of Media Implied Anaerobic Membrane Bioreactor for Domestic Wastewater Treatment

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Abstract

In this study, media implied anaerobic membrane bioreactor was used for treatment artificial domestic wastewater to investigate organic matter removal efficiency and biogas generation by monitoring water quality parameters and methane concentration for estimate reactor performance.

The anaerobic bioreactor could achieve excellent treatment performance in terms of COD removal and biogas production even at a short HRT (6 h). COD concentration of effluent was maintained lower than 20 mg/L and average removal efficiency was 95%. TOC and VFAs consumed through anaerobic treatment it means organic matters transformed to biogas. Membrane fouling was successfully controlled by scouring effect induced by media rotation. The anaerobic membrane bioreactor could be adapted to domestic wastewater treatment.

Keywords

Anaerobic membrane bioreactor; domestic wastewater treatment; media; biogas; membrane fouling

INTRODUCTION

Anaerobic wastewater treatment had been unusually used owing to the sensitive operation parameters until the advantage of anaerobic treatment which less consumption of electricity and methane production, resurfaced by global warming. The major site of electricity consumption in aerobic biological treatment systems is the aeration equipment, which consumes above 40% of whole facility consumption. The anaerobic treatment system could be adapted in traditional treatment system as a solution for energy saving. Contrary to the treatment of high-strength wastewater, the difficulty in retaining slow-growth microorganisms with short hydraulic retention time (HRT) has been concerned in the treatment of low-strength wastewater (Haandel and Lettings, 1994). The use of membrane can retain high biomass concentration in the bio-reactor without any sludge loss irrespective of short HRT. Thus, anaerobic membrane bioreactor (MBR) has been studied to treat low strength wastewater (Huang et al., 2008). However, to control fouling development in the anaerobic membrane bioreactor is an issue of concern. The Anaerobic MBR has more serious membrane fouling tendency, comparing to aerobic MBR (Pattanayak, 2007). Although of energy consumption, bio-gas recirculation is usually used to control membrane fouling in submerged type anaerobic MBR. Therefore, in this study, a media implied anaerobic MBR was attempted to reduce energy consumption for control of membrane fouling in the anaerobic MBR, and investigated the performance of the reactor on organic matter removal efficiency and biogas generation by monitoring water quality parameters and methane concentration for artificial wastewater.

MATERIALS AND METHODS

Anaerobic membranr bioreactor and media

The anaerobic MBR system was composed of two reactors, an anaerobic expended bed reactor (AEBR) and an anaerobic rotary media membrane bioreactor (ARMBR). Two rotary disks connected to the motor via a shaft were installed in the ARMBR, and the membrane (0.25 µm, PVDF) was located between the rotary disks. Both of the reactors were filled with fibrous ball media made of polypropylene. The water treated was sucked out through membrane at 11 LMH. The synthetic wastewater with 350 mg/L of COD was fed. The reactors were maintained at 30℃. The AEBR and the ARMBR were operated at 2-3h and 4h HRT, respectively.

Artificial domestic wastewater

Table 1. shows the component and concentration of artificial wastewater.

Table 1. The artificial wastewater composition and concentration

Components	Concentration (mg/L)	Component	Concentration (mg/L)
$FeCl_2$	2.92	$C_6H_{12}O_6$	100
$MgSO_4$	2.5	CH_3COONa	138.96
$CaCl_2$	3.13	Peptone	50
NH_4Cl	76.04	Beef extract	50
KH_2PO_4	20	$NaHCO_3$	100
NH_2CONH_2	10	$MnSO_4{\cdot}H_2O$	0.031
ZnC_{l2}	0.021	$NiCl_2{\cdot}6H_2O$	0.041
$CuCl_2{\cdot}2H_2O$	0.027	H_3BO_3	0.056
$Na_2MoO_4{\cdot}2H_2O$	0.025	$CoCl2{\cdot}6H_2O$	0.041

Analytical methods

The COD_{Cr} and TOC were measured for organic matter removal efficiency using Hach DR-5000 spectrophotometer (Hach, USA) and TOC-V CPN (Simadzu, Japan). The biogas volume and component analysed by water substitution method and gas chromatograph HP 6890 (HP, USA) equipped with Carbonex™ 1004 stainless steel micropacked column(Supelco, USA). The VFA was detected by LC-10 AVP HPLC system (Simadzu, Japan) DO, pH, ORP, SS and alkalinity was analysed to confirm bioreactor condition

RESULTS AND DISCUSSION

Effect of rotating media on membrane fouling

Fig 1 shows changes in trans-membrane pressure (TMP) under various rotation speed and media volume condition in the ARMBR. TMP rapidly increased at no rotation and no media condition. However, under the same condition, when only the rotation was applied at 40 rpm, increase of TMP was reduced to half level. And under that condition, if 10% of media was added in the reactor, TMP was additionally decreased to half level of no media condition, which was a quarter TMP level of no rotation, no media condition. This TMP was the same level of the TMP achieved at 100 rpm without media. It indicate that rotating media could effectively control membrane fouling since rotating media swept out fouling matters from the membrane surface.

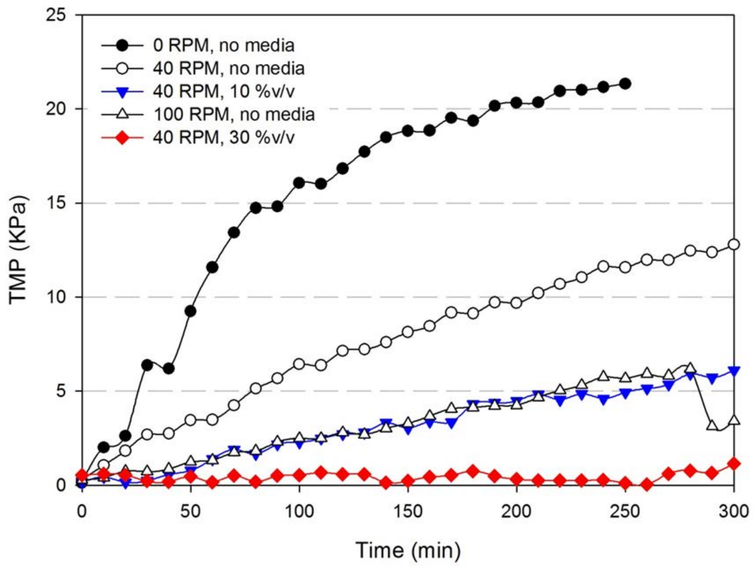

Figure 28. Effect of media rotation on membrane fouling

Characteristics of organic matter removal and biogas production

As shown in Fig. 2, the AEBR stably treated wastewater. COD concentration of effluent was maintained about 55 mg/L and average removal efficiency was 85%. To reduce reaction time, the HRT was reduced from 3h to 2 h. Even when HRT was reduced to 2hr, removal efficiency was kept about 85%.

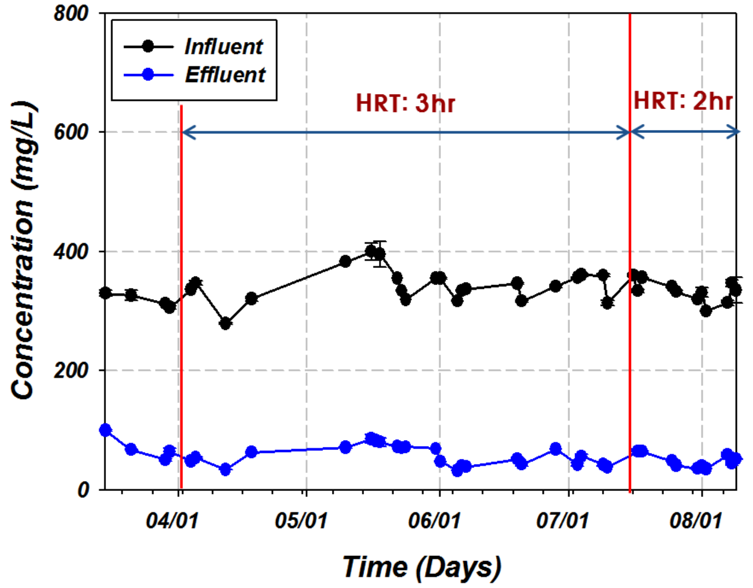

Figure 2. Changes in COD concentration of influent and effluent

Figure 3. shows methane production during the experiments. Regardless of HRT, the methane production rate and methane yield were maintained about 2.3 mol/m^3/d and 0.18 L/gCOD, respectively. The methane content was kept around 95%, regardless of HRT.

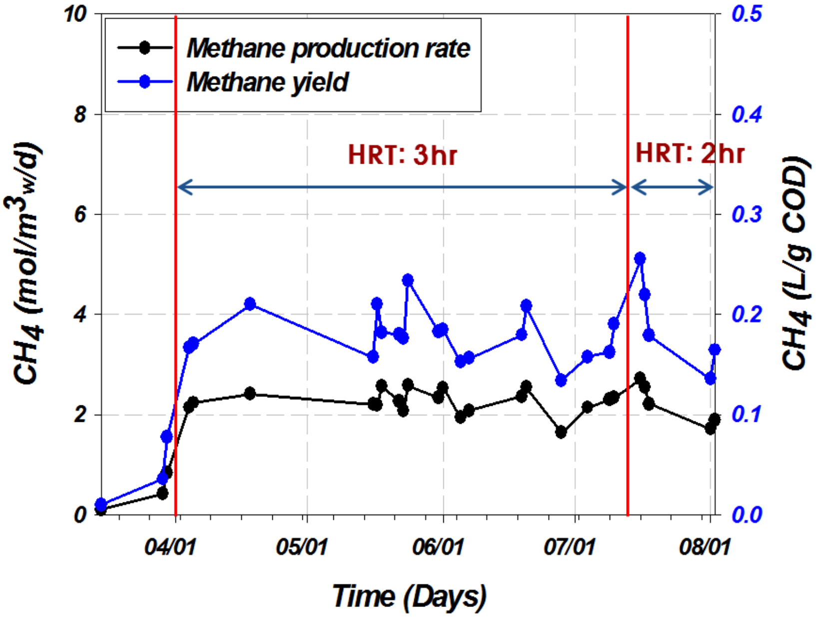

Figure 3 Changes in methane production

CONCLUSIONS

AEBR could achieve excellent treatment performance in terms of COD removal and biogas production even at a short HRT (3-2 hr). In the ARMBR, membrane fouling was successfully controlled by scouring effect generated by media rotation. ARMBR could be used for polishing of the AEBR effluent, reducing 50 mg/L of COD down to 10 mg/L and nearly zero for TSS. It is feasible to treat municipal wastewater with the anaerobic MBR system.

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(36) Phosphate removal from wastewater through hydroxyapatite crystallization

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Abstract

Phosphate removal through hydroxyapatite crystallization is an effective way for phosphate recovery during wastewater treatment processes. This study investigated the performance of phosphate removal via hydroxyapatite crystallization using different seed crystals (e.g., silica sand and slag). This study found that the release of Ca^{2+} from the steel slag reduced the cost of chemicals. The efficiency of crystallization was determined by comparing the removal of phosphate between filtered and unfiltered samples (filtering samples through 0.45 um filters). Phosphate was successfully crystallized when the slag was used. Moreover, this study attempted to investigate Ca^{2+} and phosphate molar ratio, type of seeds, and up-flow velocity to enhance the performance of hydroxyapatite crystallization using a fluidized bed reactor.

Keywords

Crystallization; hydroxyapatite; phosphate; slag

Climate change plays an important role in increasing frequency of algal bloom around the world. Recently, we observed the population of algae sharply increased to a level in rivers in Republic of Korea that public seriously concerned about their drinking water sources. Currently, there are many attempts to reduce the occurrence of serious algal blooms by government officials, but they are still under investigation if low water flow in rivers is a major factor due to four major rivers restoration project. Nitrogen and phosphorus are well known for limiting factors in the occurrence of algal bloom, and this study was conducted to reduce the phosphorus loading in the rivers by reducing phosphorus in wastewater water as low as possible (total phosphorus less than 0.3 mg/L where wastewater treatment discharge more than 50 m^3/day of treated wastewater) though hydroxyapatite crystallization. Phosphorus is a valuable resource in many applications, and many approaches address impacts of global phosphorus scarcity. Phosphate removal through hydroxyapatite crystallization is an effective way for phosphate recovery during wastewater treatment processes. This study investigated the performance of phosphate removal via hydroxyapatite crystallization using different seed crystals (e.g., silica sand and slag). This study found that the release of Ca^{2+} from the steel slag reduced the cost of chemicals. The efficiency of crystallization was determined by comparing the removal of phosphate between filtered and unfiltered samples (filtering samples through 0.45 um filters). Phosphate was successfully crystallized when the slag was used. Moreover, this study attempted to investigate Ca^{2+} and phosphate molar ratio, type of seeds, and up-flow velocity to enhance the performance of hydroxyapatite crystallization using a fluidized bed reactor.

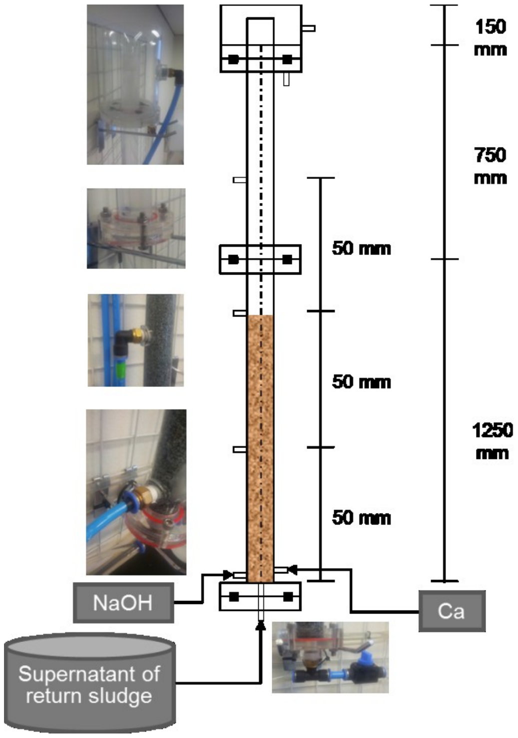

Figure 1. Experiment set-up of hydroxyapatite crystallization system

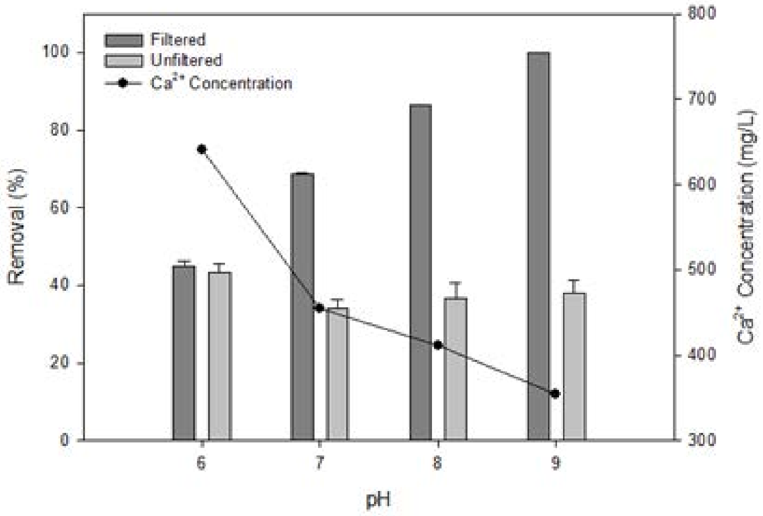

Figure 2. Phosphate removal between filtered and unfiltered samples at different pH during hydroxyapatite crystallization

ACKNOWLEDGEMENT

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(37)Effect of bioaugmentation on Ammonia Oxidizing Bacteria (AOB) kinetics

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Abstract

The aim of this work is to evaluate, through experimental monitoring and modelling, to what extension is possible to affect the kinetic parameters of Ammonia Oxidizing Bacteria (AOB) through the continuous inoculum (bioaugmentation) with AOB selected in a different reactor and characterized by different kinetics.

Two membrane bioreactors (MBR) pilot plants were used to simulate the continuous inoculum of nitrifying sludge from a side-stream reactor treating synthetic wastewater, similar to anaerobic digester supernatant, to a main-stream reactor operated with low solids retention time (SRT = 2.5 d) treating real domestic wastewater.

An activated sludge model (ASM), with two step nitrification denitrification (ASMN) was applied to carry out the evaluation in both MBRs, while conventional batch kinetic tests were performed to estimate AOB kinetic parameters.

Through modelling it was possible to clearly demonstrate that effectiveness of bioaugmentation, especially within a certain range of temperature in the seeded reactor. The nitrification process, prior to bioaugmentation, was well described using two different sets of kinetic parameters, that is the half-saturation constant for ammonia (K_{NH}) and the maximum specific growth rate ($\mu_{max,AOB}$), estimated in the side-stream (K_{NH} = 0.8±0.15 mg N-NH^4 L^{-1}; $\mu_{max,AOB}$ = 0.95±0.02 d^{-1}) and main-stream (K_{NH} = 0.39±0.17 mg N-NH^4 L^{-1}; $\mu_{max,AOB}$ = 0.84±0.019 d^{-1}) MBRs. Despite the significant difference between the K_{NH} in the reactors, the continuous inoculum of biomass from the side stream, was not followed by the expected change (increase) in the half saturation constant in the seeded reactor where the parameters remained practically unchaged (K_{NH} = 0.4±0.14 mg N-NH^4 L^{-1}; $\mu_{max,AOB}$ = 0.85±0.015 d^{-1}).

Keywords
Bioaugmentation; Ammonia Oxidizing Bacteria; kinetics; modeling;

INTRODUCTION

Bioaugmentation of activated sludge by the addition of indigenous or allochthonous strains or consortia of microorganisms is a powerful instrument to enhance biological nitrification (Bartolì et al. 2011) and, potentially, a cost-effective strategy to obtain high nitrification efficiencies at relatively low solids retention time (SRT). It consists of enriching the mixed liquor of the main-stream reactors of an activated sludge system with nitrifying biomass collected from a side stream reactor where the environmental conditions are favourable for nitrifiers growth. However, bioaugmentation is not yet easy to predict and control (Van Limbergen et al. 1998) and its success depends on the effective establishment and metabolic adaptation of the added biomass in the treatment system (Satoh et al. 2013). Several phenomena can influence bioaugmentation efficiency (i.e. predation, large temperature differences and different nitrifying biomass in the seeding and the seeded reactor) and only in few cases bioaugmentation efficiency has been accurately predicted using conventional IWA ASMs (Munz et al, 2012). The use of lumped kinetic parameters and of a unique ammonia oxidizer biomass (AOB) are often seen as limitations on bioaugmentation modeling while the use of two AOB populations with different kinetic behaviours is regarded as a possible solution (Wett and al., 2011). Despite several experiences demonstrated that the kinetics of nitrifiers vary with different reactor configuration and process conditions (Dytczak et al., 2008), how kinetic parameters changes when AOB is transferred from one environment to another is still unclear.

The aim of this work is to evaluate through experimental monitoring and modeling the effect of AOB bioaugmentation on the kinetics of nitrifying biomass in a MBR representing a main stream section of an activated sludge system continuously inoculated with the biomass deriving from a side stream MBR operated under different operational conditions as temperature, SRT and ammonia loading rate.

MATERIALS AND METHODS

The experimental set-up consisted of two MBRs as shown in Figure 1. The side-stream pilot scale MBR (MBR1- the seeding reactor) consisted of pre-denitrification, nitrification and of a filtration tank equipped with three flat membranes (DF-10 Kubota, Japan). MBR1 was fed with synthetic (with a high concentration of nitrogen) influent simulating anaerobic digester supernatant (650 mg $N\text{-}NH_4^+$ L^{-1}; 250 mg COD L^{-1}) and operated for more than 600 days with an SRT of 20 d.

The main-stream pilot scale MBR (MBR2 - the seeded reactor) was equipped with a hollow fiber filtration module (Module ZW10 GE-Zenon Environmental) and fed with real domestic wastewater continuously collected from the sewer at the Cuoiodepur WWTP (San Romano – San Miniato, Pisa, Italy). ALR was close to 18 g $N\text{-}NH_4^+$ L^{-1} d^{-1} and Dissolved oxygen (DO) concentration and pH were the same in both reactors: pH = 7.5 ±0.5, DO = 4 ± 0.5 mg L^{-1}.

In MBR1, temperature was controlled and maintained at 20 ± 0.5 °C while in MBR2 temperature depended on environmental temperature without any control and varied from 24 to 6 °C during the experiment. MBR2 was operated in steady state conditions without any external seeding for more than 435 days, with an SRT of 2.5 d. Bioaugmentation started on day 435 and seeding flow was maintained at 2.5 L d^{-1} for more than 150 d.

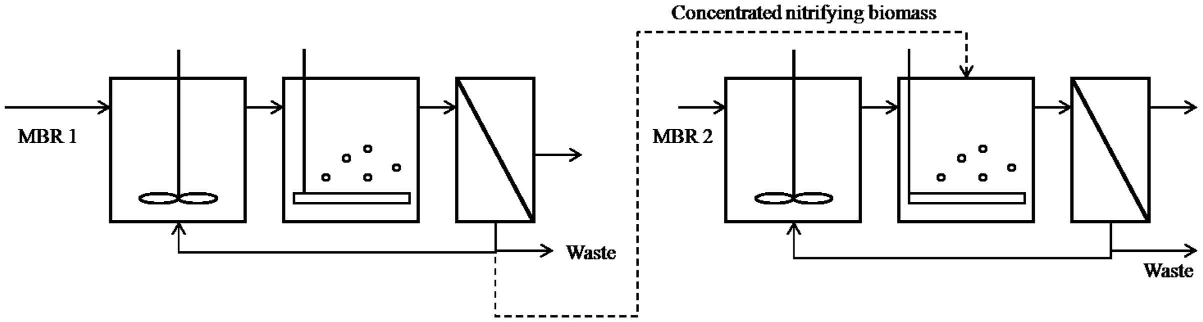

Figure 1. Schematic of the experimental pilot scale set-up

In order to study the kinetics b of nitrifying biomass in both MBRs, a series of off-line kinetic batch tests under controlled T, pH and substrates conditions were performed.

1 L of mixed liquor collected from MBR1 and MBR2 aerobic basin in both augmented and non-augmented conditions was maintained mixed and aerated until reaching endogenous. A fixed amount of NH_4Cl was dosed in order to obtain an initial concentration that will not be neither limiting nor inhibitory, based on observation and literature data. The pH was controlled at 8 ± 0.1 and the DO higher than 4 mg L^{-1} through fine bubbles aeration. A sample was collected every 10 minutes and the $N\text{-}NH_4^+$ was analyzed through colorimetric analysis. Each test was repeated in triplicates.

An activated sludge model with a two-step nitrification-denitrification (ASMN) was used to describe the processes (autotrophic and heterotrophic biomass) in both pilot plants and to estimate the amount of active AOB biomass at the time of batch tests according to Munz et al. (2011), assuming a AOB decay coefficient of 0.17 d^{-1}. The model, that separately represents AOB and NOB populations, was used to calibrate the maximum specific growth rate for AOB ($\mu_{max,AOB}$) and the half-saturation constant for ammonia (K_{NH}) with the results of batch tests.

RESULTS AND CONCLUSIONS

The AOB concentration of the samples used in conventional kinetic tests was determined through the modelling of the nitrification capacity of the MBR pilot plants during the non bioaugmented period: an AOB concentration of 520 mg COD L^{-1} and 10 mg COD L^{-1} have been estimated for MBR1 and MBR2, respectively.

AOB concentration was used to calibrate $\mu_{max,AOB}$ and K_{NH} using ASMN model on the ammonia bulk liquid concentration obtained in conventional kinetic batch tests. An example of experimental and modelled ammonia concentration for the MBR2 nitrifying biomass is reported in Figure 2.

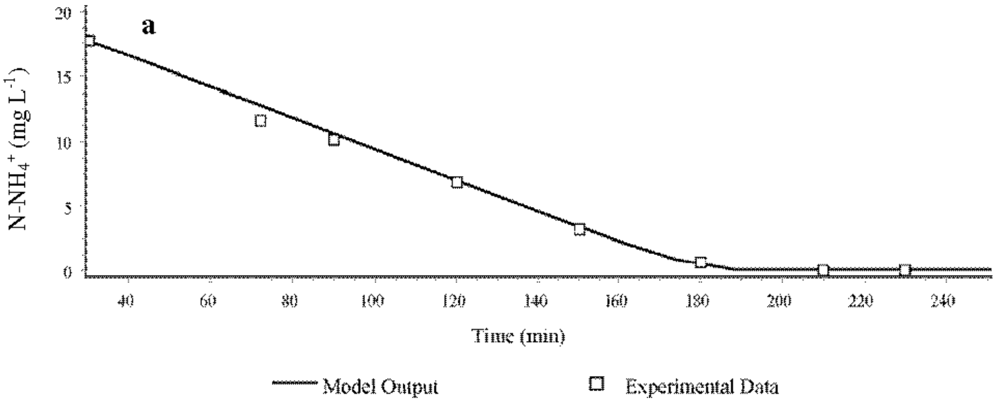

Figure 2. Experimental results and calibration with ASM1 of a test for half-saturation constant and maximum specific growth rate estimation

Average values of $\mu_{max,AOB}$ and K_{NH} obtained through kinetic batch tests are reported in Table 1.

Table 1. Calibrated ASMN parameters in batch tests

MBR1		MBR2 without bioaugmentation		MBR2 with bioaugmentation	
K_{NH} (mg N-NH_4 L^{-1})	$\mu_{max,AOB}$ (d^{-1})	K_{NH} (mg N-NH_4 L^{-1})	$\mu_{max,AOB}$ (d^{-1})	K_{NH} (mg N-NH_4 L^{-1})	$\mu_{max,AOB}$ (d^{-1})
0.8±0.15	0.95±0.02	0.4±0.14	0.85±0.015	0.39±0.17	0.84±0.019

The results obtained with kinetic batch tests and through the calibration of kinetic parameters over quality effluent experimental data confirm a selection of different AOB biomass in MBR1 and MBR2 in non augmentated period due to the different operational conditions maintained.

Kinetic test were replicated using MBR2 AOB biomass after 70 days of continuous bioaugmentation.

No significant differences have been estimated between AOB biomass in MBR2 with and without bioaugmentation and nitrification during the bioaugmented period (from day 435) were well described using the same set of kinetic parameters (Figure 3).

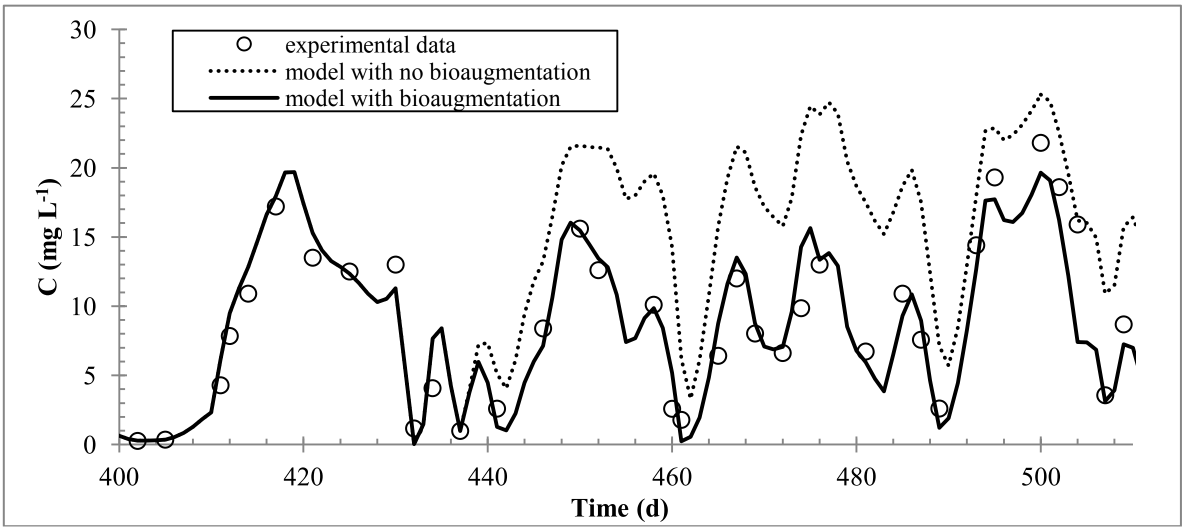

Figure 3. Experimental data and model output for MBR2 effluent ammonia

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(38) Role of Vegetation in an Ecological Hybrid Vegetation-Activated Sludge Process (V-ASP): from Mathematical Modeling to Experimental Verification

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Abstract

A hybrid vegetation-activated sludge process (V-ASP) with friendly ecological pattern was developed. Herein, the importance of installed vegetations was evaluated from the viewpoints of nutrients removal enhancement, and was simulated by a developed mathematical model. The highest nutrients removal efficiencies above 25% was obtained by *Canna indica (CI)*, whose growth kinetics and its resulted nutrients utilization rate were deemed as to conform with Monod Equation. Through batch-tests measurement and calculation, its half-saturation constant and the maximum growth rate were estimated. The comparison of experimental and simulated results revealed that the deviation of COD, TN, NH_4^+-N and TP was below 25%, 5%, 8%, and 10%, respectively, implying that the model has high feasibility. It was observed that the V-ASP system has stable pollutants removal performance and high resist to influent loading fluctuation. The results herein give a new insight for ecological wastewater treatment process configuration, and offer the direct guideline for their real application.

Keywords: Ecological wastewater treatment process; vegetation-activated sludge process; ASM2d model; nutrients removal

INTRODUCTION

The demand of decentralized wastewater management in semi-urban or rural areas brings about the increasingly development of ecological sewerage treatment technologies that possess landscaping and pollutants removal functions (Solano et al., 2004; Masi et al., 2013). Conventional ecological wastewater treatment process, such as constructed wetland and oxidation pond, have to confront the problems such as large footprint, relative stringent influent requirement, and unstable pollutant removal effectiveness deteriorated by low temperature. From last two decades, one promising ecological sewage treatment process, Living Machine (LM) technology, began to achieve more and more concerns since that it involved the vegetations into biological wastewater treatment units to affiliate their landscaping ability (Todd and Josephson, 1996; Masi et al., 2013), as well as to enhance the pollutants removal efficiencies, especially for nitrogen and phosphorus. However, the reported LM process was always used for individual apartment or small residential area that has limited wastewater flow-rate, which resulted in numerous difficulties during the system amplification to large-scale (Kavanagh and Keller, 1996; Li et al., 2013). Besides, as the major baseline for vegetation selection, their nutrients removal capabilities were often underestimated to some extent. In the present work, special attentions were paid to the role of vegetations in the vegetation-activated sludge process (V-ASP) from the viewpoints of their landscaping and pollutants removal abilities. Afterwards, a mathematical model for the V-ASP was developed based on IAWQ Activated Sludge Model No.2d (ASM2d) and the kinetic coefficients estimation, to comprehensively evaluate the contribution of vegetations, and to anticipate its effectiveness (Henze et al., 1999).

MATERIAL AND METHODS

CSTR reactor and V-ASP reactor

The batch tests were carried out in three identical continuous stirred-tank reactor (CSTR) (working volume = 48 L) to estimate the nitrogen and phosphorus removal performances by three vegetation species, *Cyperus altrnlifolius* (*CA*), *Canna indica* (*CI*) and *Spathiphyllum* (*SP*). The feeding influent was real domestic wastewater with an average COD, NH_4^+-N, TN and TP of 266, 50.9, 55.3 and 4.6 mg/L, respectively. The dissolved oxygen (DO) concentration in the bulk was kept above 2.0 mg/L. By change the influent flow-rate, the pollutants removal kinetics coefficients, including the maximum substrate utilization rate (ν_{max}), the maximum vegetation growth rate (μ_{ve}), half-saturation constant ($K_{COD,ve}$, $K_{NH4+-N,ve}$, $K_{NO3-,ve}$, $K_{PO43-,ve}$), and vegetation yield coefficient (Y_{ve}) were estimated.

A V-ASP system comprised of a sequencing batch-reactor (SBR) (L×W×H=80×40×60 cm, working volume = 170 L) and selected vegetation species that with the best nutrients removal abilities. The vegetation cultivation density in V-ASP system was around 180 cm^2/vegetation, and up to 15 cm of vegetation root was submerged beneath the bulk. The hydraulic retention time (HRT) of the V-ASP was 8 h, which included 20 min fill, 1.5 h anaerobic, 4 h aeration, 1.5 h anoxic, 30 min sedimentation and 10 min withdrawn. The solids retention time (SRT) was 15 d, and the reactor was operated at room temperature (about 22°C).

Sampling and analytical methods

The influent and effluent water samples were collected regularly, and then were filtered by 0.4 µm black polycarbonate membrane filters. The pollutants in both samples were analyzed for the COD, NH_4^+-N, TN and TP to estimate removal performance according to Standard Methods.

Evenly mixed root, stem and leaves of the vegetations were collected to estimate the vegetation mass (X_{ve}) and growth rate (ν). After the digestion by concentrated sulfuric acid and hydrogen peroxide, the TN and TP content in vegetation ($i_{N,ve}$, $i_{P,ve}$) and its components were determined.

Mathematical model development

The ASM2d was used as the basic model for V-ASP simulation (Henze et al., 2000). The parameters related with chemical phosphorus precipitation were neglected. Since that there were limited substrates available in the bulk, it is reasonable to assume that the pollutants removal kinetics by vegetation complied with Monod's equation. Accordingly, the parameters brought from vegetation function consist of X_{ve}, $K_{COD,ve}$, $K_{NH4+-N,ve}$, $K_{NO3-,ve}$, $K_{PO43-,ve}$, Y_{ve}, $i_{N,ve}$, $i_{P,ve}$, μ_{ve}, and ν_{max}.

RESULTS AND CONCLUSIONS

Enhanced pollutants removal by vegetations

A long-term experimental batch tests showed that all of vegetations could remove nutrients from domestic wastewater under an aerobic condition (Fig. 1), while they had rather limited COD removal efficiencies. The NH_4^+-N removal efficiencies by these three vegetations were indeed comparable, all of which averaged around 20%. In contrast, the maximum TN and TP removal efficiencies were obtained by *Cl*, averaged in 27.4% and 30.3%, respectively. Notwithstanding, it is highly expected that the nutrients removal capabilities would be elevated in a certain level after continuous incubation by wastewater. Considering the landscaping and pollutants removal performance, *Cl* was employed to involve with SBR for V-ASP configuration.

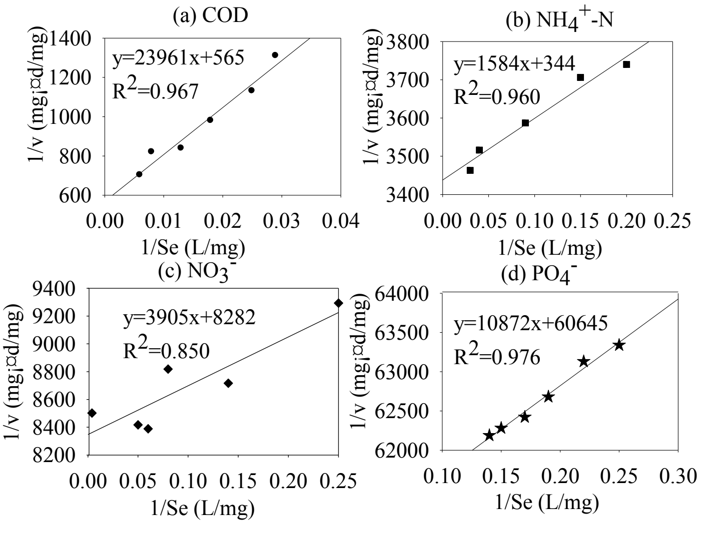

Figure2. Graphical method to estimate half-saturation constant K_s and the maximum growth rate ν_{max}

Estimation of vegetation kinetic coefficients

As that the vegetation growth kinetics could be expressed as Monod Equation, and its resulted nutrients utilization kinetics conformed to Michaelis-Menten mode, the K_s of different pollutants and the maximum vegetation growth rate could be calculated by plotting of 1/ν against with 1/S_e (S_e is the effluent pollutants concentration). As shown in Fig.2, the $K_{COD,Ve}$, $K_{NH4+-N,ve}$, $K_{NO3-,ve}$, and $K_{PO43-,ve}$ of *CI* were 42.4, 0.46, 0.47 and 0.18 mg/L, respectively. The *CI* has the maximum growth rate (μ_{ve}) about 0.0003 d^{-1} by relative growth rate method (Hadad et al., 2006), and the yield coefficient (Y_{ve}) related with nitrogen about 0.17. From the components analysis, the nitrogen ($i_{N,ve}$) and phosphorus ($i_{P,ve}$) content in the *CI* was around 0.03 gN/g*CI* and 0.005 gP/g *CI*, respectively.

Experimental verification and evidence for the role of vegetation

The developed ASM2D model was operated using Matlab compiler. The V-ASP system was operated to evaluate the feasibility and accuracy of developed model. As showed in Fig. 3, the relationship between the simulated results and measured results was quite close. The deviation of COD, NH_4^+-N, TN and TP was below 25%, 8%, 5% and 10% respectively, indicating that developed model could be suitable for estimation of V-ASP process. A Student's t-test was made to give a comparison between the simulation and experimental date by SPSS software. The results revealed that four p-value were all greater than 0.05, which helped to deem t hat there were no statistically significant difference of the model. Therefore, it is believed that the developed model based on ASM2d and kinetics coefficients measurement was capable to predict the V-ASP system accurately.

Through a long-term V-ASP system operation, it was observed that the V-ASP system has stable wastewater treatment effectiveness under a low HRT about 8 h, resulted in an effluent with the average COD, NH_4^+-N, TN and TP was 23, 0.3, 9.0 and 0.38 mg/L, respectively. The involvement of vegetation in the conventional SBR would improve the stability of the system, as well as increase the resist for system loading fluctuation. The results herein would be very useful to understand the role of vegetation in the ecological wastewater treatment process, and to give the direct guideline for the real application.

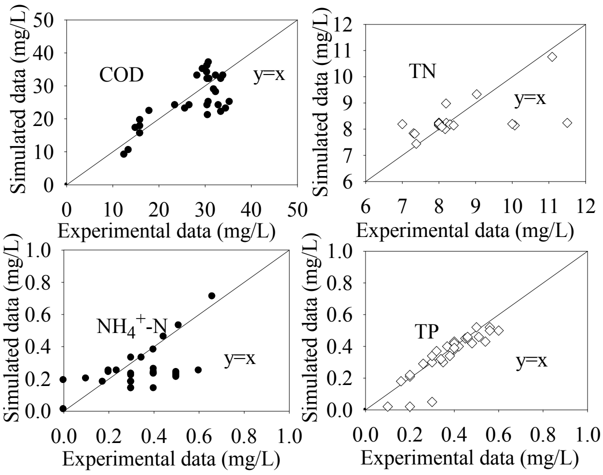

Figure 3. Comparison of simulated and experimental results for V-ASP system

ACKNOWLEDGEMENT

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(39) Biological phosphorus removal in municipal wastewater treatment plants in Flanders (Belgium): kinetic characterization of biomass and operational influences.

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Abstract

Flemish wastewater treatment plants were screened as to identify the role that several parameters have on biological phosphorous removal. The influent characterization was found the most influential aspect in favoring the Bio-P activity. In particular, presence of consistent VFAs concentrations limits the necessary anaerobic HRT in dry weather flow by concentrating the release peak in a short time-window. The relevance of other parameters (temperature, pH, nitrate), proved by lab tests, was not identified in full scale measurements, likely due to the multi-factoriality of bio-P activity. Flemish installations were characterized by co-existence of denitrifying and aerobic uptake. The two were proven in this study to be a different metabolic paths of the same organism. While anoxic P uptake was found irrelevant in terms of nitrate removal, the influence on the overall P removal was high and accounted to the 37% of the total P removal.

Introduction: Application of current state-of-the-art phosphorous recovery techniques, such as the struvite precipitation, requires good working enhanced biological phosphorus removal (EBPR) activity in wastewater treatment plants (WWTPs). In this process, the polyphosphate- accumulating organisms (PAOs) are able to store phosphorus through sequential anaerobic–aerobic conditions. Alternatively, nitrate or nitrite can be used as electron acceptors (i.e. anoxic conditions) instead of oxygen (Kuba *et al.*, 1993).

Since the late nineties, several Aquafin's installations have been equipped with anaerobic basins as to perform Bio-P activity. Due to the heterogeneity of several simultaneous processes, the different influent feeds, and eventual interferences, identification and quantification of the EBPR performances in full scale must necessarily pass through detailed lab protocols. Most studies have been carried out at lab-scale, whereas comparative data and observations from full-scale studies are still limited (Lopez-Vazquez *et al.,* 2008). Therefore, there is a clear need to verify and extend the findings of laboratory-based studies to full-scale operating plants (Seviour *et al*., 2003). The objective of the present paper is: (i) evaluate which environmental and operating conditions as well as wastewater characteristics influence the occurrence of full-scale EBPR; (ii) Characterize the contribution of dPAOs metabolism to the overall P removal.

Materials and methods: Several Aquafin municipal WWTPs were included in this survey. All systems have aeration volumes preceded by an anaerobic volumes, on line controlled aeration, and sludge retention times ranging from 15 to 25 days. The survey was carried out from 2011-2013. Daily flow-composite influent-effluent samples were collected. Samples were analyzed for BOD_5, COD, suspended solids (SS), Kjeldahl nitrogen (KJN), NH_4-N, NO_3-N and NO_2-N, PO_4–P and total phosphorus (TP). All samples were analyzed according to the Standard Methods (Apha, 1999).

Volatile fatty acids (VFA) and metals were measured in influent water samples. Multiple linear regression of several independent parameters (yearly averages of PO_4-P effluent, NO_3-N effluent, anaerobic volume, BOD and TP load) was computed by the statistics toolbox available in Matlab (Mathworks).

Batch tests were enforced with the aim of: (i) estimating the EPBR activity; (ii) =analyze the effect of VFA concentration on the anaerobic retention time. A first batch has been run with 1L recycled activated sludge mixed with 1L influent flow; After measuring the influent COD concentration, a second batch has been run with 1L of the same recycled activated sludge and 1L effluent flow and HAc (spiked until reaching the same influent COD concentration). PO_4-P concentrations and specific release rate (mgPO_4-P/gSS/h) have been measured over time for both batches; (iii) characterizing the kinetics of dPAOs /aPAOs in full scale conditions. All 3 L batch tests were stirred at 300 rpm with controlled pH (6.9-7.2), with an O_2 set-point (Osp) of 5 mg/l, and a temperature of 20°C. The spiked HAc concentration dose was carefully chosen to assure that all HAc is degraded before the consequent aPAOs uptake. The test results are extracted by considering the initial uptake and release rates (measured within the first 60 minutes). The Bio-P activity was estimated in the release time as follows: (mgPO_4-P_{final}- mgPO_4-$P_{initial}$)/time/gVSS*100.

RESULT AND DISCUSSION

Influent characterization: The influent composition plays an important role on Bio-P activity. Batch test were performed to look at the effect of VFAs rich/poor waters on the same sludge water. Two EBPR activated sludges were chosen (figure 1): (i) Dilsen WWTP, receiving a high content of industrial waters, and containing a 10-15% (COD VFA/ COD Total); (ii) Aalst WWTP, receiving few industrial waters, and containing no measurable COD VFA. The EBPR performances of these two sludges were tested by feeding their specific influent feed. A parallel test was conducted by feeding influent flow or effluent and HAc, i.e. the latter until reaching same volume and COD concentration of the municipal influent flow. Volumes, COD concentrations, and controlled conditions were also comparable. Release tests are performed with a time window comparable to the hydraulic residence time (HRT) available in full scale during dry weather flow.

In case of Dilsen sludge, the PO_4-P released was 70% of that released with an HAc based influent. A real influent feed allows a release rate peak already at 5-20 minutes from start. After the peak, a drastic drop in the release rate follows: the COD available doesn't allow high PO_4-P concentrations. We think the peak coincides with the intracellular use of the VFA. In case of an HAc based influent, the peak comes at about 5 minutes lasting for longer time than in the other test, since the HAc concentration is in fact higher. Peak intensities are comparable. However after the peak the release rate smoothly decreases. Both peaks start are delayed according to the amount of nitrate present in the sample. Only when NO_3-N drops, a strong release rate can take place.

In case of Aalst sludge, the PO_4-P released was 38% of that released by an HAc based feed. A municipal influent feed exerts no peak in the observed release rate. On the contrary, the release rate is rather slow, reaching a max of 1 mgPO_4-P/g/g MLSS after 50 minutes. This would seem to indicate a COD conversion or fermentation into products usable by Bio-P bacteria's. The rate remains slow all over the test and slowly fades at the end of the test. After 3 hours in anaerobic time, the PO_4-P released doesn't converge to a value but keeps on growing steady and slow. In case of an HAc based feed instead, the peak arrives at 10-25 minutes. Once again, in case of HAc based feed, the release rate slowly decreases.

A phosphorous release phase in municipal influent, in absence of VFA fractions, is fed through conversion processes, likely based on fermentation. In this case the phosphorous is released at a low rate (figure 1c). This drastically enlarges the time-length of the release phase, and the tank volume necessary to sustain the activity. When looking at Aalst WWTP process scheme, there is a huge anaerobic volume but without a good influent characterization it does not allow Bio-P activity.

A fix % of VFA would thus sustain the EBPR in all conditions by decreasing the necessary HRT to release. The faster/higher the release peak comes, the higher is the Bio-P activity performed in short HRT, i.e. in rain weather flow events. A release peak due to a 10% VFA presence in the influent characterization, as in Dilsen, allows to have 50% of the released P in the first 40 minutes. In this sense, anaerobic tanks have moderate dimension and serve the EBPR purpose.

Lopez-Vazquez *et al.* (2008) found no significant correlation between the amount of Bio-P biomass and VFA fractions. Flemish WWTPs were scanned for VFA concentrations. The correlation factor between VFA concentrations and bio-P activity accounts for a R^2 of 0.68 (table 1). This is the highest correlation with Bio-P activity found in full scale data of Flemish installations. The importance of influent

characterization is also highlighted by a visible correlation with regards to BOD concentration.
The present discussion has influence on the EBPR design practice. While the parameter mostly used to design anaerobic tanks is the HRT (generally within the 2-3h), this work shows how this approach doesn't match the process characteristics. Optimal anaerobic tank volume mainly depends on the release peak due to the VFA fraction, or the strength of the BOD concentration. Nitrate load, dependant on N removal and recycle ratio, increase also the anaerobic HRT.

If influent characterization proves to be so relevant in full scale EBPR, the margin of process optimization reduces. Certainly *ad hoc* step-feeding strategies and proper use of process-schemes would be as a consequence encouraged.

<u>Environmental factors affecting EBPR</u>: Parallel batch tests have been performed to check the effect of temperature on release-uptake phase of aPAOs-dPAOs. The temperature was 10.5 °C, 15 °C, 23.5 °C, so as to represent typical seasonal temperature in Flanders (Belgium). In this test, the release was clearly quicker at 15 °C and 23.5 °C than at 10.5 °C. The initial uptake rate was instead highest at 23.5 °C with similar performances at 15°C, but clearly lower at 10.5 °C. Not surprisingly low temperatures were found detrimental to the process. The dynamics of EBPR must be sought in comparison with the heterotrophic competition. While the Bio-P release difference was not so marked between the 15-23 °C, the heterotrophic activity, measured by the overall NO_3-N consumption, was found clearly higher at higher temperatures (both in anoxic and anaerobic phase). Bio-P could better compete for HAc at around 15°C than at 23.5°C. This could explain why, in some Flemish installations, EBPR performances are to large extent seasonal dependent. Highest performances are reported indeed in spring periods, where the water temperatures lay between 13-16 °C, i.e. Brugge WWTP. These results were in agreement with Baetens *et. al.* (1999). The latter demonstrated an effect of temperature on kinetics of EBPR rather than on the stoichiometry. According to the authors, the aerobic uptake has a maximum in the interval between 15-20 °C.

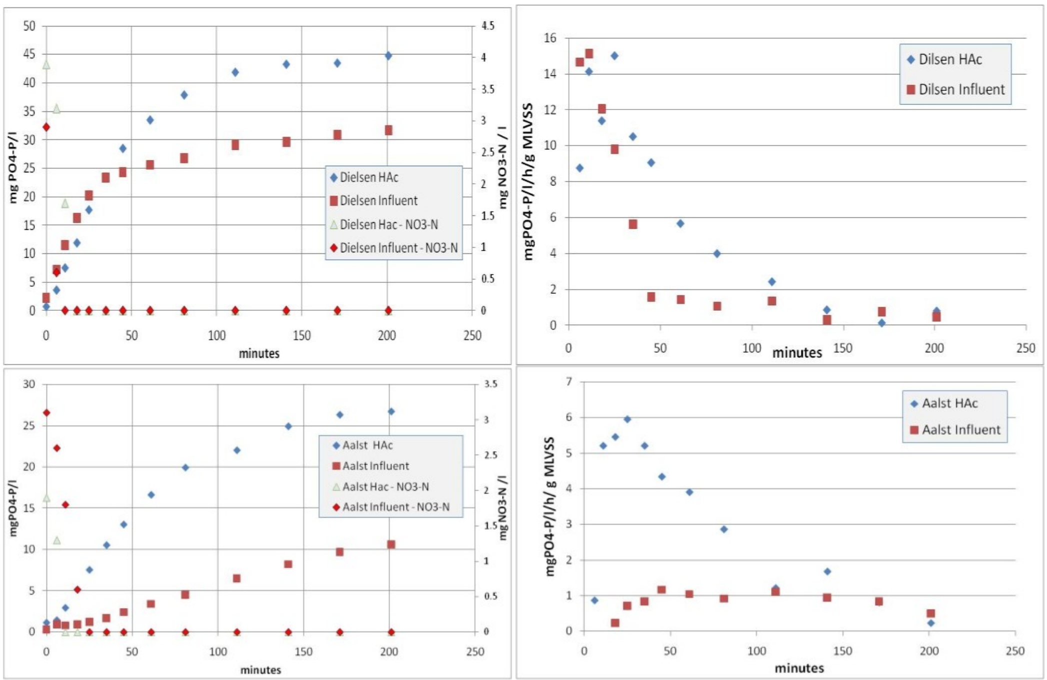

Figure 1a (top left): Released PO4-P:Dilsen influent compared to a completely vfa driven influent. Figure 1b (top right): Release rate of PO4-P:Dilsen influent compared to a completely vfa driven influent. Figure 1a (bottom left): Released PO4-P:Aalst influent compared to a completely vfa driven influent. Figure 1b (bottom right): Release rate of PO4-P:Aalst influent compared to a completely vfa driven influent.

Average PO_4-P release	Max PO_4-P release	WWTP	Anae Vol.	Anae/Aer Vol.	BOD	TP	NO_3-N eff	BOD/TP	V.F.A.
mg PO_4-P/gMLSS/h	mg PO_4-P/gMLSS/h		m^3	m^3/m^3	mgBOD/L	mgTP/L	mgNO_3-N/L	mgBOD/mgTP	mg/L
5,9	5,9	Morkhoven	2000	0,13	78	3,8	5,0	20,7	
18,3	35,0	Dilsen	1175	0,19	151	6,8	2,5	22,3	30
7,9	9,0	Leuven	6250	0,26	149	6,3	5,5	23,6	
7,0	7,0	Aartselaar	6000	1,00	122	5,9	4,7	20,7	0
6,6	6,8	Ieper	1908	0,17	117	4,8	1,7	24,4	
5,9	6,2	Tielt	800	0,15	71	3,9	3,5	18,2	
3,7	5,6	Eeklo	1100	0,12	70	4,0	1,9	17,6	
4,5	7,2	Brugge	10000	0,15	104	9,0	2,7	11,6	
4,0	5,0	Aalst	3700	0,14	102	3,9	1,7	26,3	3
4,3	4,3	Antwerpen-Z	8750	0,18	126	5,1	3,7	24,6	
9,3	9,3	Merksem	1600	0,27	94	4,0	4,0	23,5	
5,7	5,7	Deurne	10788	0,14	153	5,8	4,2	26,4	15
4,5	4,5	Malle	2000	0,65	84	4,1	4,3	20,3	
2,5	2,5	Hamme	1100	0,16	75	4,2	3,6	17,9	
3,7	3,7	Mol	1500	0,20	92	4,6	4,1	20,2	
5,0	6,0	Mechelen-N	3813	0,18	91	4,3	3,1	21,0	
20,6	30,0	Oostende	4500	0,10	172	6,5	2,8	26,3	17
7,5	7,5	Tienen	1250	0,19	135	4,0	2,8	33,6	
	R2-value			0,01	0,47	0,21	0,05	0,1	0,68

Parallel batch tests have been done to compare bio-P activity and verify the optimal pH ranges. It was found that: (i) the optimal range of the release phase is between pH 7-7.5 with optimum at 7.0. The gain in the release rate is about a 5-10% when compared to a pH 6 batch; (ii) the optimal range of the uptake phase is between pH 7-7.5 with optimum at 7.5. The gain in the uptake rate is about a 30% when compared to a pH 6 batch. The pH confirms to be a relevant parameters in full scale EBPR operations. Differently from Lopez-Vazquez *et al*. (2008), these tests suggest that the major gain in the Bio-P activity is obtained by controlling the pH during the uptake phase. Though when looking at full scale data, the R^2 factor between anaerobic pH and bio-P activity is 0.02, likely due to the multi-factoriality of the EBPR process. However pH process optimization is not applicable in big volumes, and a wise process survey would at least limit dosage of chemicals altering the pH far from the desired range, or extensive aerations.

Denitrifying P activity: A test was performed to highlight whether dPAOs and aPAOs are performed by the same organism. As hypothesis, if aPAOs and dPAOs are different species, each bacterial strain would uptake PO_4-P according to its "private" intracellular storage reserve. In other words an initial aerobic uptake rate would not be limited by a previous anoxic uptake rate. Similarly, an initial anoxic uptake rate would not be change if preceded by a previous aerobic uptake rate.

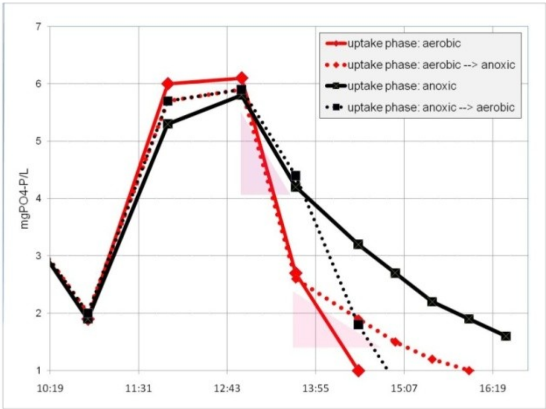

Figure 2: identification of dPAOs and aPAOs through an experiment.

In figure 2, the decrease of the PO_4-P concentrations due to an uptake phase (after 12h43m). Triangles highlight how the anoxic uptake rate significantly lowers, after 45 minutes of aerobic cycle. Similarly, the aerobic uptake rate lowers after 45 minutes of anoxic cycle. Certainly, energy consumption in an aerobic uptake is higher than in an anoxic uptake (same time-length), as reflected by the P uptaken. The more is the P uptaken, the less is the residual energy for further uptake. This explains why the decrease in rate is more significant after the aerobic uptake than after the anoxic uptake. By estimating the initial energy reserve and the amount of energy used per P uptaken (considering the uptake speed relative to anoxic/aerobic conditions), it is in fact even possible to predict the speed of uptake when switching aerobic/anoxic conditions in a long uptake phase.

Now, if aPAOs and dPAOs are 2 different bacterial strains, either their PHAs is consumed before the uptake (in any case the consumption rate would be very low), or aPAOs and dPAOs share their energy source (not possible because the polymers are intracellular). We suggest, out of our simple tests, that aPAOs and dPAOs share the energy sources because they are the same bacterial strain, and dPAOs-like and aPAOs-like behaviour represent two possible metabolic paths of the same organisms.

With regards to the dPAOs contribution to the denitrification performances, the heterotrophic rates reported in literature have been compared with the experimental rates measured with Aquafin's sludge. The experimental denitrification rate in endogenous conditions was estimated in 0.27±0.04 mgNO_3/gVSS/h. This value is in literature reported as 0.3 mgNO_3/gVSS/h at 20°C. The experimental DN rate during endogenous anoxic conditions, and in presence of PO4-P, was estimated in 0.40 mgNO_3/gVSS/h. The dPAOs denitrification rate would results, at net of the heterotrophic removal rate, 0.13±0.04 mgNO_3/gVSS/h. According to Hu *et al.* (2002), the contribution is little and, as its maximum, equal to the 20% of the endogenous DN rate. According to these results the contribution of dPAOs to denitrification is higher than reported by Hu *et al.*, but still very modest. With regards to the overall contribution the P uptake, considering the volume where this activity takes place, it could be concluded that dPAOs contribution is relevant and counts for the 37% of the overall P uptake.

(40) Quantifying filamentous bacteria in activated sludge using new image analysis procedure

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Abstract

In this work a new method based upon automated image analysis techniques was elaborated and presented. It simultaneously delivers data about aggregates and filaments in activated sludge, what is a novelty in comparison to the procedures that have been used so far. Moreover, the macroprogramme performing image processing and calculation of morphological parameters is written in the same software, which is used for grabbing of images. At the same time the previously presented procedures required using two different types of software, one for image grabbing and another one for image processing and analysis. Application of this new procedure for the quantification of filamentous bacteria in two full-scale activated sludge systems proved that it was simple, fast and delivered reliable results.

Keywords

Activated sludge; image analysis; filamentous bacteria; quantification

INTRODUCTION

The contribution of filamentous bacteria in activated sludge systems can be quantified by manual counting under a microscope or by the application of the automated image analysis techniques. Basically two different image analysis procedures and their modifications have been published so far. First one was image analysis procedures elaborated by da Motta et al. (2001), while the second one was prepared by Amaral and Ferreira (2005) and then developed by Mesquita et al. (2009). In both procedures vital slides were made and observed under 100x magnification. Then, the images were collected using the appropriate software. Next stage was image processing and analysis and it was performed with the help of different software than for image grabbing. Finally, the values of the indicators of filamentous bacteria (e.g. the total length of filaments per image, number of filaments per image or filamentous bacteria mean length) were achieved.

The aim of this work is to describe a new procedure for quantifying filamentous bacteria and basic morphological parameters of aggregates in activated sludge and check its applicability in full-scale wastewater treatment plants (WWTPs).

MATERIALS AND METHODS

Activated sludge was taken from two full-scale WWTPs in Zgierz and in Lodz. Both WWTPs treat municipal wastewater using activated sludge systems. Samples were taken once per month from the anaerobic and aerobic zone of the activated sludge chamber from each of two WWTPs.

The procedure consisted of three stages: (1) Neisser staining, (2) grabbing of microscopic images, (3) digital image processing and analysis. Three independent fixed smears were prepared from each activated sludge sample and stained in accordance with Neisser method (Eikelboom and van Buijsen, 1991). They were observed in bright field using a 10x objective (Nikon Eclipse Ni microscope). Then, at least 45 images were snapped and saved from each activated sludge sample with the use of NIS ELEMENTS AR software (Nikon, Japan). All of them were processed and analysed with the use of the macroprogramme written and operating in NIS ELEMENTS AR. The procedure comprised the following stages: (1) segmentation of the blue plane of the image and selection of all objects, (2) removal of debris, (3) transformation of the greyscale image into the binary image and calculation of the area of aggregates and filaments, (4) application of morphological filters to obtain the binary image of aggregates (without filaments) and calculation of the area of aggregates, (5) obtaining of the binary image of filaments by the subtraction of the binary image of aggregates from the binary image containing both aggregates and filaments, (6) skeletonisation of the binary image of filaments and calculation of the length of filamentous bacteria.

RESULTS AND DISCUSSION

In order to apply the procedure for quantification of filamentous bacteria two problems had to be solved. Firstly, it was estimation of the number of images to be grabbed for statistically reliable data. The collection of 45 images ensured reliability of the image analysis. Secondly, it was proved that both Neisser positive as well as Neisser negative, were detected by this procedure. It was made by the comparison of the same field of view snapped in phase-contrast and bright field. Then, three indicators to quantify filamentous bacteria, i.e. the total filamentous length per image (TL/image), the total filamentous bacteria length per volume (TL/vol) and the ratio of filaments to aggregates area (Fil/Agg) were calculated. Comparison of the values obtained by the newly elaborated procedure with literature data showed that they were in the same order of magnitude as the values obtained using the previous procedures (da Motta et al., 2001; Amaral and Ferreira, 2005). All selected descriptors of filaments proved that more filamentous bacteria were present in the WWTP Lodz than in the WWTP Zgierz. As an example the values of TL/image are presented in Fig. 1.

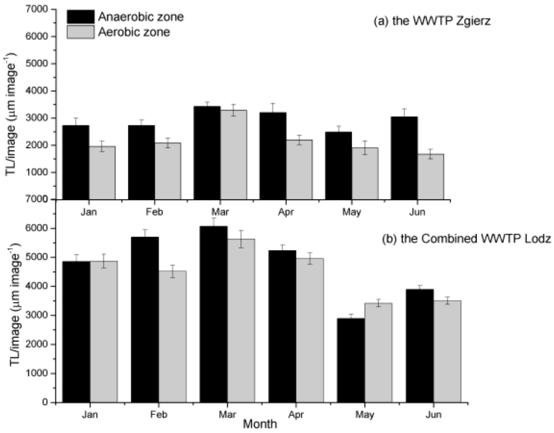

Figure 1. Variations of TL/image ± ⍰/2 in both full-scale WWTP tested.

To sum up, the elaborated procedure enables fast and reliable estimation of the quantity of filamentous bacteria in activated sludge. Its main advantage, in comparison to the previously elaborated procedures, is that both aggregates and filaments are well-visible in the individual image.

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(41) Anaerobic Digestion Modelling: Innovative Characterization Tool And Extension To Micropollutant Fate

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Abstract

Advanced dynamic anaerobic digestion models, such as ADM1, requires both detailed organic matter characterisation and intimate knowledge of the involved metabolic pathways. In the current study, a methodology for municipal sludge characterization previously developed is used to describe two key parameters: biodegradability and bioaccessibility of organic matter. The methodology is based on coupling sequential chemical extractions with 3D fluorescence spectroscopy. Experimental data, obtained from two different laboratory scale reactors, were used to validate the model. The proposed approach showed a strong application potential for reactor design and advanced control of anaerobic digestion processes. In order to complete the modified model, the organic micropollutants fate modeling is considered, since their degradation is strongly linked with the organic matter biodegradation, and addition of micropollutants kinetics terms in the overall model is proposed.

Keywords

Modelling; ADM1, organic matter characterization, bioaccessibility, organic micropollutants

INTRODUCTION

In the current context, where anaerobic digestion has become a key process for organic matter treatment and energetic valorization, precise control and prediction of process performance is a must-be. Concomitantly to the organic matter degradation and valorization, some Organic MicroPollutants (OMPs) like Polycyclic Aromatic Hydrocarbons (PAHs) have been shown to be removed during anaerobic digestion (Trably et al., 2003; Barret et al. 2012). The fate of OMPs from wastewater has become an important environmental issue due to their toxicity in the aquatic environment and their effect to the human health (i.e. endocrine disrupting effects). During the biological wastewater treatment (water line), mass balances have shown that the main pathway of degradation is the sorption of OMPs on sludge (Barret *et al*., 2012). As a consequence, anaerobic digestion of sludge has to deal with the OMPs degradation, above all from a sanitation and regulations point of view (sludge spreading for agriculture). In order to predict both organic matter and OMPs degradation, advanced mathematical models have to be implemented. Ten years ago, the International Water Association (IWA) specialist group on anaerobic digestion developed the Anaerobic Digestion Model N°1 (ADM1) (Batstone *et al.,* 2002). For a particulate and complex substrate such as municipal sludge, hydrolysis of macromolecules has been identified as the limiting step (Yasui *et al*., 2006; Mottet *et al*., 2013). In terms of organic matter characterisation, two concepts are of the most relevance: bioaccessibility and biodegradability. Both were traditionally obtained from time consuming and tedious laboratory batch tests used to determine the biochemical methane potential (BMP). An innovative methodology based on the three dimensional excitation emission matrix (3D-EEM) fluorescence spectroscopy (complexity aspect) combined with chemical sequential extractions (bioaccessibility aspect) has been developed (Jimenez *et al*., submitted). Both parameters was assessed in 5 days instead of the 30 days or more required for BMP. The results obtained from testing 52 municipal sludge samples (primary, secondary, digested and thermally treated) showed a successful correlation with sludge biodegradability and bioaccessibility. One part of this study focuses on evaluating this methodology by using the parameters obtained as input variables of a modified ADM1 model (Mottet *et al*., 2013) taking into account the bioaccessibility aspect. A second part of the paper will focus on the modeling of the OMPs fate during anaerobic digestion of sewage sludge, using the ADM1 modified model and taking into account of the partition of the OMPs into the various organic matter compartments issued from the sequential extractions.

MATERIAL AND METHODS

Organic matter characterization

Based on the floc definition, the applied sequential extraction (SE) correlates bioavailability of sludge organic matter to its chemical accessibility. The obtained fractions were Dissolved Organic Matter (DOM) obtained by centrifugation and filtration at 0.45µm, soluble Exo-Polymeric Substances (S-EPS), readily bound EPS (RE-EPS) and Humic Substances Like (HSL) obtained by chemical extractions using salt and/or soda of increasing molarity. The non extracted (NE) fraction is the non extractible fraction.Extracts were then measured by fluorescence spectroscopyas explained by (Jimenez *et al.*, submitted). Combining SE with the 3D liquid phase fluorescence (LPF) methodologies was named the 3D-SE-LPF method.

Modelling

Concerning the organic matter degradation, the modified ADM1 model from Mottet *et al.* (2013) has been chosen because (i) the limiting step is the hydrolysis (Contois equation) and (ii) two complex substrates with different hydrolysis rates are considered as Yasui *et al.* (2008) on the two-shaped curve obtained for methane production rate for sludge. The 3D-SE-LPF methodology is used in order to calculate the non biodegradable X_I, readily biodegradable X_{RC} and slowly biodegradable X_{SC} fractions through the Partial Least Square model developed by (Jimenez *et al.*, submitted) using a linear combination of COD fractionation and fluorescence intensity data. OMPs degradation modeling is based on the work made by Delgadillo *et al.* (2011) and applied to the Mottet *et al.* (2013) model.

RESULTS: VALIDATION OF THE METHODOLOGY FOR MODIFIED ADM1 IMPLEMENTATION

Using the modified model of Mottet *et al.* (2013), calibration and validation of two lab scale mesophilic continuous reactors (4 liters, hydraulic retention time of 18 days, organic load of 0.13 $gCOD.gVS_{reactor}^{-1}.d^{-1}$) were performed with few parameters change (growth rate kinetic of hydrolytic biomass). One reactor (P1) was fed with a secondary sludge and the second reactor (P2) with the same sludge but deprived of some extracted fractions (DOM, S-EPS and RE-EPS).

Concerning the methane production, PLS predicted variables used for ADM1 implementation led to a satisfying fit of experimental methane production as shown by figure 1. Changes of organic loading and organic matter characteristics were well managed by the model. Indeed, depriving the most accessible fractions of the sludge led to depriving the most readily biodegradable fractions as shown by the zoom of figure 1, as explained by Yasui *et al.* (2006). This means that the chemical accessibility fractionation defined in this study is well correlated to bioaccessibility. From the results obtained in this study, fluorescence spectroscopy will lead to main achievements for better knowledge of organic matter.

PERSPECTIVES: ORGANIC MICROPOLLUTANT MODELLING IN ADM1

Some studies related the strong correlations between OMPs degradation and organic matter degradation in anaerobic digestion (Trably *et al.*, 2003, Barret *et al.*, 2012). Moreover, Delgadillo-Mirquez (2011) has demonstrated that the OMPs biodegradation are mainly related with the upper biological pathway of anaerobic digestion (hydrolysis, acidogenesis and acetogenesis). As a consequence, the bioavailability and bioaccessibility concept of organic matter (hydrolysis considered as the limiting step) could be used for OMPs fate characterization. Consequently, the SE protocol has been applied for OMPs partition assessment into the organic matter compartments in order to estimate their bioavailability. Delgadillo *et al.* (2011) showed that combining bioavailability and cometabolism concepts on a dynamic simplified model allowed the prediction of the OMPs fate in anaerobic digestion.

Besides, Barret *et al.* (2012) and Delgadillo (2011) confirmed that the bioavailable fraction is contained in the aqueous phase (free OMPs and sorbed to colloidal matter) and that the bioaccessibility depends on the pollutants sorbed to particles. However, as shown by simulation results from Delgadillo (2011), using a first order model for hydrolysis does not fit well with experimental data. As a result, OMPs degradation modeling is impacted. From these observations, modifications and additions in the Mottet *et al.* (2013) model could be made. A schematic overview of the model is presented in the figure A.1 of Annex. Results from generated lab data will be presented at the conference in order to calibrate and validate the new model.

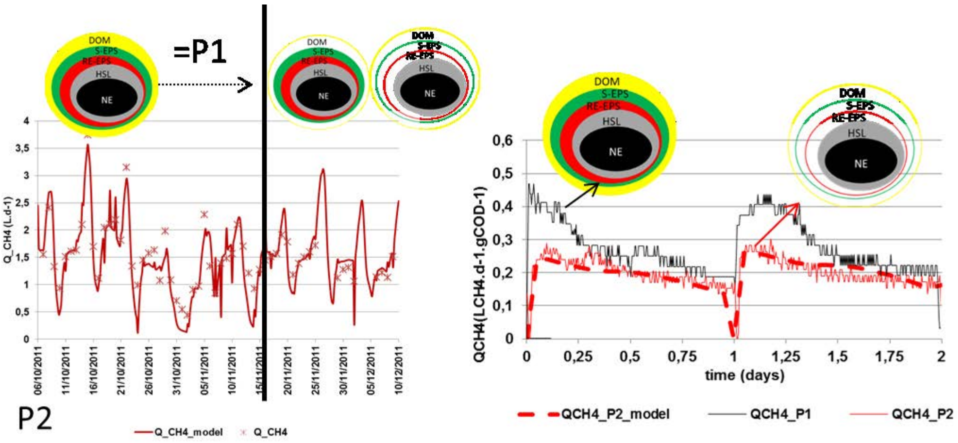

Figure 1. Results obtained on methane production: experimental data versus model

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ANNEX

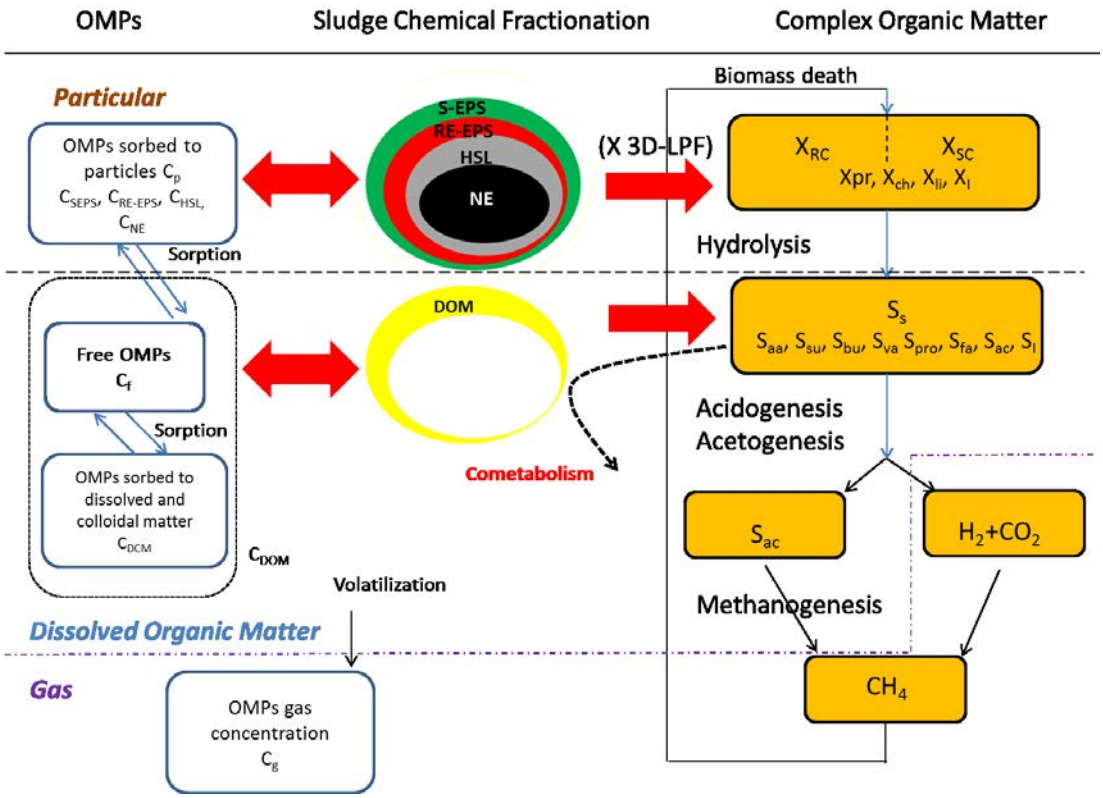

Figure A.1. Schematic overview of the modified ADM1 model for OMPs fate modeling in regards with the sludge chemical fractionation

(42) Optimisation wastewater coagulation studies using CFD

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Abstract

In this study, hydraulic behaviour of one flat blade turbine (FBT) and two pitched blade turbine (PBT) with different inclined angle are studied, these turbine could equipped in jar test unit to enhance flocculation process. This workpresent general procedure of implement CFD for mixing effect research, introduce the development of models for flocculation simulation and demonstrates the advantageof use CFD in flocculation optimization.

Keywords

Flocculation; CFD; jar test; FBT; PBT

Introduction

Coagulation process is becoming more popular in wastewater treatment. For example, 70% of all wastewater is treated in wastewater treatment plants (WWTP) with coagulation processes. Non-optimised dosing of coagulants has negative impacts on the environment not only due to poor treatment efficiencies, but also due to production of unnecessary chemical sludge, which can be costly as well as ecologically negative. Thus it is important to define the optimal dosages and operational conditions for the best and ecological performance.

The “Jar test” is the most common method used in laboratory scale coagulation studies, by researchers and treatment plant operators.Both the rapid mixing where the coagulants undergo hydrolysis and other chemical reactions, as well as the slow mixing stage where the particleagglomeration takes place,are vital stagesin process optimization where hydraulics play a critical role. The computational fluid dynamics (CFD) is the mostsuitable method to explore hydraulic mechanism of flocculation.Bridgeman (2010) used CFD simulate mixing in lab scale cylinder and square vessels for jar tests, while Driss (2010) reported that besides the configuration of vessel, the geometry of paddle is also essential and influent performance of flocculation process.This study takes the above research further in optimisinga lab scale flocculation device using CFD approach including the velocity gradient of Flat blade turbines (FBT) and Pitched blade turbines (PBT) with different inclined angles.

Materials and Methods

Bridgeman (2012) studied mixing effect of a lab-scale sewage sludge digester, where he found thatmultiple reference frames (MRF)could balance computing time and accuracy. MRF divide the whole zone into two sub-zone, moving zone and static zone. Wu (2012) evaluated performance of six turbulence models for mechanical mixing. He concluded that the Realisable k-ε model could predict mixing effect more accurate than other models.In this study, MRF and Realisable k-ε model is chosen.Inpresent work, a jar test unit produced by Kemira was used. It had paddlewith length 56 mm, width 2 mm and height 30 mm, which was located 45mm above bottom of beaker and the shaft had a diameter 4 mm and length 165mm. The beakers were 175mm tall and diameter 90 mm. In further discussions, we use PBT with inclined angle 45°as PBT45 and PBT with inclined angle 60°as PBT60.


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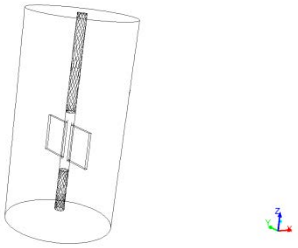

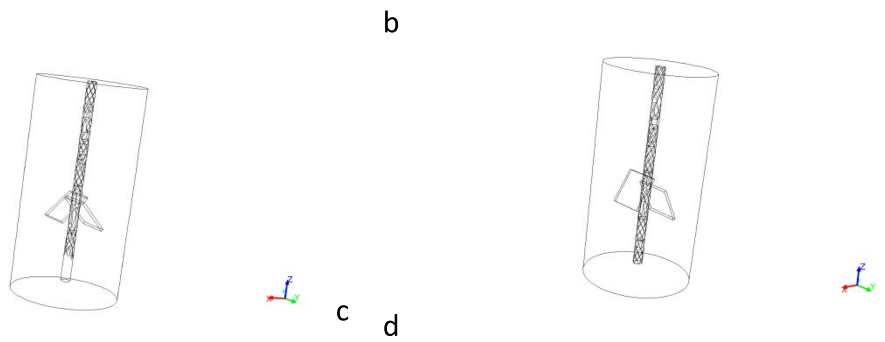

Figure 1.Schematic of : (a) Jar- test unit (b) FBT, (c) PBT 45 and(d) PBT 60

Governing equations

Fluids and particles are governed by continuity equation and Navier-Stokes equation.

Continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho \cdot u) = 0$$

Where ρ is density, u is velocity and t is time.

Navier-Stokes equation:

$$\rho \frac{\partial u}{\partial t} + \rho \nabla \bullet uu = -\nabla P + F + \mu \nabla^2 u$$

Where P is pressure, F is body force and μ is viscosity

Turbulence model

Realisable k-ε modelhave better performance for flow with strong swirling and circulation.

For turbulence kinetic energy k:

$$\frac{\partial(\rho k)}{\partial t} + \frac{\partial(\rho k u_i)}{\partial x_i} = \frac{\partial}{\partial x_j}[(\mu + \frac{\mu_t}{\sigma_k})\frac{\partial k}{\partial x_j}]$$

$$+ P_k + P_b - \rho\varepsilon - Y_M + S_k$$

For dissipationenergy ε:

$$\frac{\partial(\rho\varepsilon)}{\partial t} + \frac{\partial(\rho\varepsilon u_i)}{\partial x_i} = \frac{\partial}{\partial x_j}[(\mu + \frac{\mu_t}{\sigma_\varepsilon})\frac{\partial \varepsilon}{\partial x_j}]$$

$$+ \rho C_1 S\varepsilon - \rho C_2 \frac{\varepsilon^2}{k + \sqrt{\nu\varepsilon}} + C_{1\varepsilon}\frac{\varepsilon}{k}C_{3\varepsilon}P_b + S_\varepsilon$$

Where P_k generation of turbulence kinetic energy due to the mean velocity gradients, P_b is the generation of turbulence kinetic energy due to buoyancy and μ_t is Turbulent Viscosity. Other parameters such as $C_{1\varepsilon}$, σ_ε, σ_k and C_2 are constant.

Result and Conclusions

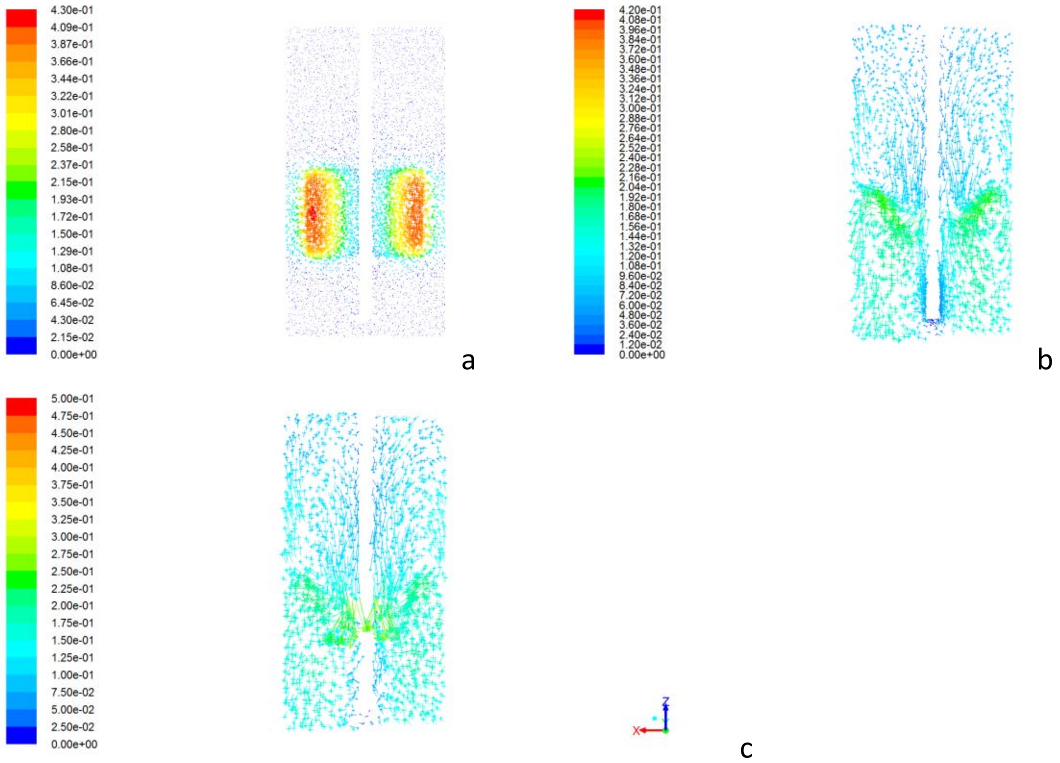

Figure 2.Velocity vectorswith different paddles and angles: (a) FBT, (b) PBT 45and (c) PBT 60

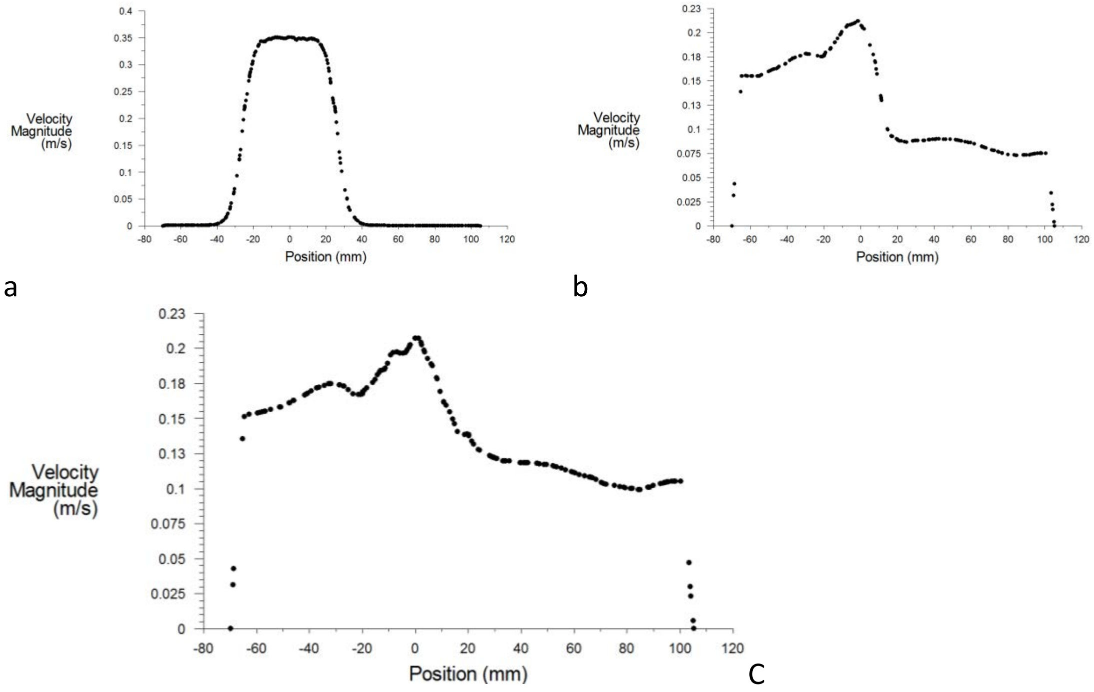

Figure 3.Plot of velocity gradient with different paddles and angles: (a) FBT, (b) PBT 45, (c) PBT 60

Fig. 2 shows the velocity vectors of different paddles. In fig. 3,position refers to the point where the velocity gradient information was collected, which werelocatedmidway of shaft and beaker wall, along longitudinal direction of the beaker.Assume liquid inside beaker is water and mixing speed of paddle is 150rpm.

According to fig. 2, thehighest velocities are limited to the paddle zone. Fig. 3a shows that velocity is around 0.35m/s within the paddle zone, while it decrease to near zero in other zones, indicating a poor mixing.Fig. 2b shows an enhancement in mixing by PBT45, where larger vectors indicating higher velocitiesalso outside paddle zone. The direction of velocity vector indicatesan increase movement of liquid. Fig. 3b shows improved velocity distribution compared with FBT, where the velocities vary 0.15-0.2 m/s from the bottom of beaker to paddle zone, while 0.075m/s above paddle zone. Fig. 2c and fig. 3c follow tendency similar to PBT45, but superior performance.

Our conclusion is that CFD gives a unique insight to the hydraulics in jar tests as well as suggestions for improvements, which should be considered in construction of mixing units, since it is necessary to secure even and immediatemixing of the coagulants with the whole water mass to optimally utilize the hydrolysis spices produces within fractions of seconds in coagulation processes.

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(43) On-Line Control of an Industrial SBR Treating Wastewater with Variable Load and Composition.

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Abstract

On-line control of the biological treatment process is an innovative tool to cope with variable COD and nutrient concentrations in industrial wastewater. In the present paper we propose a dynamic control strategy based on the redox potential profile (ORP) and the oxygen uptake rate (OUR) to determine the duration of the anoxic feeding phases and the subsequent aerobic phases in a nutrient-removing sequencing batch reactor (SBR). As a result, the sludge loading rate (F/M ratio) and the SBR cycle length are adapted to the activity of the activated sludge and the actual characteristics of the wastewater, without affecting the final effluent quality.

Keywords
Real-time control; nitrate knee; tank truck cleaning

INTRODUCTION

Quite a number of industrial wastewaters are characterized by a high degree of variability in composition, load and degradability (Eckenfelder *et al.* 2009). A typical example is wastewater originating from tank truck cleaning (TTC) activities. The wide range of transported cargo, ranging from food products to hazardous chemicals, results in wastewater with a highly variable composition (Dries *et al*. 2013). Since treatment plants have a fixed volume, large safety factors are applied in the design phase to guarantee an effluent quality within the discharge limits. As a result, the water treatment process in many facilities is often not very efficient. By introducing on-line control schemes, the wastewater treatment process may adapt itself dynamically to the varying influent conditions (Olsson *et al*. 2005). Such an approach offers great potential to save energy and time.

In the present study, we designed and applied a dynamic control strategy based on signals from 2 common low-cost and reliable sensors, i.e. dissolved oxygen (DO) and oxidation reduction potential (ORP).

MATERIALS AND METHODS

A lab-scale SBR (total volume = 20 L, volume after discharge = 12 L) treating real TTC wastewater was set-up to validate the control strategy. The SBR was inoculated with the nutrient-removing activated sludge from a full-scale industrial wastewater treatment plant in the harbour of Antwerp (Belgium).

The reactor was equipped with pH, ORP and DO sensors from Hach-Lange, connected to a SC1000 transmitter. The SBR process operation was controlled by a Siemens PLC connected to I/O modules from WAGO Kontakttechnik. The operator interface, including visualisation of sensor signals and the process control settings, was programmed using LabView software (National Instruments). The SBR was operated in a step-feed mode consisting of a (variable) number of consecutive anoxic feeding and aerobic reaction phases.

RESULTS AND DISCUSSION

Wastewater characteristics

Table 1 shows the variation in COD and ammonium concentration in the influent TTC wastewater fed to the SBR, during an experimental period of about 100 days.

Table 1. Variable composition of the TTC wastewater fed to the SBR.

Parameter	Min.	Max.	Avg. ± SD	% CV
COD (mg/L)	1024	3000	2078 ± 409	20
NH_4-N (mg/L)	57	194	115 ± 30	26
COD/N (-)	9	33	19 ± 5	28

Control principles

The principle of the control strategy is illustrated in Figures 1 and 2 for a typical SBR cycle. The duration control of the anoxic feeding phases was based on the on-line detection of the "nitrate-knee" in the ORP profile (Plisson-Saune *et al*. 1996, Olsson *et al*. 2005, Marsili-Libelli *et al*.2008). A sharp decrease on the ORP indicates the complete removal of nitrate (Figure 1).

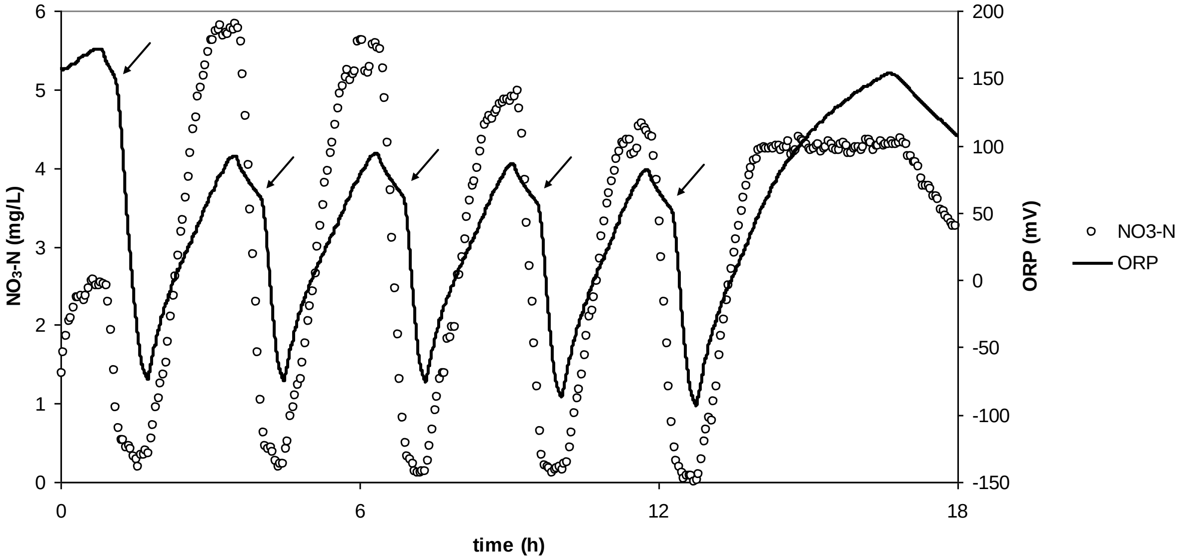

Figure 1. Online ORP profile and corresponding NO_3 concentrations for a typical SBR cycle treating TTC wastewater; the arrows in the ORP graph indicate the "nitrate-knee".

The duration of the aerobic phases was based on the absolute value of the oxygen uptake rate (OUR), which was calculated online in the aeration tank. A "low" OUR value corresponds to complete nitrification and COD removal (Figure 2; Puig *et al*. 2006).

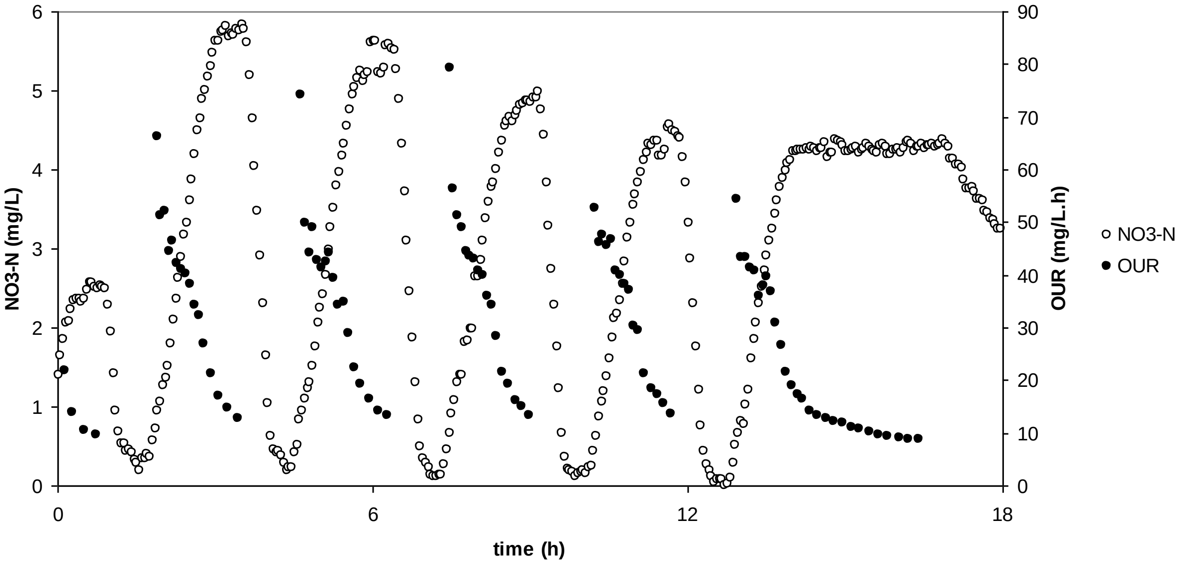

Figure 2. Online OUR profile and corresponding NO_3 concentrations for a typical SBR cycle treating TTC wastewater.

Impact of the control strategy

The control strategy described above was implemented in a lab-scale SBR treating real TTC wastewater (composition as reported in Table 1). Table 2 shows the average COD and NH_4-N removal efficiencies during an experimental period of about 100 days. The average sludge loading rate (F/M ratio) and cycle length are also shown.

Table 2. Characteristics of the dynamically operated SBR process treating TTC wastewater.

Parameter	**Min.**	**Max.**	**Avg. ± SD**	**% CV**
COD removal (%)	85	97	92 ± 3	3
NH_4- N removal (%)	91	98	95 ± 2	2
F/M (g COD/g MLSS.d)	0.05	0.19	0.12 ± 0.03	26
Cycle length (d)	0.8	1.4	1.1 ± 0.2	14

The result of the control strategy is a SBR cycle with variable length and sludge loading rate, depending on the characteristics of the wastewater (such as nitrogen content) and the activity of the sludge (as indicated by the OUR). Importantly, the implementation of the real-time control strategy had no adverse impact on the efficiency of the biological treatment of TTC wastewater (Table 2).

CONCLUSION

Although reliable on-line nutrient sensors are available on the market today, they are very expensive and require intensive servicing. Therefore, on-line nitrogen monitoring is not a realistic option for most small enterprises. The results of the present study indicate that on-line control based on common and cheap sensors is a robust way to implement dynamic processes in industrial activated sludge plants.

ACKNOWLEDGEMENTS

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(44) Adsorption of Boron from Aqueous Solution by Using Vermiculite Clay in the Presence of HDTMA

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Abstract

In this study, boron was removed from water by adsorption using vermiculite as the adsorbent and hexadecyltrimethylammonium bromide (HDTMA) as the adsorption agent. Boron solutions were prepared synthetically from H_3BO_3. At the first part of the experiments, HDTMA sorption on vermiculite clay was investigated in batch system. HDTMA solution concentration was changed from 5 to 100 mmol/L. Langmuir and Freundlich isotherm models were analyzed sorption of HDTMA on vermiculite. The maximum HDTMA sorption percentage on vermiculite surface was 99% and Freundlich isotherm model was fitted well with the experimental data. Batch studies were performed to investigate the effects of various experimental parameters on boron removal such as, HDTMA concentration, contact time, pH, initial boron concentration and inert electrolyte. It was found that 50 mmol/L HDTMA concentration was enough for boron adsorption. Contact time experiments were run between 2-24 h. 15 h end-over-end shaking was enough to reach the adsorption equilibrium. pH experiments were run between 2-12 and it was observed that maximum boron adsorption was occurred at pH 8.5-9. To obtain the adsorption isotherms, initial boron solution concentration was changed between 50-8000 ppm. Langmuir and Freundlich isotherm models were used to model the experimental data. At last, 0.5 and 1M NaCl were used as inert electrolytes. Adding the inert electrolyte into boron solutions did not show any significant change on boron adsorption.

Keywords

Boron, adsorpsiton, HDTMA, vermiculite.

INTRODUCTION

Increased industrialization and human population have led to a progressive degeneration of the existing environment. Pollutants in the physical and biological environment are subject to redistribution, deterioration and transformation [1].Boron pollution in water is a serious problem and can occur due to both natural reasons and human activity.

There are several physicochemical treatment processes typically used to remove boron from water and wastewater. The main process that have been studied are; precipitation-coagulation, adsorption on oxides, adsorption on activated carbon or cellulose [2], ionexchange with basic exchangers [3], solvent extraction after complexation [4], and use of boron selective resins with diols as boron complexing agents [5-7].

Vermiculite has high exchange capacity with 2:1 cyristalline structure, in each cell layer structure, the middle layer is an Al-O(OH) octahedral layer, the upper and lower layers being a silicon-oxygen tetrahedron layer [8].

In this study, boron was removed from water by adsorption using vermiculite as the adsorbent and hexadecyltrimethylammonium bromide (HDTMA) as the adsorption agent. Batch studies were performed to investigate the effects of various experimental parameters on boron removal such as pH, initial boron concentration, contact time, inert electrolyte. Equilibrium isotherms of batch system were also analyzed by Langmuir and Freundlich isotherm models.

MATERIAL and METHODS

Characterization of clay

The cation exchange capacity (CEC) of vermiculite was determined by sodium acetate method. To prepare homoionic form of vermiculite, it was mixed with 50 mL 10% HCl during 30 min and washed with distilled water. Then, hydrogenated clay was shaken with 50 mL 1M NaCl solution. After 30 min end-over-end shaking, the clay suspension was filtered and fresh 50 mL 1M NaCl solution was added on the solid phase. This procedure was repeated two times, followed by washing with distilled water. The solid phase was dried at room temperature.

Boron adsorption

Hexadecyltrimethylammonium bromide (HDTMA-Br) (purity 99%) supplied by Fluka was used as the adsorption agent for boron removal. Vemiculite was supplied from Agrekal Agricultural Company and particle size was 1mm.

At first part of the experiments, HDTMA sorption on vermiculite clay was investigated in batch system. HDTMA solution concentration was changed from 5 to100 mmol/L.

Batch studies were performed to investigate the effects of various experimental parameters on boron removal. From 5 to100 mmol/L HDTMA concentrations were used to find the optimum HDTMA concentration for boron removal. Contact time experiments were run between 2-24 h. One of the most important parameter to express the boron adsorption behaviour was pH. pH experiments were run between 2-12. To obtain the adsorption isotherms, initial boron solution concentration was changed between 50-8000 ppm. At last, 0.5 and 1M NaCl were used as inert electrolytes. Boron concentrations were measured by spectrophotometer (Shimadzu UV Spektrophotometer UV-1800) according to curcumine method.

RESULTS and DISCUSSION

HDTMA sorption

Cation exchange capacity of vermiculite clay was found 49.43 meq/100 g according to sodium acetate method.

Initial HDTMA solution concentration was changed to find the HDTMA sorption capacity of vermiculite clay. Sorption isotherm of HDTMA was given in Fig. 1. According to Table 1 Freundlich isotherm model was well described HDTMA sorption onto vermiculite clay.

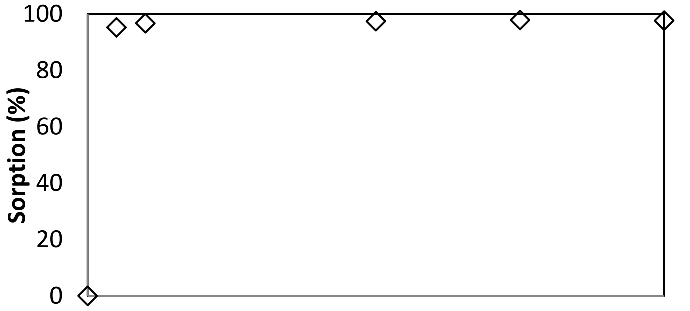

Figure 1. Sorption of HDTMA on vermiculite

Table 1. Isotherm model parameters for HDTMA sorption onto vermiculite clay

Isotherm model	Linear equation	Isotherm constants
Langmuir isotherm	y= 2.487x+1.097	Q_m = 0.402 b = 2.267 R^2 = 0.95
Freundlich isotherm	y= 0.885x-1.153	K_F = 0.858 n = 1.129 R^2 = 0.99

Boron adsorption

To find the HDTMA concentration used in boron adsorption experiments, initial HDTMA concentrations were changed and boron adsorption percentages were calculated. Results were shown in Fig. 2.

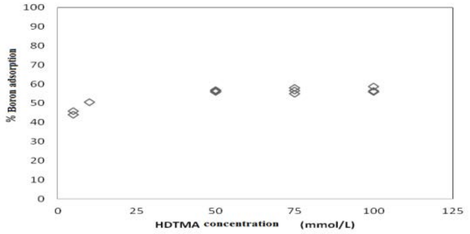

Figure 2. Adsorption of HDTMA on vermiculite

50 mmol/L HDTMA concentration was enough for boron adsorption. After that concentration value, boron adsorption reached a plateau.

Contact time experiments were run between 2-24 hours and as seen from Fig. 3, after 15 hours end-over-end shaking, boron adsorption did not changed.

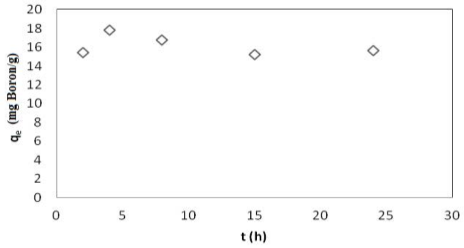

Figure 3. Contact time of boron adsorption in the presence of HDTMA onto vermiculite clay

pH value was changed between 2-12. It was found that boron adsorption reached a maximum in basic medium, Fig.4. Boric acid converted to its anionic form (borate ion, $B(OH)_4^-$) in basic medium, and HDTMA adsorbed borate ion with electrostatic interactions.

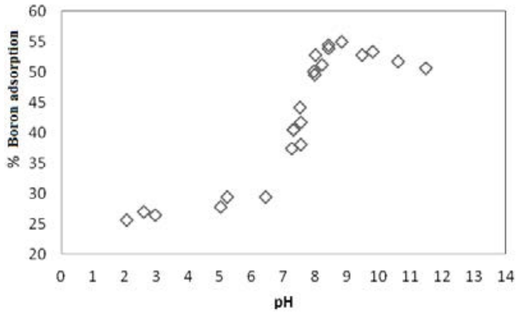

Figure 4. pH effect of boron adsorption in the presence of HDTMA onto vermiculite clay

Boron adsorption isotherm was obtained by changing the initial boron concentration and it was found that increasing initial boron concentration resulted with an increase of boron adsorption until it reached to a plateau, Fig. 5. Langmuir and Freundlich isotherm models were also analyzed in Table 2.

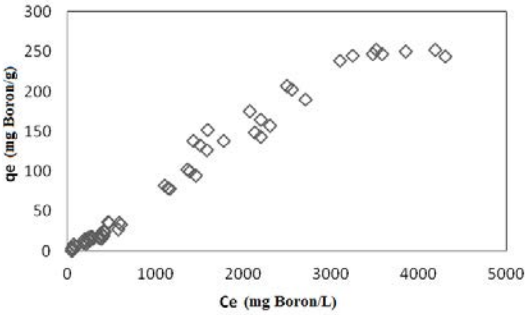

Figure 5. pH effect of boron adsorption in the presence of HDTMA onto vermiculite clay

Table 2. Isotherm model parameters for boron adsorption onto vermiculite clay

Isotherm model	Linear equation	Isotherm constants
Langmuir isotherm	y=14.58x+0.0046	Q_m = 217.40 b = 0.315 R^2 = 0.94
Freundlich isotherm	y=1.065x-1.365	K_F = 0.043 n = 0.94 R^2 = 0.98

At last, inert electrolyte effect on boron adsorption was investigated and results were shown in Fig.6.

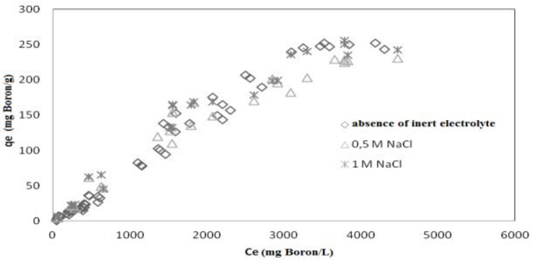

Figure 6. Inert electrolyte effect on boron adsorption

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(45) Removal of Boron by Using Perlite Clay in the Presence of Gallic Acid

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Abstract

Removal of boron was performed by using perlite clay. Gallic acid is used as the adsorption agent since raw perlite does not have boron adsorption capacity. Boron solutions were prepared synthetically from boric acid (H_3BO_3). Perlite cation exchange capacity and gallic acid sorption capacity of the perlite were determined. Initial gallic acid solution concentrations were changed between 2.5-100 mmol/L and Langmuir and Freundlich isotherm models were applied to the data. Batch studies were performed to investigate the effects of various experimental parameters on boron removal. GA concentration, contact time, pH, initial boron solution concentration and inert electrolyte effects were investigated. Langmuir and Freundlich isotherm models were applied to experimental data. According to R^2 values, Freundlich isotherm model was well fitted with the isotherm data. 0.5 and 1M NaCl were used as inert electrolytes. Adding the inert electrolyte into boron solutions did not show any significant change on boron adsorption.

Keywords

Boron, adsorpsiton, gallic acid, perlite.

INTRODUCTION

Boron pollution in water is a serious problem and can occur due to both natural reasons and human activity. Boron is also an important micro nutrient for the plants to vegetate but if it exists in high concentrations, it could have toxic effects. Toxic effects of boron should be noted especially for dry regions, thus, increasing attention has been paid to remove the boron from waste waters.

There are several physicochemical treatment processes typically used to remove boron from water and wastewater. The main process that have been studied are; precipitation-coagulation, adsorption on oxides, adsorption on activated carbon or cellulose [1], ion exchange with basic exchangers [2], solvent extraction after complexation [3], and use of boron selective resins with diols as boron complexing agents [4-6].

Perlite is a glassy volcanic rock and expands to about 20 times its original volume upon heating within its softening temperature range of 760 to 1090 °C. Perlite is essentially a metastable amorphous aluminium silicate [7].

In this study, boron adsorption onto perlite clay was investigated in the presence of gallic acid. At first part of the experiments, gallic acid sorption capacity onto perlite clay was studied. All the experiments were run in batch system. At the second part of the experiments, boron adsorption was studied by changing the experimental parameters such as pH, initial boron concentration, contact time, inert electrolyte. Equilibrium isotherms of boron adsorption were also analyzed by Langmuir and Freundlich isotherm models.

MATERIAL and METHODS

Characterization of clay

The cation exchange capacity (CEC) of perlite was determined by the ammonium acetate method. To prepare homoionic form of perlite, it was mixed with 50 mL 10% HCl during 30 min and washed with distilled water. Then, hydrogenated clay was shaken with 50 mL 1M NaCl solution. After 30 min end-over-end shaking, the clay suspension was filtered and fresh 50 mL 1M NaCl solution was added on the solid phase. This procedure was repeated two times, followed by washing with distilled water. The solid phase was dried at room temperature.

Boron adsorption

Gallic acid supplied by Fluka was used as the adsorption agent for boron removal by using perlite. Perlite used in the experiments was supplied from Genper Perlite Company and particle size was 0.5-1.5 mm.

At the first part of the experiments, gallic acid sorption onto perlite clay was investigated in batch system. Gallic acid solution concentration was changed from 2.5 to100 mmol/L.

Batch studies were performed to investigate the effects of various experimental parameters on boron removal. 0.05 g perlite clay was used in the experiments. From 2.5 to 100 mmol/L gallic acid concentrations were used to find the optimum gallic acid concentration for boron removal. Contact time experiments were run between 2-24 h and pH experiments were run between 2 to 12. To obtain the adsorption isotherms, initial boron solution concentration was changed between 50-8000 ppm. At last, 0.5 and 1M NaCl were used as inert electrolytes. Boron concentrations were measured by spectrophotometer (Shimadzu UV Spektrophotometer UV-1800) according to curcumine method.

RESULTS and DISCUSSION

Gallic acid sorption

Cation exchange capacity of perlite clay was found 5.049 meq/100 g according to ammonium acetate method.

As seen from Fig. 1, sorption of gallic acid onto perlite clay was around 80%.

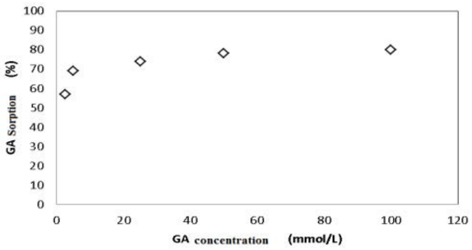

Figure 1. Sorption of gallic acid on perlite

Table 1. Isotherm model parameters for gallic acid sorption onto perlite clay

Isotherm model	**Linear equation**	**Isotherm constants**
Langmuir isotherm	y=11.98x+0.404	Q_m = 0.083 b = 29.66 R^2 = 0.79
Freundlich isotherm	y=0.912x-0.968	K_F = 0.380 n = 1.097 R^2 = 0.95

Boron adsorption

Boron adsorption experiments were run by changing the initial gallic acid concentration to find the optimum gallic acid concentration. Results were shown in Fig. 2.

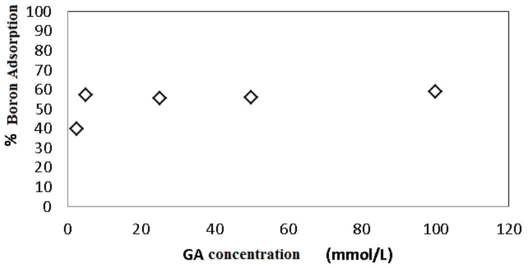

Figure 2. Adsorption of gallic acid onto perlite clay

5 mmol/L gallic acid concentration was found enough for boron adsorption because after that concentration boron adsorption reached a plateau.

Optimum contact time was chosen according to the time that boron adsorption did not change. Therefore, 15 hours end-over-end shaking was found enough for boron adsorption experiments, Fig. 3.

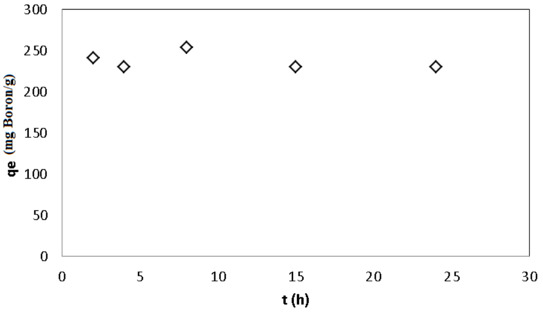

Figure 3. Contact time of boron adsorption in the presence of gallic acid onto perlite clay

pH experiments were run between 2-12, and it was found that there was slight increase in boron adsorption between pH 7-9, Fig.4. Gallic acid adsorbed boron from hydroxide parts, while gallic acid sorption onto perlite clay occurred by electrostatic interactions.

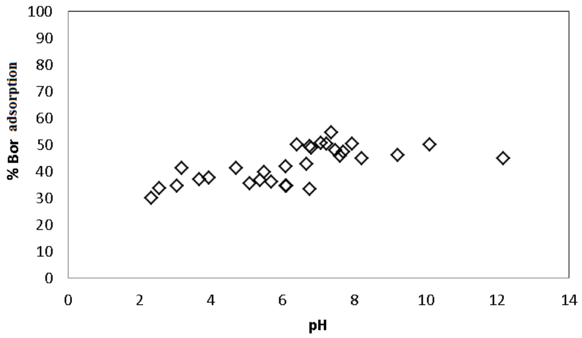

Figure 4. pH effect of boron adsorption in the presence of gallic acid onto perlite clay

Table 2. Isotherm model parameters for boron adsorption onto perlite clay

Isotherm model	Linear equation	Isotherm constants
Langmuir isotherm	y=2.277x+0.0004	Q_m = 2500 b = 0.176 R^2 = 0.83
Freundlich isotherm	y=0.896x-0.109	K_F = 0.896 n = 1.115 R^2 = 0.86

Initial boron concentrations were changed until a plateau was reached. It was found that increasing initial boron concentration was resulted with an increased in boron adsorption, Fig. 5.

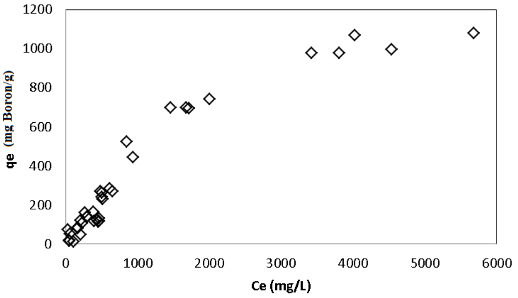

Figure 5. pH effect of boron adsorption in the presence of gallic acid onto perlite clay

At last, inert electrolyte effect on boron adsorption was investigated and results were shown in Fig.6.

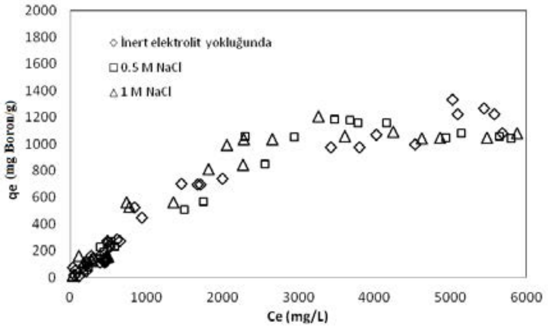

Figure 6. Inert electrolyte effect on boron adsorption

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(46) Combined physicochemical and biological processes for the treatment of an agrochemical industry wastewater

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Abstract

The aim of this work was the treatment of an agrochemical wastewater by coagulation/flocculation and subsequent biological process. The physicochemicalpre-treatment allows ca.53% and 66% of TOC and COD removals,decreasing the organic loading from 6300 and 24500 mg/L to 3100 and 8150 mg/L, respectively. Then, theresultant effluent was treated in a sequencing batch rector (SBR) by mixing with a simulated influent of biological wastewater treatment plant. The contribution of the pre-treated agrochemical wastewater in the feed of the SBR was increased from 2 to 50% of the inlet total organic carbon.The gradual increase of the pre-treated effluent during the biological treatment has allowed the acclimation of the biomass, achieving remarkable TOC removals with the maximum loading of 50% ofthe organic matter from the pre-treated wastewater.

Keywords
Agrochemical wastewater, SBR, coagulation, sludge biotic index, sludge bioindication

INTRODUCTION

The huge amounts of wastewaters generated in agriculture and industry have motivated the study and development of alternative water regeneration and reuse technologies. Soluble pesticides, herbicides and insecticides are of great importance, since their high solubility makes extremely easy their propagation in the environment. Moreover, most of them are resistant to conventional treatments at environmental conditions (Burrows et al., 2002). Thus, there are many works focused on the evaluation of different techniques for the treatment of model pollutants included in the family of pesticides, herbicides and insecticides. In some cases, these techniques have been assessed as pre-treatment before final biological treatments (Pariente et al., 2013). In this work, a real agrochemical wastewater that contains some of these pollutants was studied by coagulation/flocculation process usinga prehydrolized inorganic coagulant based on iron polyferric chloride (PFC)following by a biological treatment, operating as SBR.The PFC coagulant was prepared by partial neutralization of iron chloride under controlled basic conditions (Wang et al., 2008). During this process, the condensation of prehydrolized iron species produces polymeric iron species characterized by the range of hydrolysis and polymeric degree of Fe(III), including monomers ($[Fe(OH)_x]^{(3-x)+}$) and polymers $[Fe_m(OH)_x]_n^{(3m-x)n+}$ (Fan et al. 2002). These coagulants are considered more effective than monomeric iron salts under a variety of water quality conditions, especially at lower temperatures and broader pH range, with less coagulant dosage and metal residuals(Shi et al. 2004).On the other hand, the SBR is a fill-draw biological systemwhich provides a remarkable flexibility for perturbations of the feed composition. The SBR can be easily adapted to variations of pollutant concentrationsby appropriate design of the operation stepswithout modification of the hydraulic retention time of the wastewater during the process (Mace et al., 2002).

EXPERIMENTAL

The coagulant used in this work(polyferric chloride, PFC), was prepared as described elsewhere (Gao et al. 2008). It consists in an initial $FeCl_3$ aqueous solution of 6.7% w/w of the iron source. Following, $Na_2CO_3$was added to set anOH/Fe molar ratio of 2.0 and the solution was stirred until complete homogenization. Afterwards, Na_2HPO_4wasalso added with a Na_2HPO_4/Fe molar ratio of 0.08.Typically, coagulation experiments were carried out in a 4x1L jar-test set-up filled with 500 mL of the as-received wastewater. The dose of PFC coagulant (1 g/L) and wastewater were vigorously mixed for 30 seconds at 150 rpm, followed by settling for 5 min.The SBR is a 2 L glass tank, equipped with a compressed air inlet to provide the oxygen uptake and homogeneous suspension of the biomass.The feeding and drawingloadings ofthe SBR wereperformed with a peristaltic pump. Dissolved oxygen (DO), temperature and pH were continuously monitored along all the experiments.Initially, the SBR was inoculated with activated sludge from a full-scale urban wastewater treatment plant located in Móstoles, Madrid (Spain). The sludge was adapted during a 30-day period to a synthetic wastewater described elsewhere (Carrera et al.,2001) using glucose, saccharose and sodium acetate as the main organic sources. After theadaptation period, the pre-treated agrochemical wastewater wasfed to the SBR with a gradual increase of the organic matter in the inlet total organic carbon of 2, 4, 10, 20 and 50%.The C:N:P ratio was maintained in 100:3:1 during every experiments. The operation of SBR consisted in cycles of 12 h. with an aerobic reaction phase of 10.9 h (including the filling step divided in 5 sub-phases of 5 min each one during the first 10 h.), a settling phase of 0.7 h., a draw phase of 0.2 h. and an idle phase of 0.2 h. The exchange volume in each cycle was 50% of the total volume, being the hydraulic retention time (HRT) 1 day. The purge was calculated to maintain a sludge retention time (SRT) of30 days. The pH was maintained at 7.5 by a buffer solution in the feeding influent.The temperature was set at 25± 2 ºC. The dissolved oxygen (DO) concentration was between 1-2 mg/L during the filling sub-phases and around 7.5 mg/L in the rest of the cycle.Total organic carbon (TOC) before and after the coagulation/flocculationand SBR operations and volatile suspended solids (VSS), ammonia nitrogen, nitrites and nitrates before and after the SBR operation were measured for all the cycles. Biodegradability and toxicity of as-received and pre-treated wastewater by coagulation/flocculation was evaluated by respirometric tests. Microfaunabioindication and sludge indexes (Jimenez et al., 2001; Madoni, 1994) were determined for samples at 5 days and 60 days of cycles with 10% and 50%of TOC in the inlet SBR from the pre-treated wastewater (samples 10%_5d, 10%_60d and 50%_5d, 50%_60d, respectively).

RESULTS AND DISCUSSION

Table 1 shows the main characterization data of the as-received and pre-treated wastewater after physicochemical treatment with the PFC coagulant. Although,respirometrytests evidenced a partial biodegradability of as-received wastewater, the toxicity and the high organic concentrationmakes necessary apre-treatment prior to biological treatment.The physicochemical treatmentachieved a remarkable decrease of the TOC and COD concentrations. Additionally,the biodegradability increased and the toxicity significantly reduced. However, the organic loading was still too high as compared to typical values of influents of biological processes inurban wastewater treatment plants (TOC and COD of ca. 500 and 1300 mg/L).Thus, the pre-treated wastewater was fed to the SBR by mixing with asynthetic urban wastewater in order to achieve those values in the feed of the biological reactor. Proportion of the pre-treated wastewater was progressively increased in order to vary from 2 to 50% of the inlet TOC content.Figure 1 displays TOC and NH_4^+ concentrations in the influent and effluent of the SBR along the operation for the different organic loadings from the pre-treated wastewater. Carbon and nitrogen were consumed during the operation and once reaching steady-state conditions (commonly after 1.5 SRT days), the TOC and NH_4^+ removalswere in the range of 85-97 % and >99%, respectively. Thebiological performance regarding the TOC removal decreased for the highest loading of pre-treated wastewater in the influent of SBR (50%), even after 50-60 days (ca. 2xSRT) of operation.The remaining TOC concentration for those conditions (ca. 75 mg/L) could beassociated to the poorly biodegradable organic fraction of the pre-treated wastewater, although therespirometrytest indicated a low contribution (Table 1). Thus, these results are attributed to the influence of other factors related to the complex composition of the pre-treated wastewater as the proportion in the feeding influent is increased.

Table 1. Characterization ofas-received and pre-treated agrochemical wastewater by PFC.

	Raw wastewater	**Pre-treated wastewater**
COD (mg/L)	24500	8150
TOC (mg/L)	6300	3100
Biodegradability (%)	65	97
Toxicity (%)	36	4

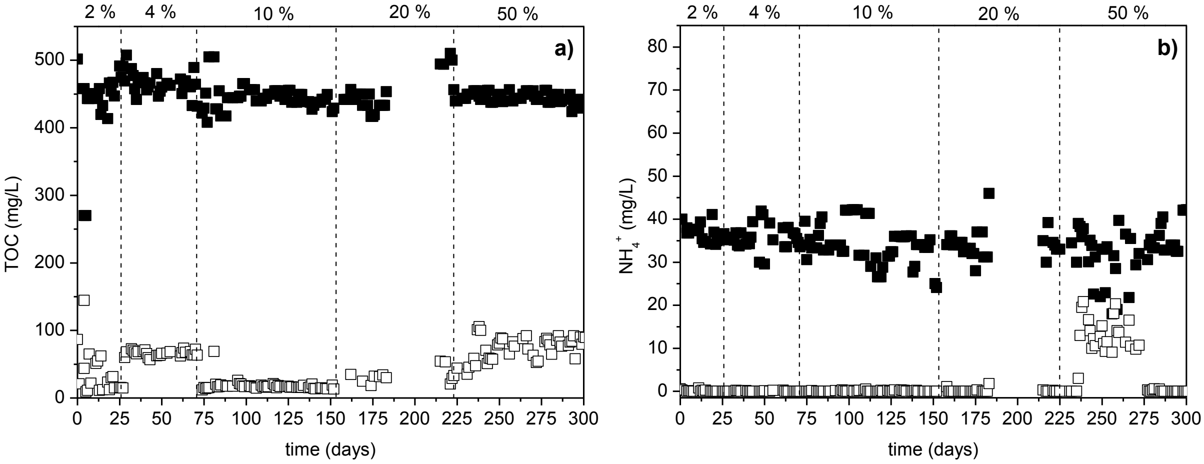

Figure 1.a) TOC and b) NH_4^+ concentrations in the influent and the effluent for the 300 days of the SBR operation (■ Influent; □ Effluent)

On the other hand, the sludge of the SBRwas characterized by the sludge index(SI)and the sludge biotic index(SBI), both of them normally used to evaluate the performance of activated sludge. The SIis based on the evaluation of different macroscopic (turbidity, suspended flocs, odour, among others) and microscopic (shape, cover, filaments in flocs, protozoa abundance) parameters.In contrast, the SBI is based on the evaluation of the biodiversity for different microfaunakeygroups andthe abundance of their morphological species. According to these indexes, the sludge characterization at 5 and 60 days of operation with 10% and 50% of the inlet TOC from the pre-treated wastewater is shown in Table 2.

Table 2. Sludge characterization indexes

Samples	**10%_5d**	**10%_50d**	**50%_5d**	**50%_50d**
Sludgeindex (SI, Jimenez et al., 2001)	46.5[a]	56[b]	39[a]	66[c]
SBI (Madoni, 1994)	3[a]	3[b]	3[a]	2[c]

[a]Low performance but abundance of species; [b]Low performance and higher abundance of species: better biological quality; [c]Good performance

The calculated sludge indexes (SI and SBI) showed a clear improvement of the sludge quality and biological performance at longer operation times for both10% and 50% of the inlet TOC content from the pre-treated wastewater. Thus, the SI and SBI indicated a low performance of the sludge after 5 days, with a decrease of the number and density of biological species as well as a disaggregation of the flocs in the sludge. However, after 50 days (higher than one SRT), the microfaunawas stabilized to better biological quality, achieving values of really good performance of the sludge with a significant abundance and density of species. Thus, the results show the gradual acclimation of the biomass to the increasing carbon source of the pre-treated wastewater. It should be also pointed out that the SBR operational conditions allow achieving similar results of wastewater depuration even during the acclimation period, according to the results shown in Figure 1.

Finally,the biological SBR process (including all the sequencing steps, fill-reaction-settling-discharge) was fitted to the IWA ASM1 model. A reasonably good agreement was obtained between experimental and predicted values by using the default parametersset of typical municipal cases. These results indicate the feasibility of treating the agrochemical wastewater at different organic loadings and after preliminary physicochemical treatment by a biological process operating as SBR.

CONCLUSIONS

A preliminary physicochemical treatmentusing polyferric chloride as coagulant,and following biological process in a SBR,is proposed as a good alternative to treat an agrochemical wastewater. The physicochemical treatment achieved a significant reduction of the organic loading. This is an important issue in order to achieve less concentrated effluents amenable to biological treatments. The SBR was able to operate with feedings of50% of the inlet TOC from the pre-treated wastewater with a remarkable biological performance. The gradual acclimation of the biomass for the increasing organic loading of the pre-treated wastewater evidenced the viability of the biological process in the overall treatment.

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(47) Experimental design for removing phosphorous from water reservoir by phyllosilicates

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Abstract

We executed experimental designs “central composite”-type aiming to define optimal conditions for sorption studies and to compare the retention of total phosphorus in water using phyllosilicates as auxiliaries in the treatment of drinking water. Phyllosilicates talc, pyrophyllite, and kaolinite were studied by means of particle size, pH, ionic strength and mass of phyllosilicate. Mathematical modeling ensured reliability for the analysis of experimental matrixes of each phyllosilicate because the errors of the main effects were <5%. It was possible to predict the capacity retention yield of 83.59% (weight) with pyrophyllite, 84.60% with kaolinite and 71.64% with talc. Kaolinite showed more linear behavior and better defined factors for phosphorus retention. There are interactions among the factors studied that helped us to predict the maximum possible retention of phosphorus, as well as the proper conditions for future sorption studies.

Keywords

Phosphorus removing, water treatment, chemometric design

INTRODUCTION

The excess of phosphorus in water reservoir frequently induces algal blooms, resulting the eutrophication and decreasing the water quality, which increase costs for water treatment. The main sources are fertilizers, domestic sewage, industrial wastewater and atmospheric deposition. Anthropogenic introduction of phosphorous can be exacerbated in urban reservoirs where the domestic sewage and industrial effluents are not properly collected and treated.

Phosphorous treatments reported in literature involve physical (filtration for particulate P, membrane technologies), chemical (precipitation) and biological (assimilation) process, which demand thorough monitoring of the process and considerable operating cost. The employment of cheap materials can be an attractive alternative, which could be after used as source of phosphorus for agricultural purposes. Phyllosilicate is a class of minerals where the crystallographic units are arranged in sheets, with great importance for geology, agriculture and industry. They are essential constituents of a lot of metamorphic, magmatic, sedimentary rocks and soils, being widely used in industry as filler material for ceramics, cosmetics, electronics, paints, deodorants etc. In this study three phyllosilicate (talc, pyrophyllite, and kaolinite) were evaluated, considering properties such as dimensional versatility of the surface area, sorption sites, presence of silanol groups capable of chemical modification and presence of hydroxyl (for metals uptake). The mineral talc is a hydrated magnesium phyllosilicate ($Mg_3(Si_2O_5)_2(OH)_2$ or 3 $MgO.4SiO_2.H_2O$) and pyrophyllite is a hydrous aluminum ($Al_2(Si_4O_{10})(OH)_2$), both from Brazilian mineral industry (around 500.000t/year). The kaolinite is a hydrated aluminum silicate ($Al_2Si_2O_5(OH)_4$) with a production of 2.6 million t/year (about 5 % of global production).

EXPERIMENTAL

An experimental planning central composite-type was performed to comparatively evaluate the performance of the three phyllosilicates retention (sorption) of total phosphorus (as orthophosphate) in water. The matrix was established as shown in Table 1:

Table 1. Experimental parameters evaluated and the established levels of variation.

	Level		
Parameter	(-1)	(0)	(+1)
Particle Size (μm)	44 – 63	63 – 74	74 – 105
pH	3	7	10
Mass (g)	0.25	0.50	1,00
Ionic strength (mgL^{-1} NaCl)	0.75	0.075	0

Experimental Planning

Central composite experimental design type 3 $^{(k-p)}$ was used. The levels were defined by square points or hub and star points or axial points, and two replicates at the center point were established. The processing algorithm applied a function for the rotational model of second order (quadratic), ie, it is constant on the circles around the origin, totaling by experimental design (for study of each phyllosilicate) 4 factors (independent variables), 28 runs (cases, experiments) 25 unique runs. The experimental designs were validated by model selection and pure residual error.

Materials and methods

Step 1 - Characterization of minerals depending on the origin by x-ray diffraction (Talc - Xilolite S/A – Brumado, BA; Pyrophyllite as agalmatolite - Lamil Lage MinériosS/A - Pará de Minas, MG; Kaolinite - Imerys Rio Capim Caulim S/A - Ipixuna do Pará, PA); Step 2 – granulometric analysis by sieve and discrimination by particle size; Step 3 - Sorption with stirring and rest for sedimentation of a fixed mass of phyllosilicate suspended in water with the total phosphorus concentration set by addition of 7.50 mgL^{-1} as sodium orthophosphate) under the described experimental conditions; Step 4 - Filtering and analysis of phosphorus in the liquid phase.

Phosphorous total analysis

The method was applied for determination of total phosphorus as the Standard Methods for Examination of Water and Wastewater (22nd Ed.), differential spectrophotometric method phosphorus vanado molybdic acid, range 400 at 470 nm. The minor and higher ranges of concentration were, respectively, 0 to 5.00 mgL^{-1},(N = 6, R^2 = 0.998179) and 0 to 15.00 mgL^{-1} (N = 5, R^2 = 0.998003) for total phosphorous, the analytical or calibration curves were obtained from sextuplicates (LD = 0.09 mgL^{-1}, LQ = 0.30 mgL^{-1}), for the curve employed to quantification after sorption-minor range of total phosphorous e concentration.

RESULTS AND DISCUSSION

The selected model used to analyze the central composite experimental design considered quadratic and linear components of principal effects (two ways). It was proceeded the analysis of variance and the simulation of the optimal point by response surface. The good performance of the planning conducted for the three phyllosilicates was evidenced by the better linearity with the smallest error with pyrophyllite (R^2 = 0.9031, Error = 2.8%), talc (R^2 = 0.7281, Error = 0.7%) and kaolinite (R^2 = 0.755, Error = 3.1%). Although the relative errors of the main effects were <5% in all the schedules, data were fitted to the model with respect to variability in the experimental matrix.

Pareto's diagrams obtained from the respective variance analysis tables (Figure 1) showed that pH and ionic strength are significant factors for the application of the three phyllosilicates. The kaolin was less susceptible to the variations of these factors. The particle size was less significant factor, relevant only for talc. In all cases, there are significant interactions between the factors, *i.e.*, there is synergy among factors in the process of competition for sorption sites. The response surfaces made possible to determine the maximum experimental yield in terms of retention capacity and to project the maximum retention with adjustment of the parameters (Figures 2, 3 and 4).

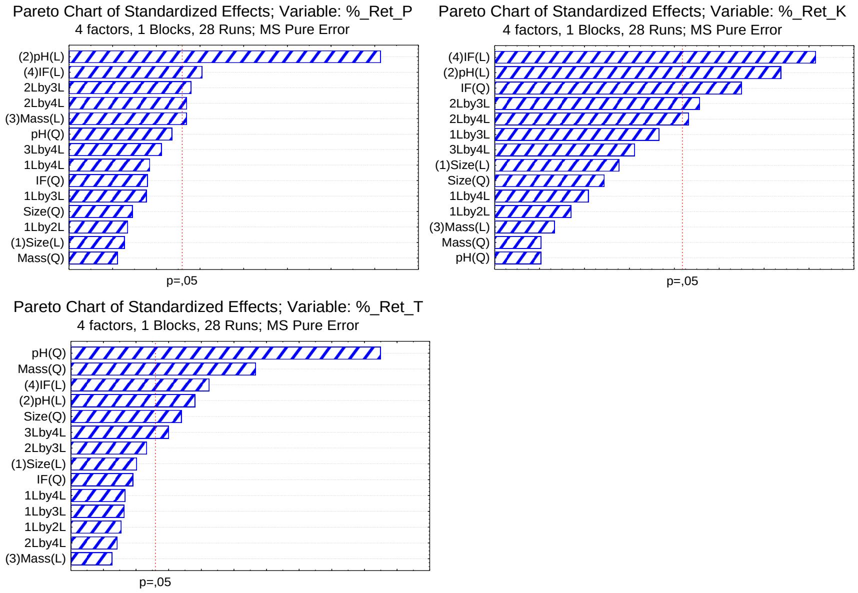

Figure 1. Pareto's diagrams representing the factor that presented significant effects.

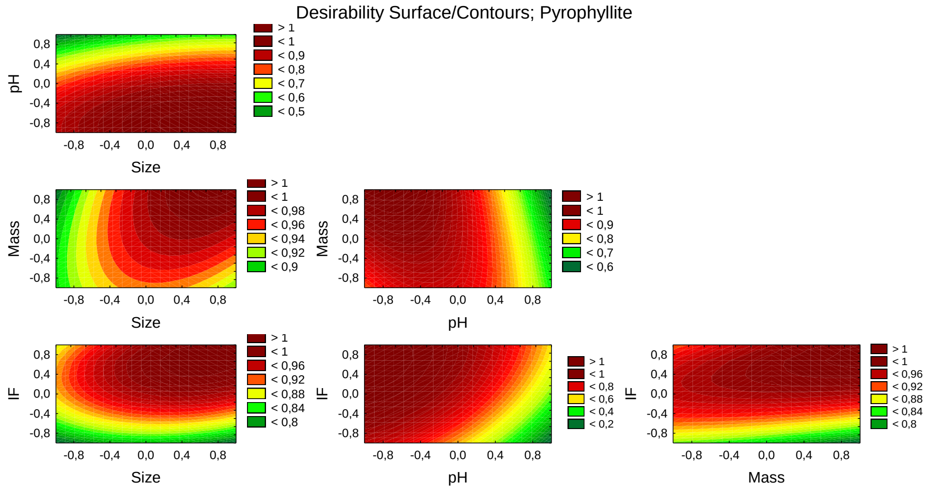

Figure 2. Response surfaces with optimum adjustment to the percentage (% mass) of phosphorus retention by pyrophyllite.

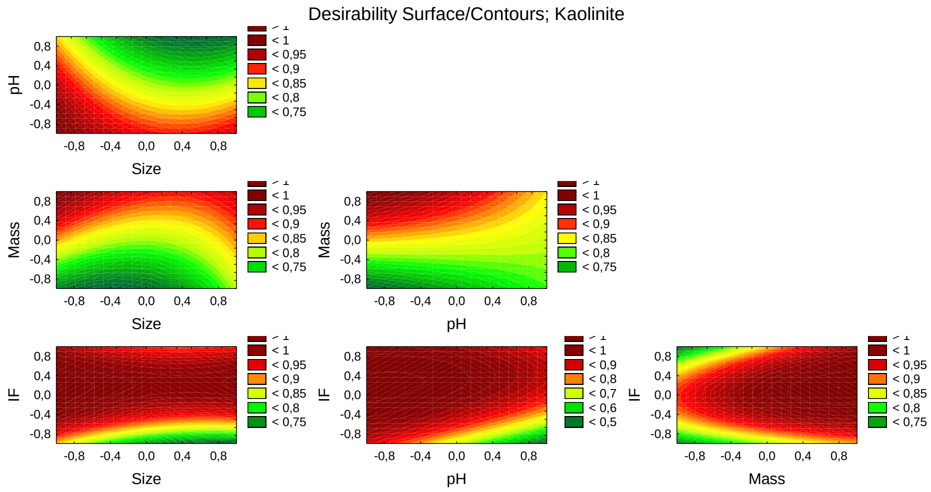

Figure 3. Response surfaces whit optimal point adjustment for the uptake of phosphorous from caulinite (% mass).

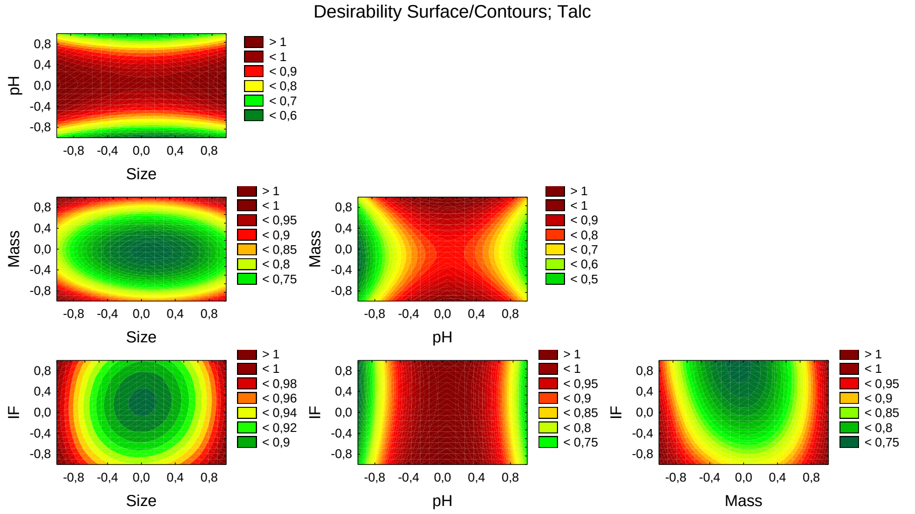

Figure 4. Response surfaces whit optimal point adjustment for the uptake of phosphorous from talc (% mass).

Table 2 provides a comparative analysis of the capabilities of total phosphorus retention of the three phyllosilicates.

Table 2. Comparison of uptake capacities of phylossilicates obtained from experimental design.

	Pyrophyllite	**Kolinite**	**Talc**
Critic values of prediction (% mass)	83.59	84.60	71.64
Particle Size	+1	-1	-1
pH	-1	-1	0
Mass	+1	+1	-1
Ionic Force	+1	0	-1
Maximum experimental up take (% mass)	82.23	100.0	91.41

CONCLUSIONS

The experimental design was satisfactory for the study of the retention of total phosphorus from water using phyllosilicates process. The results were compared to the reduced reliable mathematical modeling errors. The kaolinite showed better performance in terms of phosphorus retention, which process had a more linear and higher prediction at 80% retention of phosphorus behavior. It was possible to establish optimal conditions for future studies of sorption.

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(48) Bioremediation of phenol containing wastewater by aerobic granules in sequencing batch reactor

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Extended Abstract

The use of aerobic biological treatment can be traced back to the late nineteenth century. The most common and longest standing methods of aerobic treatment has been the activated sludge process. These days a new innovation in aerobic process has been developed known as aerobic granular sludge technology. It has many advantages over the conventional activated sludge process i.e. it can withstand fluctuating loads; lesser space requirement; lower biomass production due to high biomass retention. These aerobic granules are cultivated inside the sequencing batch reactor (SBRs) in which the separations of sludge and effluent takes place inside the same reactor

A laboratory scale SBR with an effective volume of 2 L was used to cultivate aerobic granules. The internal diameter of the reactor was 5 cm and the working H/D (Height/Diameter) was about 20. Fine air bubbles for aeration and mixing were supplied by diffusers placed at the reactor bottom. Superficial air velocity was maintained in the range of 2-3 cm/s. A reactor was operated sequentially in 8 h cycles which consist of 5 min of influent filing, 472-447 min of aeration, 5-30 min of settling and 3 min of effluent withdrawal. Effluent was discharged at 50 cm from the bottom of the reactor with a volumetric exchange ratio of 50%.

The cultivation and hydrodynamic properties such as morphology, fractal dimension, porosity, size distribution, and settling velocity of stable aerobic granules, developed in a sequencing batch reactor SBR was investigated in this study. A column type SBR was operated with organic loading rate of 0.3 kg phenol /m^3day with phenol as a sole carbon source. The phenol loading rate was then increased to 1.8 kg phenol/m^3day and an efficiency of 79% was achieved. . In the final phase of the reactor the MLVSS, SVI, MCRT, F/M and size of granule in the reactor was 8.9g/L, 63 ml/g MLVSS, 19.8 days, 0.40 and 4.5-5.5 mm respectively. Aerobic granules were visible within 30 days of operation of the reactor. The granules were larger and stronger and had a compact structure. The granules were fractal and porous aggregates and had a fractal dimension and porosity of 2.47 and 0.7-0.9 respectively. The settling velocities of aerobic granules were in the range of $2.38x10^{-02}$m/s-$7.1x10^{-02}$m/s. This was in good agreement with the settling velocities predicted by Stoke’s law for porous but impermeable spheres. It may be due to the EPS (Extracellular Polymeric Substances) produced by bacteria form a gel matrix that clogs the pores within the granules. The results suggested that fast settling aerobic granules can be cultivated on toxic substrate in SBR which can favoured for its industrial wastewater treatment application.

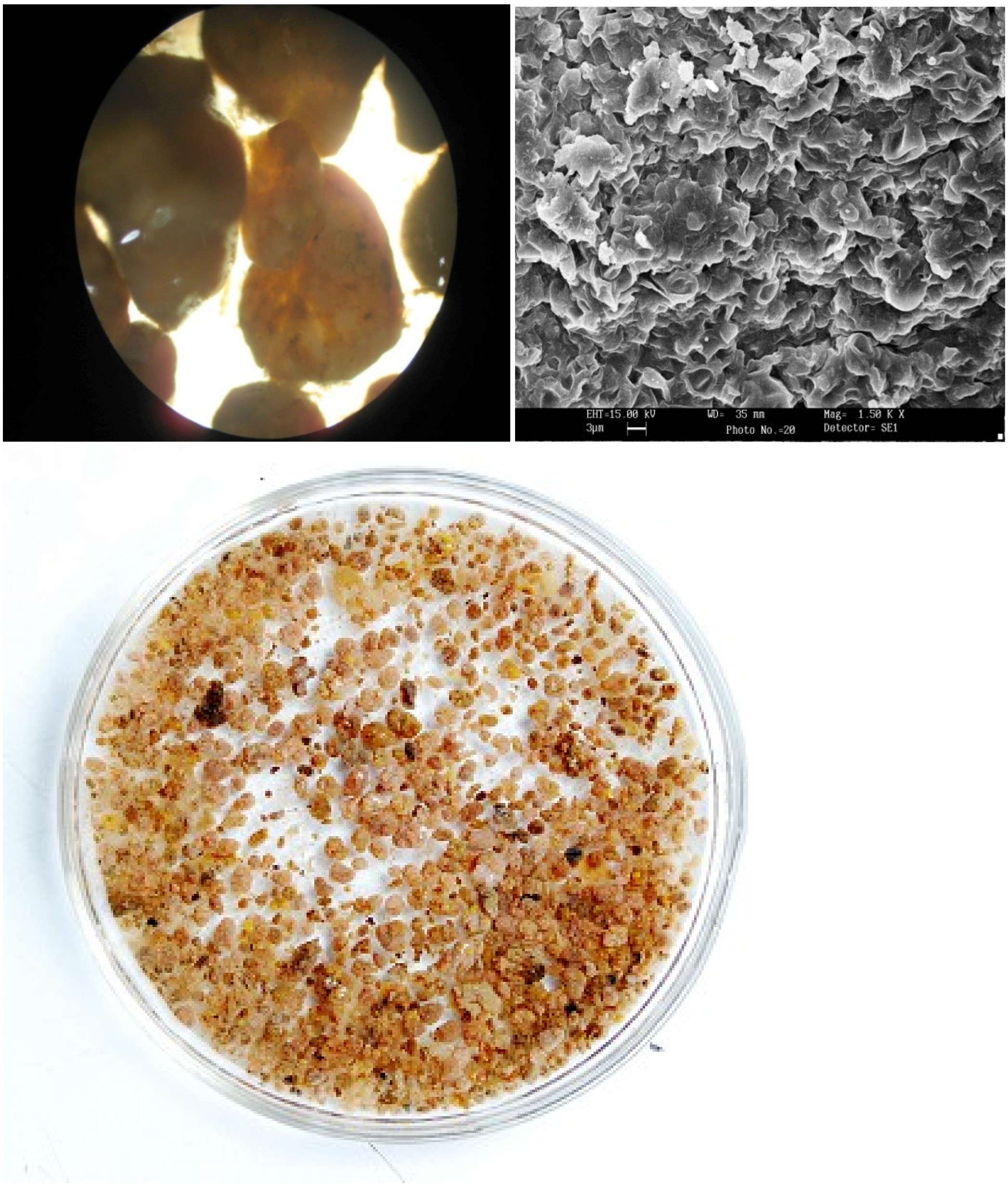

Figure 1 Microscopic and SEM image of fully developed granules on day 45 and Macrostructure photo of granules in 90mm Petri dish on day 45.

Keywords: Aerobic Granules; Phenol; Sequencing Batch Reactor (SBR); Settling Velocity

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(49) Evaluation of industrial pollutants removal using membrane bioreactor

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Abstract

The water demand is vast, whether it is for human consumption, agricultural application, or industrial use. Industrial wastewaters contain high concentration of organic matter, different kinds of chemical substances, including dissolved organic compounds and total suspended solids including fat, grease, manure, grit, undigested feed and etc. Membrane bioreactors were used for removal of organic substance from industrial wastewater.

Different types of industrial wastewater contain some refractory organic matter that cannot be removal easily. In this context the biological treatment methods are viable options among the other treatment systems. Membrane bioreactor (MBR) system is one of them. In this study the removal of some industrial pollutants in wastewater, such as pharmaceutical, slaughterhouse, were examined using submerged membrane bioreactor.

A membrane bioreactor (MBR) system comprises a conventional activated sludge process coupled with membrane separation to retain the biomass. Since the effective pore size can be below 0.1 µm, the MBR effectively produces a clarified and substantially disinfected effluent. Submerged type membranes were used in the treatment studies. COD, TOC, total phosphorus, total nitrogen analyses were conducted to determine the removal efficiencies of membrane bioreactor system.

Keywords

Membrane bioreactor; industrial pollutants; wastewater; submerged membrane

INTRODUCTION

There are some advantages associated with the MBR which make it a valuable alternative over other treatment techniques. First of all, the retention of all suspended matter and most soluble compounds within the bioreactor leads to excellent effluent quality. The possibility of retaining all bacteria and viruses results in a sterile effluent, eliminating extensive disinfection and the corresponding hazards related to disinfection by-products. Since suspended solids are not lost in the clarification step, total separation and control of the solid retention time (SRT) and hydraulic retention time (HRT) are possible enabling optimum control of the microbial population and flexibility in operation. The absence of a clarifier, which also acts as a natural selector for settling organisms, enables sensitive, slow-growing species, such as nitrifying bacteria, bacteria capable of degrading complex compounds, to develop and persist in the system even under short SRTs.

EQUIPMENTS AND EXPERIMENTAL CONDITIONS

A submerged type ultrafiltration membrane was placed in the tank bioreactor in the experimental studies. The raw wastewater was taken from the feed tank and loaded to the bioreactor which consisting membrane unit. Activated sludge which was taken from a domestic biological treatment plant was inoculated to the bioreactor. At the beginning, the bioreactor was operated as a batch activated sludge process. Then the membrane module was inserted to the reactor and MBR studies were conducted. At the bottom of the membrane unit, an aerator was taken place for the cleaning of membrane surface and also for supplying oxygen to the mixed liquor. A peristaltic pump was used to draw the filtrate from membrane unit. The transmembrane pressure (TMP) of the system is measured and control during the experiments.

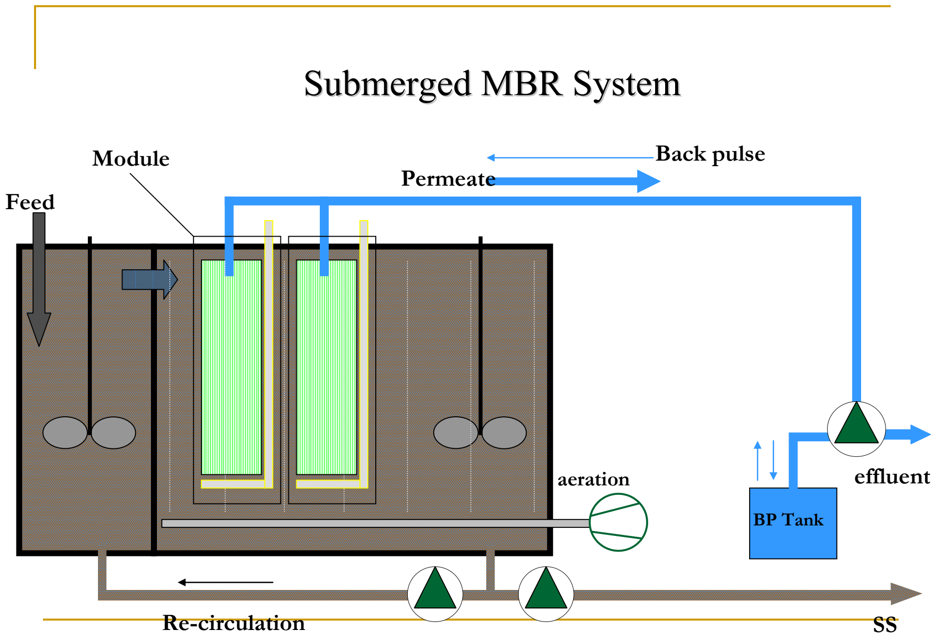

Figure: Membrane bioreactor system

Biological treatment by MBR

After the treatment studies made by conventional activated sludge (batch system without membrane), membrane unit was submerged to bioreactor, and the wastewater was begun to fed to the bioreactor continuously. The long hydraulic retention time was chosen at the light of previous preliminary test results. The wastewater drawn from membrane unit was transferred to the filtrate storage tank. The most suitable pH range for the biodegradation of organic substances by activated sludge was 6-9. Therefore, pH value of the wastewater was tried to keep in the range of 6.5-7.5.

CONCLUSION

The industrial wastewater treatment by using membrane bioreactor was investigated. An ultrafiltration membrane was used as membrane unit in the studies. The parameters such as COD, TOC, TN, TP and turbidity were studied to determine the treatment performance of this membrane bioreactor process. According to the tests made, the removal efficiency of COD and TOC was found on average 96% and 85% respectively. When the performance was observed, it was seen that the TOC removal was accomplished with an efficiency of for related industrial wastewaters. Beside the organic parameters, nutrient removal efficiencies were also examined. It was observed from the treatment results that membrane bioreactor system was very successful for removing several contaminants from industrial wastewaters. MBR provide a superior effluent quality compared to conventional methods.
In frame of assessment of MBR technology, it can be listed, the advantages and disadvantages as follows.
Advantages: 1) High effluent quality, 2) No sludge settling problems, 3) Reduced volume requirements.
Disadvantages: 1) Membrane fouling, 2) Increased operational costs.

(50) Human cell-based reporter gene assays for endocrine disrupters, POPs, obesogens and other toxic pathways for drinking water, surface water and WTP effluents

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Abstract

Traditionally, chemical monitoring systems are utilized to determine the presence of high risk chemicals to protect wildlife and humans. However, this approach has significant limitations, as it detects only a limited number of (priority) chemicals/pharmaceuticals, which can only associate risk with compounds if toxicological information is available and does not address the potential synergistic effects. This lack of information, together with that of proper analysis tools to screen with the same laboratory equipment for a wide variety of relevant toxicity endpoints (such as cytotoxicity, genotoxicity, endocrine disruptors, POPs and obesity) makes it favourable to work with high-throughput robotics and effect-based human cell-based reporter gene assays.

We present here an overview on current status of human cell based reporter gene assays for several pollutants applied to different types of waters, presenting some case studies in which the authors organizations have been involved, thus showing the potential and drawbacks of such assays to monitor complex mixtures/effects of all kinds of potential pollutants present in such matrices.

Keywords

In vitro reporter gene assays, CALUX®, endocrine disruptors, hormone–like pollutants, emerging POPs, water pollution, water treatment, STP optimization

INTRODUCTION

There are compounds present in the aquatic environment that can disturb endocrine processes, for example via interaction with the endogenous hormone receptors. Such pollutants may not only bind to the estrogen and/or androgen receptor, but also to other ones (Van Der Linden et. al., 2008).

The reporter gene assays for the detection of endocrine disruptors (ED) and/or hormone-like substances using the CALUX® technology are based on a simple principle: human ER/AR/TR receptors are integrated in the human U2OS cell line. If an ED is binding on the receptors, luciferase is as well activated to the standards (estradiol, DHT and T3) and can be measured by a luminometer. Other CALUX tests work on a similar, all of them are usually rapid and highly sensible. They are usable for a wide variety of matrices (environmental, biological, food, etc.), including waters and sludges. A list of the available CALUX bioassays is listed in Table 1.

We present here an overview about CALUX tests usable for the detection and quantization of hazardous pollutants with an hormone-like or endocrine disruptor effect as well as for the characterization of waste streams effects on physiological pathways (e.g. estrogenicity, androgenicity, progestinicity, glucocorticoid, thyroid activity, oxidative stress, obesity, cytotoxicity, genotoxicity and POPs-like activity). At present, a broad initial screening on the ca. 50 available CALUX cell lines allows to detect relevant toxic endpoints from several known environmental pollutants such as endocrine disrupters (e.g. bisphenol A, phthalates), POPs (dioxins/dl-PCBs), obesogens (PFOA/PFOS, TBT), oxidative stress (organometals) or genotoxic compounds (PAHs).

SOME CASE STUDIES

Following we briefly report three case studies in which reporter gene in vitro assays have been successfully used for investigations of emerging pollutants in waters and determination of the best technology for water treatment. CALUX results generally fit well with those of chemical methods usually adopted for hormone-like substances (e.g GC-MSD, Avberšek et al., 2011).

Table 1. Overview of human cell-based reporter gene assays for endocrine disrupters, POPs, obesogens and other toxic pathways applied on drinking water, surface water and effluents of WTPs

Addressed pollutants	Test	Detection
Endocrine Disrupting Chemicals and POPs	HTPS CALUX	Pathway
C- and N-Dioxins PXDD/Fs, dl-PXBs (X= Cl, Br, F, methyl)	DR CALUX	Dioxin receptor
Carcinogenic PAHs (such as Benzo(a)pyrene)	PAH CALUX	Dioxin receptor
Estrogens, EDCs, Bisphenol A, Phthalates, Pesticides, Pharmaceuticals, cosmetics	ER CALUX	Estrogen receptor mix
Androgens, EDCs, Bisphenol A, Pesticides, Pharmaceuticals, triclosan	AR CALUX	Androgen receptor
Progestins, EDCs, Anti-babypill, Pesticides, Pharmaceuticals	PR CALUX	Progesterone receptor
Glucocorticoids, cortisol-like compounds, EDCs, Asthma spray, Immune-suppressive agents	GR CALUX	Glucocorticoid receptor
Thyroid hormones, EDCs, Brominated flame retardants	TR CALUX	Thyroid receptor
Retinoids, Pesticides, Pharmaceuticals	RAR CALUX	Retinoic acid receptor
Obesogens, fluorinated compounds PFOA/PFOS, Anti-diabetic pharmaceuticals	PPARα, δ and γ CALUX	Peroxisome proliferator receptor
Pro-inflammatory cytokines	NFkappaB CALUX	NFkappaB activation
Cytotoxic/static agents, Genotoxic compounds like PAHs, Pharmaceuticals, dyes	p21 CALUX	p21 activation
Cytotoxic/static agents, Genotoxic compounds like PAHs, Pharmaceuticals, dyes	p53 CALUX	p53 transcriptional activity
Electrophiles, oxidative stress, heavy metals	Nrf2 CALUX	Nrf2 transcriptional activity
β-Catenin/ involved in development and carcinogenesis	TCF	TCF transcriptional activity
Carcinogens, UV	AP1 CALUX	AP1 transcriptional activity
Hypoxia-mediated angiogenesis	HIF1alpha CALUX	HIF1α transcriptional activity
Endoplasmatic reticulum stressors	ER, stress CALUX	XBP1 transcriptional activity
Cytotoxic agents, Non-specific luciferase modulators	Cytox CALUX	Constitutive transcriptional activity

Case 1 – Characterization of the effectiveness of enhanced STP in hospital effluents

In 2012 Maletz et al. performed a study about the effluent of a medium sized country hospital in western Germany, addressing the efficiency of advanced treatment processes to remove potential toxic substances from sewage. They compared membrane bioreactor (MBR) and ozonation for the removal of endocrine disruptors. Estrogenic effects were characterized by the Estrogen Receptor mediated Chemical Activated LUciferase gene eXpression (ER CALUX®). The raw effluent contained estrogen receptor (ER)-mediated potential measurable by ER CALUX, which was reduced after treatment by MBR (0.2 ± 0.11 ng/L) and ozone (0.01 ± 0.02 ng/L).

The tests demonstrated efficient removal of most of the measured compounds by ozonation. On the one hand, generally the treatment of sewage by use of MBR successfully reduced estrogenicity of hospital effluents as well as substances that are able to alter sex steroid production. On the other hand, ozonation, needs further investigation because of the formation of endocrine active metabolites due to strong oxidation. The results obtained as part of this study demonstrated applicability of in vitro assays for monitoring of endocrine-modulating potency of treated sewage.

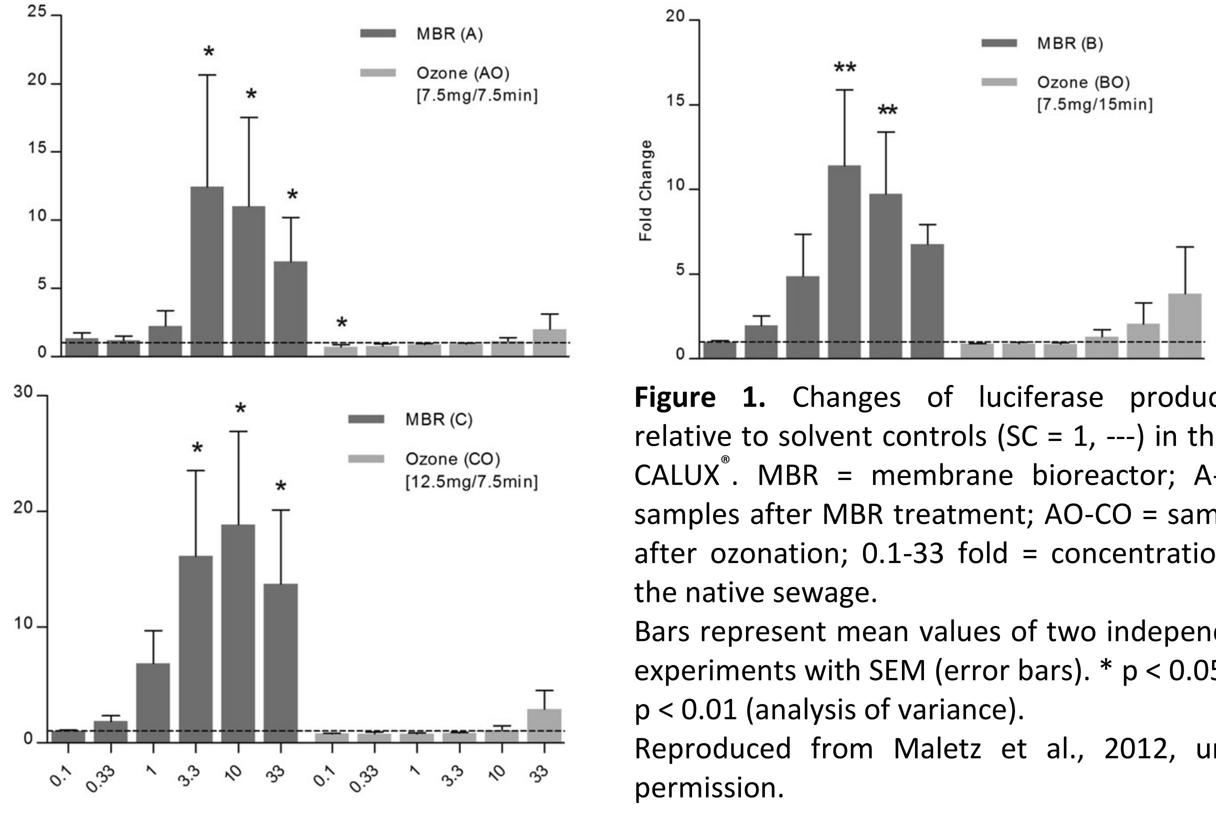

Figure 1. Changes of luciferase production relative to solvent controls (SC = 1, ---) in the ER CALUX®. MBR = membrane bioreactor; A-C = samples after MBR treatment; AO-CO = samples after ozonation; 0.1-33 fold = concentration of the native sewage.

Bars represent mean values of two independent experiments with SEM (error bars). * $p < 0.05$, ** $p < 0.01$ (analysis of variance).

Reproduced from Maletz et al., 2012, under permission.

Case 2 – A comparison of CALUX® with chemical analysis

CALUX® bioassays show in general good correlation with their chemical classical counterparts. As the former gives an indication about the total toxicity of contaminants able to bind a specific cell receptor, several papers confronted the results of the different techniques. A very interesting one is that from Schriks et al. (2010) which shows that we cal look further than estrogenic effects only. They not only used CALUX to reveal glucocorticogenic activity in several types of wastewaters collected at various sites in The Netherlands (industry, hospital, paper mill treated WW, STP effluent), but also to compare results with LC-MS/MS, finally finding a good correlation. In a non-treated hospital effluent several glucocorticoids were identified (cortisol 275-301 ng/L, cortisone 381-472 ng/L, prednisone 117-545 ng/L, prednisolone 315-1918 ng/L, and triamcinolone acetonide 14-41 ng/L). Instrumental analyses allowed the calculation of a relative potency balance calculation of the individual glucocorticoids (REPs), suggesting that triamcinolone acetonide, dexamethasone, and prednisolone are the main contributors to the glucocorticogenic. The sum of REP found was 136 ng/L in accordance with the value of 96 ng dex

EQs/L found with CALUX by Van Der Linden et al. (2008) in similar effluents.

Case 3 – Using CALUX panel tests to compare water treatment techniques

CALUX® *in vitro* essays offer comparable results with biological *in vivo* essays and a CALUX panel test can be used in a rapid and efficient way to compare the efficiency of different STPs, e.g. PAC-UF vs. biological treatment plus ozonation for water depuration (Kienle et al., 2011).

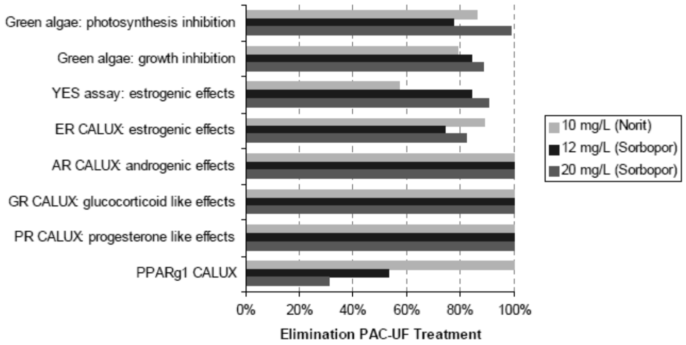

Figure 2. Elimination efficiencies (%) in the PAC-UF (packed activated carbon ultra-filtration) treatment for each of the four measurement campaigns regarding specific effects measured in *in vitro* bioassays.
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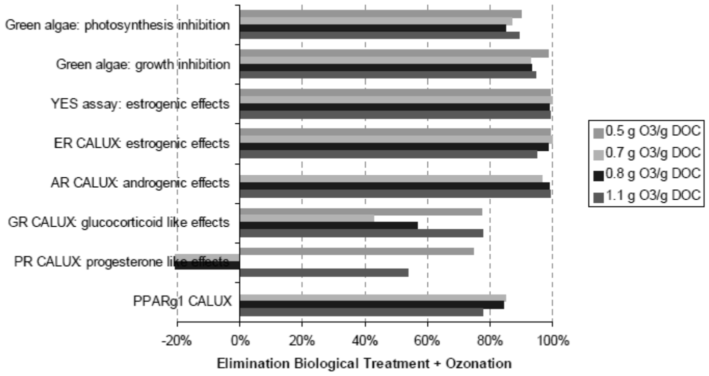

Figure 3. Elimination efficiencies (%) in the biological treatment plus ozonation for each of the four measurement campaigns regarding specific effects measured in *in vitro* bioassays.
Reproduced from Kienle et al., 2011, under permission.

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(51) Fate and Effects of Oxytetracycline in Drinking Water Reservoirs

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Abstract

Antibiotic pollution is an emerging problem due to extensive use by humans. OTC is a common antibiotic belonging Tetracycline family which is commonly used both on humans and animals. In this study, mimicry of antibiotic pollution in drinking water reservoirs was simulated by microcosm experiments. Surface water and sediment microcosm were built to monitor fate and effects of OTC in aerobic and anaerobic aquatic conditions. Both water and sediment samples were collected from two drinking water reservoirs which are active and operational. OTC was added in form of OTC containing manure in different amounts for aerobic and anaerobic conditions, respectively. An incubation period of 60 days has been set to monitor the system. In water microcosms, OTC was decreased beyond detection limit (<0,01 mg/l) after 30 days indicating a half-life 18-22 days. In sediment microcosms, OTC was more stable and had a half-life of 77-100 days very similar to soil environments. Bacterial diversity in water microcosms changed drastically possible due to bacterial content of manure. Sediment microcosm'sbacterial diversity was also affected by manure's bacterial content but effect was very low in respect to water microcosms.

Keywords
Oxytetracycline, water reservoirs, half-life, bacterial diversity, molecular techniques

INTRODUCTION

Antibiotics were discovered in 1900s and since then they are used extensively on treatment of both humans and animals. Most of antibiotics leave animal body without or slightly changed (60-90%) in form of urine and manure (Kemper, 2008).Oxytetracycline (OTC) is a broad spectrum antibiotic of tetracycline group which is widely used to treat livestock animals due to its low cost and low side effects.

OTC presence in environment is due to human use. OTC is consumed both by humans and animals to prevent infection and diseases. OTC is excreted in form of urine and faeces where it eventually end up in final receiving environments, water reservoirs. Although there are many studies concerning presence and occurrence of OTC in different environments, studies combine fate and effect of OTC in these environments are rather scarce.

The objective of this study is, therefore, to monitor fate of OTC in surface water and sediments. Effect of OTC on bacterial community in these environments are also investigated

MATERIALS AND METHODS

Chemicals and OTC detection

Oxytetracycline was purchased from Acros Organics N.V (NJ, USA). HPLC grade chemicals were obtained from Merck (NJ, USA). Extraction of antibiotic was performed as described elsewhere (Yuan et al., 2010)with slight modifications. The HPLC instrument (Schimadzu LC-10 AD) was equipped with an UV detector; (UV VIS Detector, SPD 10-A), a degasser (DGU-14A) and a system controller (SCL-10A). The column used in this study was Inertsil ODS-3 HPLC column, (25 cm x 4.6 mm). Degassing of the solvents was achieved by sonication in a transonic ultrasonic bath (ELMA D-78224, Singen/Htw) prior to use. The mobile phase consisted of 75% 0.1 M oxalic acid buffer and 25% Methanol:Acetonitrile (1:1.5) solution which was delivered isocratically at a flow rate of 1 ml/min. Total run time was 20 min. Wavelength for the detection of OTC was 357 nm, at which the retention time was 8.4±0.8 min. All results were analysed by the system software, LC Solutions (Schimadzu Scientific Instruments Inc., MD, USA). In order to determine extraction efficiencies, triplicate samples of non-medicated manure were spiked with different OTC concentrations (5, 20, 200, 1000 mg/L) and incubated for 3 hours and extracted as described above. Recovery results were calculated as a means of triplicate samples at each concentration.

Microcosms setups

Two sets of microcosm were built to mimic aerobic surface water and anaerobic sediment environments. Two surface water samples were collected from Elmali and Omerli water basins in which bacterial diversity is low and high, respectively. Sediment sample was taken from Omerli water basin. 2000 ml surface water was mixed with 10 gr of sediment and 10 gr of manure and incubated for 60 days in room temperature in vicinity of sunlight. Sediment microcosms were set in 120 ml serum bottles. 30 gr of sediment, 30 gr of manure and 40 ml surface water were mixed and anaerobic conditions were met by helium flushing. Sediments were incubated in room temperatures in dark conditions. For each sampling time, one microcosm was set. Sampling times were every 30 days for both microcosm sets and samples were collected for analytical and molecular analysis.

Monitoring of effect of OTC on bacterial communities

Bacterial Diversity Analysis

Bacterial diversity analysis was performed by DNA targeting DGGE. The procedure is described elsewhere. (Effect of SED) DNA spin kit for soil (MP Biomedicals,USA) was used to extract total GDNA and PCR reactions were carried out with Fermentas kit in Techne 5000 thermal cyclers.

RESULTS AND DISCUSSION

Fate of OTC in Microcosms

OTC concentrations in microcosm sets were monitored by HPLC analysis during incubation period. As mentioned in other researches (Kümmerer, 2008;Garcia-Rodrguez et al., 2012), OTC concentration decreased rapidly in water microcosms exposed to sunlight. After 30 days of incubation, OTC level decreased below 0,01 mg/l which was our detection limit. In sediment microcosms, OTC was more resistant to elimination and calculated half-life was 77-100 days. This half-life is parallel to other reported half –lives reported (Jacobsen andBerglind,1988; Coyne et al., 1994)

Table 1. OTC elimination, concentrations and half-life of OTC in surface water microcosms

	Sampling Day 0th day	11th day	22th day	30th day	45th day	60th day	Elimination (%)	Half-life (Day)
	OTC concentration (mg/L)							
Elmali	0,05	0,04	0,01	0,01	<0,01	<0,01	100	18
Omerli	0,02	0,02	0,01	0,01	<0,01	<0,01	100	22

Table 2. OTC elimination, concentrations and half-life of OTC in sediment microcosms

	Sampling Day Seed	0th day	30th day	60th day	Elimination (%)	Half-life (Day)
	OTC concentration (mg/kg)					
Elmali	-	6,4	4,7	4,5	30	100
Omerli	0,2	6,4	4,5	3,9	39	77

Experiments on OTC concentrations in water reservoirs showed that OTC do not pose a threat in water bodies since it is quickly eliminated in presence of sunlight. On the other hand OTC in sediments showed a pattern like in soil where OTC is highly resistant to elimination and have a half-life greater than 75 days.

Effect of OTC on microbial population

Bacterial diversity change analysis

Bacterial diversity change was monitored by DGGE on DNA level. Extracted genomic DNA was used as template to amplify 16S rRNA region of bacterial domain. Selected piece of amplified DNA was used in DGGE analysis. Analysis showed an increase in bacterial diversity due to sediment and manure addition to surface water. Elmali water sample which was selected due to its low diversity and its low diversity increased great after addition of OTC containing manure and sediments. OTC containing manure and sediment addition not only increased diversity but also increased bacterial population as shown in Q-PCR analysis. Omerli water sample which was selected due to its high diversity and after addition of OTC containing manure and sediments it diversity changed. In Omerli samples, it has been monitored that diversity is not increased but changed drastically.

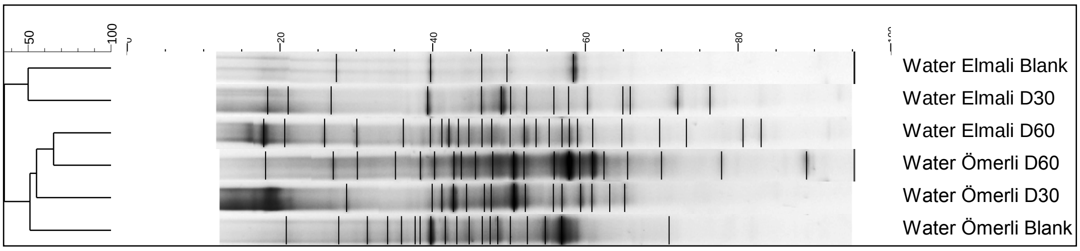

Figure 1.Bacterial Diversity analysis of water microcosms according to Dice correlation

Omerli seed sediment showed a high diversity and it's changed upon manure addition. The bacterial diversity became an amalgam of both sediment and manure diversity and remained so during incubation. The dominant band was found to be affiliated with a *Clostridium lituseburense* which was found as dominant bacterial species on our previous studies (data not shown).

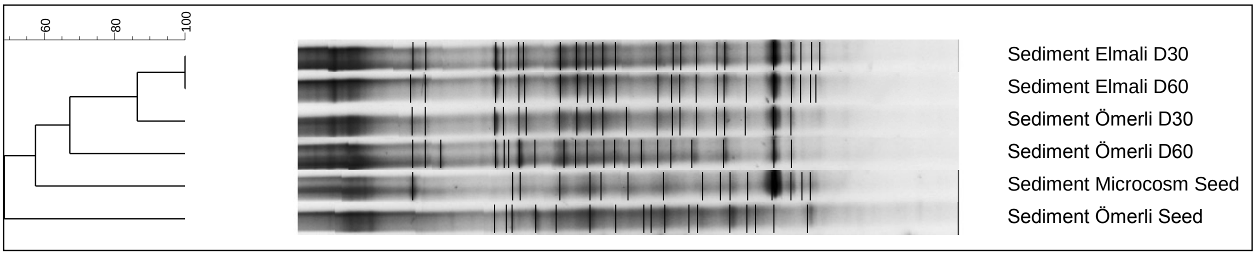

Figure 2.Bacterial Diversity analysis of sediment microcosms according to Dice correlation

Microbial experiments showed that bacterial diversity and population is highly susceptible to change in addition of foreign bacterial communities. But it is assumed that most common way to introduce of OTC to water bodies is due to leakage of OTC containing liquids rather than OTC containing solid like manure. Therefore, bacterial diversity changes do not pose a serious threat.

CONCLUSION

In this study, fate of OTC in aquatic environments was monitored along with its effect on bacterial populations. It has been found that OTC does not pose a threat in surface waters due to photodegredation but it is persistent in sediments with a half-life of 77-100 days. Bacterial diversities changed drastically in water samples. Impact of foreign bacterial population is much smaller in sediment samples.

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(52) Sulfamethoxazole biodegradation by a specific bacterial strain and investigation of its proteome

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Abstract

Antibiotic compounds, like sulfamethoxazole (SMX), are only partially removed during wastewater treatment and often detected at µg L^{-1} levels in treated effluents and receiving water bodies. Little information on SMX biodegradation is still available. Recently bacterial strains were isolated and proven to at least partially mineralize SMX. For the better understanding of SMX biodegradation mechanism, the overall proteome of *Microbacterium* sp. strain BR1 was searched for potential candidate proteins involved. We claimed that the protein expression profile will change once *Microbacterium* is exposed to SMX. An almost complete removal of SMX was observed within 24h. The protein patterns, originating from cells either exposed to SMX or not, were compared and analysed by difference gel electrophoresis and detailed statistical analysis. Protein profiles homogeneity was observed and the comparison over time allowed the identification of potential changes in the proteins' expression levels.

Keywords

Activated sludge; Biodegradation; DIGE; pharmaceuticals; proteomics; pure culture; Sulfamethoxazole (SMX).

INTRODUCTION

Antibiotics are a major pharmaceutical category and have been detected in the influent and effluent of sewage treatment plants and surface waters (Miège *et al.,* 2009). Among them, sulfamethoxazole (SMX), has become of concern because of its effects, its persistence in the environment and its low biodegradability. Antibiotics may result in various, direct and indirect, toxicological effects on the aquatic environment and on human health and it might favour the development of antibiotic resistant bacteria (Boreen *et al*., 2004). SMX removal in conventional wastewater treatment plants is largely variable and it ranges from 0% to 90% (Joss *et al.,* 2006). Few studies have focused on the role of specific bacterial strains capable of biodegrading SMX. Recent studies provided evidence for partial mineralization of SMX and related sulphonamide antibiotics by five different pure strains and with special focus on *Microbacterium* sp. BR1 (Bouju *et al.,* 2012; Ricken *et al.*, 2013). Other recent studies reported *Microbacterium* strains capabilities to degrade sulphonamide antibiotics (e.g. Tappe *et al.*, 2013).

The aim of this research is twofold. First, to investigate the ability of the single strain *Microbacterium* sp. strain BR1, previously found and isolated from activated sludge and conditioned with up to 126.5 mg_{SMX} L^{-1}, to degrade the antibiotic at more environmentally-relevant concentrations, as well as to study the strain proteome in order to identify potential proteins involved in the antibiotic biodegradation process. The expected results might give hints on proteins involved in the SMX biodegradation.

MATERIAL AND METHODS

Bacteria and biodegradation experiment

Microbacterium sp. strain BR1 was kindly provided by the Institute for Ecopreneurship from the University of Applied Sciences and Arts Northwestern Switzerland (FHNW). *Microbacterium* sp. BR 1 was grown and acclimatized to SMX by incubating the cells in 25% (v/v) Standard I medium with 125mg L^{-1} of SMX (48h, 28°C, 130 rpm) and stored at -80ºC as glycerol stocks.

The biodegradation experiment was carried out at 1 mg L^{-1} of SMX in a mineral salts medium (MMO), containing SMX as the sole carbon source. The culture was used to check the ability to degrade SMX at low mg L^{-1} concentrations.

For proteomic purposes different batch experiments were prepared. The first batch test (6 replicates) was inoculated with SMX at 1mg L^{-1} while a second batch test (6 replicates) was without SMX or carbon source. Additionally, a control flask accounted for any abiotic degradation which could lead to overestimation of the final biodegradation rate (same condition, in MMO, no pure strain). All the flasks were incubated, at 28ºC and 130rpm, and sampled over one day at times: 0, 1, 3, 6 and 24h for liquid SMX analysis and at 0, 1 and 24h for sludge samples of proteome analysis.

Analytical methods for SMX

SMX stock solutions were prepared on a weight basis in methanol at 1 mg mL^{-1} and kept frozen at -20ºC. Calibration standard solutions of the target compound were prepared by appropriate dilution. Chromatographic separation was carried out with an ultra-performance liquid chromatography system (Waters Corp. Mildford, MA, USA) coupled to an to a 5500 QqLit, triple quadrupole–linear ion trap mass spectrometer (5500 QTRAP, Applied Biosystems, Foster City, CA, USA) using an analytical method adapted from Gros *et al.*, 2013. The method showed a LOD of 0.05 µg L^{-1} and a LOQ of 0.18 µg L^{-1}. No matrix effects were observed.

Analytical methods for proteomic analysis

For protein extraction, the samples (15ml) were spun down in centrifugation tubes. The pellets were then frozen and immediately stored at -80ºC until their analysis. Pre-treatment, quantification and 1D-SDS-PAGE gel electrophoresis were performed to control the quality of the samples. The gels were then stained, quantified and an internal standard was introduced into every gel. Thus, a mixture of all samples was labelled with one of the three dyes (Cy2, Cy3 and Cy5), treated as another sample, and used to normalize the signalling and to improve the image alignments. The samples to be loaded into the 2D gels were pooled in pairs. Gel image was scanned, processed and analysed (Image Master 2D Platinum 6.0 software, Pharos FX Plus Imager instrument - Bio-Rad, SameSpots software). Accurate matching and properly spot detection were done with a semiautomatic method, with manual correction and edition of spot features created by automatic default spot analysis settings. Images were automatically aligned, spots were detected and volumes were normalized towards each internal standard.

RESULTS AND DISCUSSION

Evaluation of *Microbacterium* sp. strain BR1 biodegrading capacity

No abiotic SMX degradation was observed in the controls and a substantial biotic SMX degradation, by *Microbacterium* sp. strain BR1, was proven (as expected taking into consideration the higher tested concentrations results from Bouju *et al.*, 2012). An almost complete removal was obtained after 24h experimental period, accounting for 96% removal efficiency (Table 1). These results, referring to the liquid phase samples were specifically useful as a first step to guarantee a high biodegradation activity throughout the test to further analyse the proteome of the pure strain.

Table 1. SMX degradation values within 24h experimental period.

Time (h)	[μg_{SMX} L^{-1}]
0	1310
1	1056
3	837
6	558
24	58

Proteome analysis and statistical study

The main goal of this proteomic experiment was to compare the proteomes to observe any overexpression, of candidate proteins involved in the SMX biodegradation process, compared to the samples at time zero and the blanks monitored along the experiment. The biomass samples taken for proteome analysis were run in 2D gels and were subsequently subjected to statistical analysis to account for any possible and significant variation on the proteins expression. The majority of protein spots in all gels were well focused in the molecular weight (15 to 100 kDa) and the isoelectric point (4.0 to 7.0) range. No remarkable protein variations were observed among the different samples taken throughout the experimental period, except for eight specific proteins (showing a differential expression over time and possibly correlating with the SMX degradation) that were selected for a deeper and individualised statistical analysis (Figure 1).

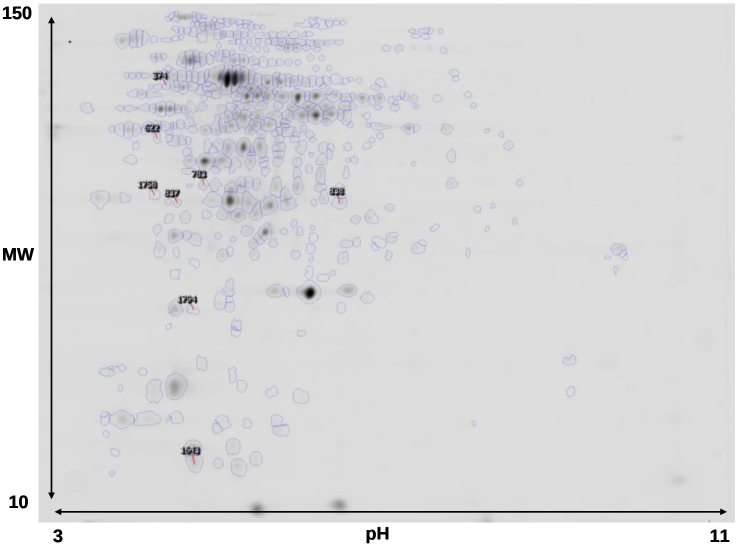

Figure 1. Pure *Microbacterium* sp. strain BR1 proteome 2D gel image. All blue circled spots refer to all the proteins detected, and those numbered to those of interest.

According to the initial hypothesis of the study, these specific proteins might play a potential role in the SMX biodegradation pathway, because their expression was altered when the antibiotic biodegradation occurs. However, in this case, it has to be taken into account that when comparing these target protein expression profiles with the blank samples (with no exposure to SMX), the latest patterns tend to overlap the interesting trends mentioned above. Thus, there is no protein in the treated samples whose expression profile changes in a significant manner between different time points; neither in the test samples nor the blank samples. This may led to the conclusion that some of these trends were more likely caused by time variability rather than SMX exposure. Alternatively this phenomenon might be related to a stress reaction (due to the antibiotic) or carbon starvation.

A possible explanation could be that the initial hypothesis to find newly expressed or overexpressed process within the SMX biodegradation process, is, in some way, not valid. This would be the case of housekeeping proteins involved (even if unlikely), while executing many other cell functions. In this case, no specific changes would be highlighted and, in the absence of more information, the proteomic approach alone would not be sufficient. Moreover, the lack of target proteins also increased the complexity of the study, since no reference could be used to track them.

CONCLUSIONS

In this study, the use of proteomics to survey a large number of proteins, was supposed to significantly speed up the discovery of new proteins involved in a target pharmaceutical biodegradation pathway, in this case SMX. This work attempted to analyse a pure *Microbacterium* sp. strain BR1 proteome, which was exposed to a single pharmaceutical compound, as a close-fitting approach to get a deeper insight into the proteins involved in the SMX biodegradation process. Significantly high biodegradation efficiency was obtained by *Microbacterium* sp. strain BR1 exposed to 1 mg L^{-1} of SMX.

The identification of unknown proteins involved in the SMX degradation pathway by DIGE was not successful in this study. Previous studies have already shown, that the identification of unknown proteins, involved in the degradation of inhibitory substances like antibiotics can be challenging (Collado *et al.* 2013). Besides other factors the diverse up and down regulation of proteins, not involved in the degradation but induced by those substances, hampers the identification.

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(53) Effect of Temperature and pH on Anaerobic Biodegradability of Diclofenac

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Abstract

The effect of pH and temperature on the anaerobic biodegradation potential of diclofenac, non-steroidal anti-inflammatory pharmaceutical was investigated with a mixed fermentative/methanogenic culture developed from a contaminated sediment sample. Culture series were incubated at a temperature range from 10 to 45°C at pH 7.2±0.1 and at a pH range from 3.1±0.1 to 13.1±0.1 at 22°C. Glucose and methanol served as the electron and carbon source. Diclofenac concentration was determined by solid phase extraction (SPE) followed by liquid chromatography tandem mass spectrometry (LC-MS/MS). Remarkable diclofenac degradation was not observed in none of the experimental setups operated under different pH and temperature conditions. Therefore, in order to eliminate uncontrolled micropollutant release into the receiving bodies additional precautions should be taken in wastewater treatment plants.

Keywords
Emerging contaminant; environmental conditions; LC-MS/MS; micropollutant

INTRODUCTION

Diclofenac is an anti-inflammatory drug found mainly in domestic wastewater treatment plants' both influent and effluent streams. It is one of the most commonly used non-steroidal anti-inflammatory drugs (NSAID) with annually 940 tonnes global consumption (Zhang et al., 2008). Potential toxic effects of diclofenac were reported at environmentally relevant concentrations on aquatic organisms (Hong et al., 2007; Hoeger et al., 2005). Continuous release of diclofenac into the aquatic environment may result in long-term chronic exposure (Garcia-Lor et al., 2012). In addition, diclofenac is listed in the high priority category by Global Water Research Coalition (GWRC, 2008). Diclofenac degradation potential in wastewater treatment plants is very low and it is often incomplete with treatment efficiencies ranging between 20–80% (Zhang et al., 2008). Diclofenac was identified as a potential problem for the water cycle because of its low removal rate during wastewater treatment processes (Huber et al., 2012). In the literature, most of the previous studies were performed at constant temperature and pH values and at concentrations relatively high which may not reflect actual conditions. However, incubation temperature and pH are expected to have a significant effect on diclofenac (bio)transformation. To our knowledge, this important area of research has not previously been explored. Depending on the location and climate, diclofenac-contaminated environments may have a wide range of temperature and pH values. The objective of the research reported here was to assess the effect of pH and temperature on the diclofenac anaerobic (bio)degradation potential.

MATERIALS AND METHODS

Culture Development

An enrichment cultures was developed from a contaminated sediment sample and acclimated to diclofenac. The culture was initiated by diluting 80 g of the sediment in 2 L of mineral media in a N_2-flushed, 3 L glass flask reactor, capped with a Teflon-lined stopper. At the beginning of each 7 day feeding cycle, glucose, yeast extract, and diclofenac in methanol were added resulting in initial concentrations of 300 mg/L, 17 mg/L, 10 µg/L, and 53 mg/L, respectively. The fresh media was added to the reactor by wasting 350 mL culture from the completely mixing reactor every two weeks. The culture was kept in the dark in a 22°C constant temperature room and constant pH was achieved (pH=7) by $NaHCO_3$ addition.

Temperature Assay

The effect of temperature on diclofenac biodegradation was assessed using four culture series incubated at 10, 22, 35, and 45°C. Three replicates were used in this part of the study. Control reactors were also set up in the presence of mineral media without biomass to understand abiotic degradation potential of diclofenac under different temperatures. Assays were conducted in 240-mL serum bottles sealed with Teflon-lined septa and flushed with nitrogen gas. Before the addition of electron donor and diclofenac, all cultures were incubated at their respective temperature for one day. All cultures were then amended with the same initial amount of glucose (300 mg/L), yeast extract (15 mg/L), and diclofenac (50 µg/L) dissolved in methanol (100 µL). Total COD introduced to the cultures was 1000 mg/L. In order to eliminate any electron donor limitation, cultures were fed again with glucose, yeast extract and diclofenac (in methanol) at 34 days of incubation.

pH Assay

The effect of pH on diclofenac biodegradation was assessed using six culture series with the following pH values (mean±stand. dev.; n = 3): 3.1±0.1, 4.6±0.1, 5.9±0.1, 7.3±0.2, 8.2±0.1, and 13.1±0.5. Three replicates were used in this part of the study. The initial pH was adjusted using 1 N H_2SO_4 or 1 N NaOH filter sterilized stock solutions. pH buffers were not used in these culture series. All cultures were amended with the same initial amount of glucose (600 mg/L), yeast extract (30 mg/L), and diclofenac (10 µg/L) dissolved in methanol (20 µL). All cultures were incubated in a 22°C constant temperature room in the dark and were manually shaken.

Instrumental analyses

Liquid samples were purified and concentrated by using OASIS HLB SPE cartridges (200 mg, 6 cc) (Waters, Millford, MA, USA). Diclofenac-*d₄* (internal/surrogate standard, 50 µg/L final concentration) injected samples were loaded to the cartridges. Diclofenac adsorbed onto cartridges were eluted using 2 mL acetonitrile and 2 mL methanol, respectively. Solvents were evaporated under gentle N_2 stream (TurboVap II, Caliper LifeSciences) to dryness. Residues were dissolved in 1 mL methanol:water (10:90). Quantification of diclofenac was performed with a triple quadrupole tandem LC-MS/MS (Thermo Accela UPLC coupled with Thermo Quantum Access tandem MS, USA). Details for the extraction procedure and quantification were given elsewhere (Topuz et al., 2013). Methane and carbon dioxide concentrations were determined by a GC unit (Agilent Technologies, Model 7890A) equipped with two columns and two thermal conductivity detectors. VFAs were measured via a gas chromatograph (Agilent Technologies, 6890N) equipped with a flame ionization (FID) detector and capillary column (DB-FFAP 125-3232).

RESULTS AND DISCUSSION

Temperature effect on diclofenac (bio)degradation

The effect of temperature on the diclofenac (bio)transformation was investigated with the mixed enrichment culture at an initial diclofenac concentration of 50 µg/L and a temperature range from 10 to 45°C. The initial pH of the cultures varied from 6.9 to 7.5 and the initial biomass concentration was 750±100 mg VSS/L (mean±stand. dev.; n = 8). Diclofenac profile in the culture series were given in Figure 1. In all of the cultures, in the first 10 days of the incubation period approximately 20 % diclofenac removal was observed. However, at the end of the 30 days incubation period where all of the organic carbon was consumed the concentration of the diclofenac reached to the initial value indicating no degradation in the culture. In the culture incubated at 35°C, although relatively higher (40%) removal was achieved at the beginning of the incubation, at the end of the incubation period diclofenac reached again to the initial concentration. After second feeding, a small increase in the diclofenac concentration was observed for cultures incubated at 10°C and 45°C compared to the initial concentration whereas diclofenac concentration remained constant in the cultures incubated at 22°C and 35°C. In the control reactors incubated at related temperatures diclofenac removal was not observed (data not shown). In the cultures incubated at 35° and 22°C the methane production rate was higher than the culture incubated at 45°C (Figure 2A). However, after second feeding methane production rate of the culture incubated at 45°C was higher than the other cultures. VFA profiles reflected that acetic acid was consumed very fast in the first feeding whereas an accumulation of acetic acid was observed in the culture incubated at 22°C reflecting temporary inhibition of methanogens in this culture. As a result of the methanogenic activity decrease at low temperatures acetic acid reached to 1000 mg/L in the culture incubated at 10°C.

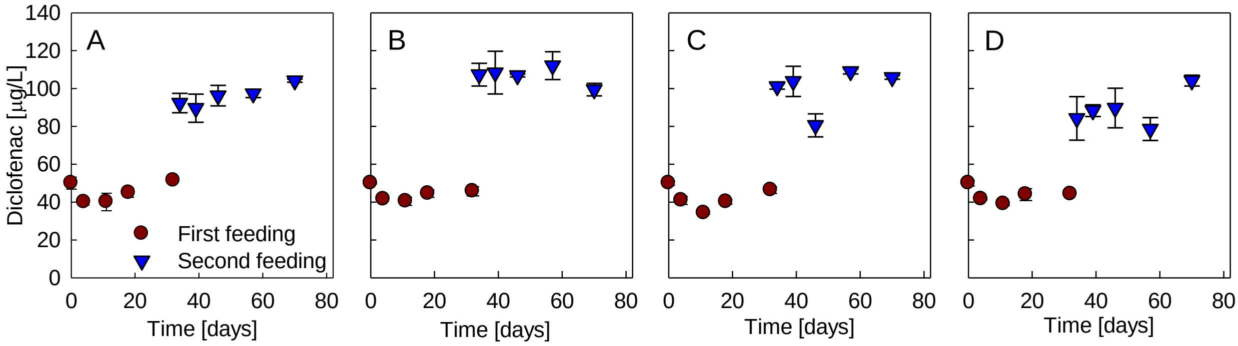

Figure 1. Time course of diclofenac during a batch biotransformation assay conducted at 10°C (A); 22°C (B); 35°C (C); and 45°C (D) using the diclofenac-enriched culture.

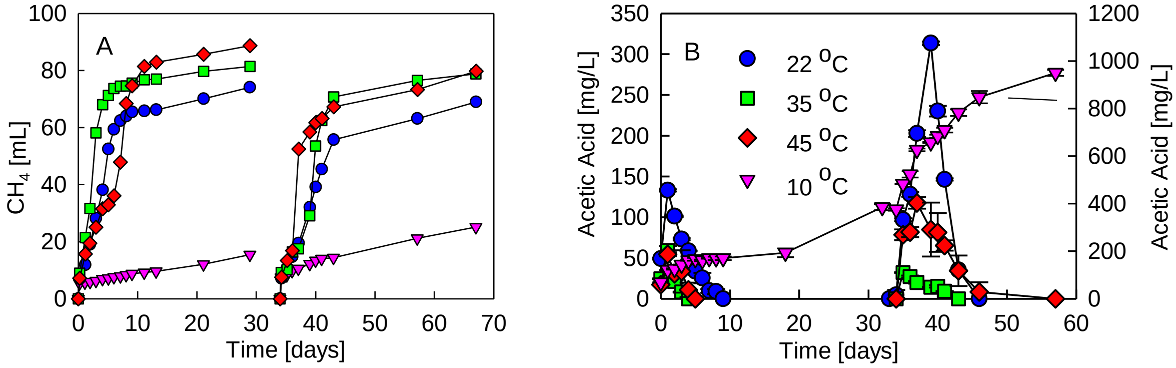

Figure 2. Cumulative methane production (A) and VFAs profile (B) in the cultures incubated at different temperatures.

pH effect on diclofenac (bio)degradation

The initial biomass concentration in these cultures was 390±50 mg VSS/L (mean±stand. dev.; n = 12). In the control reactors (without biomass) diclofenac concentration remained constant (Figure 3) indicating no degradation is possible under abiotic conditions. However, in the culture as well as in the control reactor incubated at pH 3.1±0.1 measured diclofenac concentration was half of the added concentration. This decrease can be explained by either chemical decomposition at low pH values or sorption to the solid phase (Narumiya et al., 2013). Moreover, an increase in the diclofenac concentration was observed as the incubation pH increased. The highest methane production rate was observed in the pH 7.3±0.2 culture (Figure 4A). Although there are methanogens that live in extreme pH environments, the optimum pH observed for methanogenesis was at pH 7.3±0.2 and 8.2±0.1. At the end of 31 days incubation a decrease in biomass was observed in cultures incubated at pH values of 3.1±0.1, 4.6±0.1, and 13.1±0.1 (Figure 4B). Meaningful diclofenac removal was not observed in any of the culture series during incubation. According to these results, it could be concluded that diclofenac is a very recalcitrant compound and its anaerobic (bio)degradation cannot be achieved even at changing environmental conditions. The results indicate that further investigation is required to achieve complete degradation of diclofenac as well as other persistent micropollutants before uncontrolled direct release to the receiving environment.

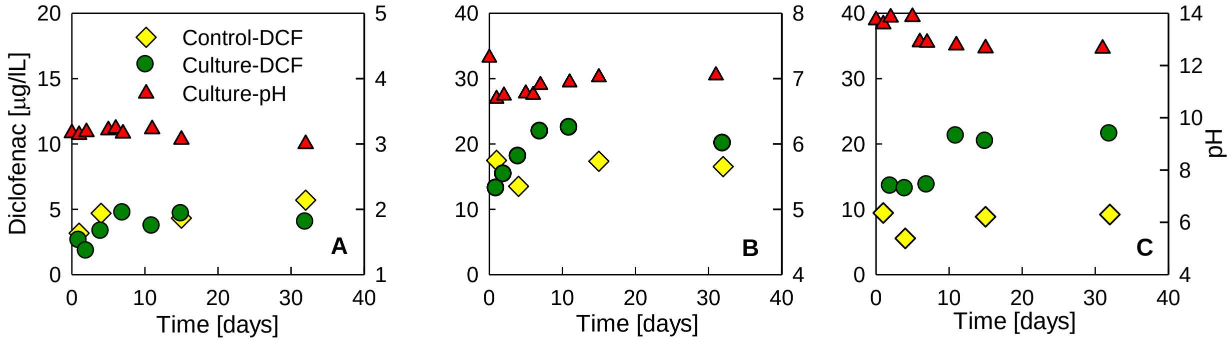

Figure 3. Time course of diclofenac and pH during a batch biotransformation assay conducted at pH 3.1 ± 0.1 (A), 7.3 ± 0.2 (B), and 13.1 ± 0.1 (C) using the diclofenac-enriched culture and culture media (control) at an incubation temperature of 22°C.

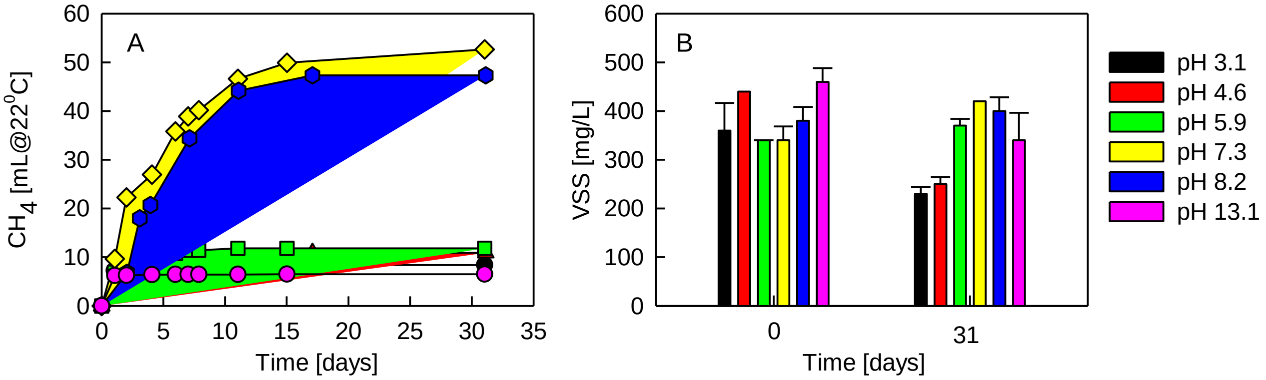

Figure 4. Cumulative methane production (A) and VSS profile (B) in the cultures incubated at different pH.

ACKNOWLEDGEMENTS

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(54) Removal of Phthalate Esters in Sewage Sludge by a Novel Filter Press Electrodewatering System

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Abstract

The objective of this work was to evaluate the feasibility and performance of removing phthalate esters (PAEs) from a biological municipal sludge by electrodewatering using a modified filter press system. Many studies show that PAEs are easily adsorbed on the sludge particles. Through such an application of biosolids as a soil modifier in agricultural activities, PAEs might end up in the last part of food chains, namely human beings. In this study it was found that the electrodewatering process employed in this work was capable of removing PAEs of concern from a biological municipal sludge. As for the most frequently detected di-n-butyl phthalate (DnBP) and di-(2-ethylhexyl) phthalate (DEHP), their average removal efficiencies were 85.63% and 75.38%, respectively.

Keywords

Biological municipal sludge; emerging pollutant; phthalate esters; filter press; electrodewatering

INTRODUCTION

Phthalate esters (PAEs) are considered as one type of endocrine disrupting chemicals that would pose potential risks to human health and the environment. The abuse of such substances has already spread in various environmental media [1]. Many studies show that PAEs are easily adsorbed on the sludge particles because of the hydrophobicity of PAEs [2]. Due to rather high concentrations of phosphorus and potassium in the biosolids, sewage sludge cake is usually reused as a soil modifier in agricultural activities. Through such an application of biosolids, PAEs might end up in the last part of food chains, namely human beings. Thus, it is worth developing a novel treatment technology for the removal of PAEs from sewage sludge when it is treated. The objective of this work was to evaluate the feasibility and performance of removing PAEs from a biological municipal sludge by electrodewatering using a modified filter press system.

MATERIALS AND METHODS

The sludge sample was collected from a sewage treatment plant in southern Taiwan. A filter press coupled with carbonaceous electrodes was employed for electrodewatering tests. In each test, 50 min of mechanical dewatering (MDW) followed by 20 min of electrodewatering (EDW) were practiced. Eight tests carried out under various operating conditions were given below: normal application of the electric field strength of 30 V/cm or 45 V/cm; with or without polarity conversion; and adjustment of the electric field strength from 30 V/cm to 45 V/cm or from 45 V/cm to 60 V/cm. Ultrasonic solvent extraction and silicone purification procedures were employed for the pre-treatment of raw sludge and sludge cake after freeze-drying. Then the analysis of eight concerned PAEs was conducted by liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS). On the other hand, the filtrate obtained from the dewatering process was subjected to solid-phase extraction instead using the Oasis^{TM} HLB cartridge. In this work PAEs of concern were dimethyl phthalate (DMP), benzyln-butyl phthalate (BBP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), diisononyl phthalate (DiNP), and diisodecyl phthalate (DIDP).

RESULTS AND DISCUSSION

Table 1 shows the average concentrations and detection frequencies of eight PAEs resulted from electrodewatering of a biological municipal sludge in this work. The average concentrations of the filtrate samples obtained from MDW and EDW were in the range of 0.01-1360 μg/L, whereas 137.84-5114.25 μg/kg for raw sludge and sludge cake. As for the detection frequency, it ranged from 0% to 100% for different PAEs. Of which, DnBP and DEHP were detected in all liquid and solid samples. Therefore, DnBP and DEHP were selected for the evaluation of their removal efficiencies in this novel electrodewatering process. The results are given in Table 2. The overall removal efficiency of DnBP ranged from 60.68% to 95.94%, whereas 44.39-89.40% for DEHP removal. This finding is in line with the general understanding that DEHP is relatively stable and recalcitrant compound as compared with other PAEs.

Table 1. The average concentrations and detection frequencies of eight PAEs in a biological municipal sludge subjected to the novel electrodewatering system under various operating conditions.

Item	DMP (ppb)	BBP (ppb)	DEP (ppb)	DnBP (ppb)	DEHP (ppb)	DnOP (ppb)	DiNP (ppb)	DiDP (ppb)
Filtrate from MDW	0.01 (1)	0.20 (4)	-	0.19 (8)	5.08 (8)	789.80 (4)	-	-
Filtrate from EDW	0.02 (5)	0.16 (5)	0.02 (7)	1.45 (8)	32.97 (8)	1360.12 (5)	-	-
Raw sludge	-	-	-	160.46 (8)	2755.88 (8)	-	-	-
Sludge cake	-	-	-	137.84 (8)	5114.25 (8)	-	-	-
Detection frequency, % (n)	**18.8(6)**	**28.1 (9)**	**21.9 (7)**	**100 (32)**	**100 (32)**	**28.1 (9)**	**0.0**	**0.0**

Table 2. The overall removal efficiencies of DnBP and DEHP of a biological municipal sludge subjected to the novel electrodewatering system.

	Removal efficiency (%)								
	Test 1	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**	**Test 7**	**Test 8**	**Ave.**
DnBP	89.90	94.92	81.08	60.68	92.44	95.94	78.46	91.67	85.63
DEHP	82.90	79.49	83.75	77.51	89.40	82.54	44.39	62.06	75.38

CONCLUSIONS

Based on the test results obtained, it was found that the novel electrodewatering system employed in this work was capable of removing PAEs of concern from a biological municipal sludge in addition to a great reduction in moisture content of the sludge cake. As for the most frequently detected DnBP and DEHP, their average removal efficiencies were 85.63% and 75.38%, respectively.

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(55) Identification of new transformation products during enzymatic treatment of tetracycline and erythromycin antibiotics at laboratory scale

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Abstract

During last decades, antibiotic compounds have been considered "emerging contaminants" due to their high consumption and pseudo-persistence in the environment being waste water treatment plants (WWTPs) one of the main inputs into the environment, since their elimination is far to be 100% for many of these compounds. This mild elimination represents an environmental problem since antibiotics can find their way to natural environment trough the effluent wastewaters, since they are directly discharged into the river.

This work describes the use of enzymatic decontamination process at laboratory scale for two highly consumed antibiotics (tetracycline (Tc) by laccase from *Trametes versicolor* and erythromycin (ERY) by EreB esterase) as a complementary treatment in WWTPs. The analysis of the samples was carried out by a fast and simple method based on the novel configuration of the on-line turbulent flow system coupled to the hybrid linear ion trap - high resolution mass spectrometer LTQ-Orbitrap in order to monitor the presence of any relevant transformation product (TP)

Degradation rates obtained for Tc and ERY without the presence of mediators were ~78% and ~50%, respectively. Concerning the identification of transformation products after enzymatic treatment, three suspected TPs of Tc and five of ERY have been proposed. In addition, the evaluation of the antibiotic activity of the samples along the enzymatic treatments showed a decrease around 100% in both cases.

The promising results of enzymatic treatment (quantitative decrease of antibiotic concentration and antibiotic activity in the samples treated) allows us to recommend the enzymatic decontamination approach, as a reliable complementary water treatment for elimination of antibiotics.

Keywords

Turbulent flow chromatogarphy; High resolution mass spectrometry Orbitrap; Enzymatic decontamination; Tetracycline antibiotic; Erythromycin antibiotic; Transformation products

EXPERIMENTAL SECTION

Biodegradation experiments

Biodegradation of tetracycline. Tc biodegradation experiments were performed in 20 ml volumes with Tc at 100 µg/ml and 0.5 mg/mL of Sigma 51639 product (i.e. 17.5 µg/ml of laccase enzyme based on the SDS-PAGE analyses of the Sigma product), at 20°C ± 1°C, in 50 ml Falcon tubes (n = 4) and without shaking. The complete reaction was acquired after 18 h of treatment based on the results of the antibiotic activity test (bioassay based from quantification methods used to determine Minimal

Inhibitory Concentrations (Wiegand *et al.* 2008)).

Biodegradation of erythromycin. The experiments were performed at lab-scale in 20 ml shake flasks with EreB esterase at 1.8 µg/ml and 100 µg/ml of ERY along 16 h. A turbidimetric antibiotic assay (Sohng *et al.* 2008) was used to monitor the antibiotic activity of ERY along the experiments.

Evaluation of transformation products generated during the treatment

The on-line turbulent flow chromatography technology coupled to a hybrid linear ion trap – high resolution mass spectrometer (TFC-LTQ Oribtrap) was used for the direct analysis of the samples. The high resolution mass spectrometer allowed the identification of the compounds with an error below 2 ppm and the elucidation of the molecular structure due to the hyphenated analyzer.

RESULTS

Biodegradation processes. The results of the study based on degradation of Tc with laccase and ERY with EreB esterase at lab-scale and without the presence of mediators can be seen in Figure 1. The antibiotic activity reached *c.a.* 0% after both processes. The promising results showed that this decontamination process could be transferred as a supplementary water treatment.

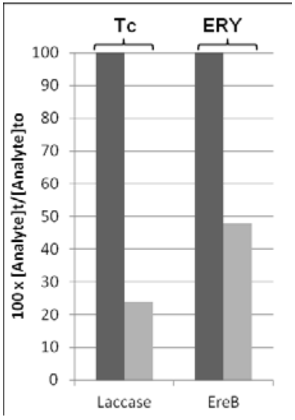

Figure 1. Biodegradation rates of 100 µg/ml of Tc by Laccase from *Trametes versicolor* (17.5 µg/ml) after 18 h and 100 µg/ml of ERY by EreB esterase (1.8 µg/ml) after 16 h.

Identification of transformation products. Concerning the identification of transformation products after enzymatic treatment, three suspected TPs of Tc and five of ERY have been proposed. In the case of Tc, the tentative molecular formulas of $[M+H]^+$ include $C_{20}H_{19}N_2O_9$ (TP 431), $C_{20}H_{14}NO_8$ (TP 396) and $C_{26}H_{30}N_6O_{12}$ or $C_{24}H_{28}N_9O_{11}$ (TP 618), with mass errors within 2 ppm in most of the cases. The postulated structures have been based on the hypothesis of dehydroxylation, (bi)demethylation and oxidation of the rings A and C as major reactions. In contrast, the major TP detected for ERY has been identified as the “dehydration ERY-A” (TP 734), with the same molecular formula of its parent compound and a mass error of 0.317 ppm, identified in a previous study (Pengelly 2010).

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(56) Chronic effects of the antimicrobial and antibiotics on microbial community structure and development of antibiotic resistance genes

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Abstract: The presence of antibiotic in wastewaters may negatively affect biological processes either by influencing the composition of the microbial community and/or direct inhibition of pollutant degradation. Besides these effects, release of antibiotics into the environment increases the risk of bacterial resistance development. The objective of this study was to investigate effects of different concentrations of tetracycline, sulfamethoxazole and erythromycin combinations on the microbial community structure and development of antibiotic resistance genes in a lab-scale anaerobic sequencing batch reactors. Polymerase chain reaction coupled with denaturing gradient gel electrophoresis analysis was used to detect the structural changes of the microbial community in terms of bacterial and archaeal 16S rRNA genes. Additionally the variations of eight tetracycline resistance genes *tet*(A), *tet*(B), *tet*(C), *tet*(D), *tet*(E), *tet*(M), *tet*(Q), *tet*(S) and *tet*(W), three sulfamethoxazole genes *sul1, sul2* and *sul3* and four eryhtromycin genes *erm*(A)*, erm*(F)*, erm*(B) during the operation was determined by and quantitative real time polymerase chain reactions. The results indicated that, antibiotics concentrations could substantially change the structure of the microbial community. At the higher antibiotic concentrations, the accumulation of resistance genes in the sludge is greater.

Keywords: Antibiotic mixture; resistance genes; microbial community

1. Introduction

Antibiotics resistant bacteria and drug resistance genes have become an important environmental contamination issue that is receiving increased attention The connection between antibiotic use and the emergence of antibiotic resistant bacteria is well reported (Wang and Schaffner, 2011).It is known that antibiotic contaminated wastewaters directly affect the microbial community structure, their activities on the degradation of pollutants in the biological treatment plants and also natural ecosystems. The study aimed to provide useful information about the combined effects of antibiotics on anaerobic microbial community structure and development of antibiotics resistance in an engineered designed environment.

2. Material and Methods

Two of 1,75 L anaerobic sequencing batch reactors (ASBRs) were set up and operation of the reactors was performed using the method described by Cetecioglu et al. (2013). Two reactors were operated at 35±2°C with a hydraulic retention time (HRT) of 2,5 days, a solids retention time of 30 days, and an organic loading rate of 2,5 kg COD/ (m^3/day). One rector, as control, was fed with synthetic wastewater while the other was fed with synthetic wastewater with ETS mixture. The influent antibiotics concentration was increased in a stepwise manner during 3 operational phases and tested antibiotic concentrations are given at Table 1.

Table 1. Tested antibiotic concentrations

	Sulfamethoxazole	*Erythromycin*	*Tetracycline*
Phase 1	5 mg/L	0,5 mg/L	0,5 mg/L
Phase 2	10 mg/L	0,5 mg/L	0,5 mg/L
Phase 3	10 mg/L	1,0 mg/L	1,0 mg/L

Each phase was operated during 1 sludge age (30 days). Samples which were taken from full mixture of ASBRs at 10th, 20th and 30th days for determining microbial community and quantifying antibiotic resistance genes. Community profiles Archaea and Bacteria within the reactors were obtained using DGGE analysis of PCR amplification as described by Cetecioglu *et al.* (2009). Antibiotics resistance gene were quantitatively studied with Q-PCR as described by Munir *et al.* (2011).

3. Results and Discussion

3.1 The influence of ETS on the structure of the ASBR microbial community

The DGGE results of the ASBRs revealed that the microbial diversity dramatically changed, particularly in phase 3 and control reactor. The similarity between control reactor and phase 1 was the highest at 73,7%. The similarity between control reactor and phase 3 was the lowest at 53,1% During three antibiotics phase, the differences in archaeal community were more remarkable. Antibiotics concentrations causes the microbial community to undergo great changes. These results are in accordance with the study by Liu *et al.* (2012) who found that microbial communities sequencing batch reactors of dramatically changed under the pressure of O-Nitrobenzaldehyde in mg L^{-1}.

3.2 Effect of ETS on the Antibiotic Resistance Genes of ASBR

Tetracycline resistance gene *tet*(M) and *tet*(Q), erythromycin resistance gene *erm*(F) and sulfamethoxazole resistance genes *sul1, sul2* and *sul3* were detected in samples taken Phase1, 10th day of operation, while erythromycin resistance gene *erm*(A) and *ere*(A) were seen at Phase 2, 10th day of operation and tetracycline resistance gene *tet*(S) were seen at Phase 3, 10th day of operation. The rest of the targeted genes were not determined during the operation period. At the phase 3, the total number of resistance genes in the sludge was the highest, which means that antibiotics may accumulated in the sludge and pose a pressure on the microbial gene due to the removal mechanism of antibiotic was mainly attributed to adsorption onto the sludge, which is consistent with other reports (Kim *et al.*, 2005; Li *et al.*, 2010). The highest maximum number was ribosomal protection genes, *tet*(M) at 5.58×10^2 copies mL^{-1} in reactor ETS, phase 3. The maximum number of resistance genes in the sludge during the phase 3 were in the order of *tet*(M)› *tet*(Q) › sul1 › sul2 › sul3 › ermF› ermA ›tet(S) ; the lowest concentration of resistance genes was $9{,}32 \times 10^{-2}$ copies mL^{-1} for enzymatic modification gene *ere*(A).

4. Conclusions

During three antibiotics phase could substantially change the structure of the microbial community. ARGs in the reactor will proliferated under lowest antibiotics concentration and reached their highest concentration when ETS concentration was the highest at Phase 3.

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(57) Catalytic oxidation of clofibric acid and ibuprofen using bimetallic nanoparticles supported on Alumina and TiO_2 with in-situ generation of H_2O_2

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Abstract

Micro-pollutants are a special class of compounds, which have a toxic effect at very low concentration. The efficient removal of emerging hazardous and toxic organic micro pollutants belonging to the class of pharmaceuticals, pesticides, aromatic hydrocarbons etc. from water is going to be a challenging endeavour. The development of efficient Advanced Oxidation Processes (AOPs) for removal of such compounds is thus of great interest. This study investigates the efficiency of bimetallic nanoparticles (NPs) in decomposition of pharmaceuticals compounds like Clofibric acid (CFA) and Ibuprofen (IBP) by simultaneous "in-situ" generation of hydrogen peroxide from formic acid (FA) and oxygen. Clofibric acid and Ibuprofen degradation study was carried out using magnetite-Palladium and Fe-Palladium NPs synthesized by two different protocols and supported on γ-Al_2O_3 and TiO_2 catalysts at ambient conditions. Almost 90% conversion of CFA was observed with different concentration of FA using γ-Al_2O_3 supported magnetite-Pd NPs. In case of IBP, high conversion was observed in presence of 10% Fe-0.5% Pd NPs on γ-Al_2O_3 and 30% magnetite-Pd NPs on TiO_2 for 6h of reaction. All NPs were characterized by XRD, ESEM and TEM techniques.

Keywords:
Clofibric acid; Ibuprofen**,** formic acid; Fe-Pd NPs, "In-situ" H_2O_2; AOPs.

INTRODUCTION

The increase in concern regarding the presence of environmental xenobiotics such as pharmaceuticals and personal care products in surface and groundwater is due to their adverse effects on aquatic life and potential impact on human health. Non-Steroidal Anti-Inflammatory Drug (NSAID) Ibuprofen (IBP) is one of the most consumed medicine and several reports have indicated its presence in effluents of wastewater treatment plant. In spite of its significant biodegradation rate, risk remains still high due to generation of toxic by-products during its biological oxidation [1]. Clofibric acid (CFA), a primary metabolite of lipid regulator drug clofibrate, occurs in surface and groundwater due to its polar character. Although its biological effects are not completely understood, it is associated with endocrine disruption through interference with cholesterol synthesis [2]. Different AOPs in combination with different technologies have been employed for the removal of above compounds. Heterogenous Fenton- like process in combination with "in-situ" generated hydrogen peroxide could be an interesting approach towards the removal of these persistent pharmaceutical compounds. This process is preferable over bulk feeding processes as H_2O_2 is generated "in-situ" and it is consumed at an appreciable controlled rate prior to its decomposition and improves the performance of oxidation reaction. High mineralization degree of organic compounds was achieved by in situ generated H_2O_2 from formic acid (FA) and oxygen by a novel Pd–Fe catalytic system [3]. In this study we have developed bimetallic (Fe-Pd) nanoparticles as an efficient catalyst using different synthesis protocols and studied its activity in degradation of CFA and IBP by in situ H_2O_2 generation from FA and oxygen.

Catalyst preparation:

Two types of nanoparticles (NPs) were synthesized using different protocols:

Magnetite-Palladium NPs: Magnetite ($Fe^{2+/}Fe^{3+}$)-Pd NPs were prepared using appropriate amounts of $FeSO_4.7H_2O$, $Fe(NO_3)_3.9H_2O$, ammonium hydroxide, hydrazine hydrate as reducing agent and PVP as stabilizer (molar ratio Fe^{2+}/Fe^{3+}: PVP -1:3) in water at 80°C. NPs obtained were cooled and recovered by centrifugation after several washes with water, and kept in ethanol for overnight with continuous stirring. The required quantity of Pd $(NO_3)_2$ was further added to obtain the Fe: Pd molar ratio of 50:1 and reduced with hydrazine hydrate. NPs were supported on Ƴ-Al_2O_3 and TiO_2.

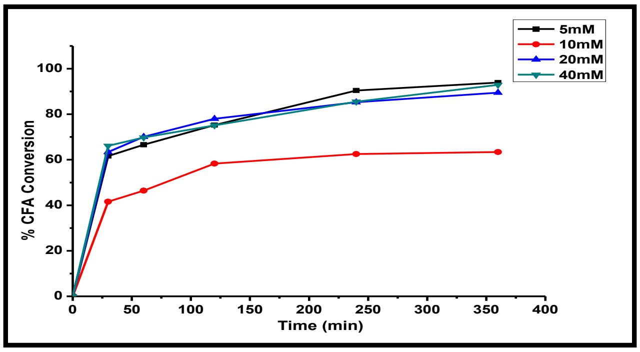
10%Fe-0.5%Pd on Ƴ-Al_2O_3 and TiO_2: 10% Fe and 0.5% Pd NPs on TiO_2 and Ƴ-Al_2O_3 were prepared using required amount of Fe $(NO_3)_3.9H_2O$, PVP as stabilizer and [Fe: PVP-1:5 molar ratio] with ethanol:DI water (50: 10 v/v) as solvent in Argon atm. $NaBH_4$ in ethanol was used to reduce Fe. After complete reduction of Fe salt, known volume of $Pd(NO_3)_2$ solution dissolved in ethanol was added. Volume was reduced by removing solvent on rota vac and further these NPs were impregnated on TiO_2 or Ƴ-Al_2O_3. After complete impregnation, sample was dried by removing solvent by rotavac and then calcined at 400°C for 3-4 h. Finally the material obtained was reduced with ethanolic solution of $NaBH_4$, centrifuged and washed with ethanol 2-3 times and again dried by removing ethanol by Rota vac.

Catalytic test

The degradation reaction of CFA (50mg/L) was carried out with 50 ml of volume, 2g/l catalyst and FA -5 to 40 mM (FA was added in two steps) in presence of 30% magnetite-Pd /Ƴ- Al_2O_3 catalyst. While degradation of IBP (30mg/L) was carried out using magnetite-Pd and 10% Fe-0.5% Pd NPs supported on Ƴ-Al_2O_3 and TiO_2 catalyst with 1L volume, 2g/L catalyst, and 10 mM FA. Oxygen was passed bubbling in both set of the reactions (20 ml/min). All the reactions were performed in darkness at ambient conditions (25°C and atmospheric pressure). Ibuprofen, clofibric acid and formic acid were monitored by HPLC.

Results and Conclusions

From Fig 1 it can be observed that almost at any concentration of FA above 90% conversion of CFA is obtained. No effect of FA concentration on CFA decomposition was observed. In spite of low conversion of CFA, complete decomposition of FA was observed with 10mM conc. Taking into account this result, decomposition of CFA with optimal concentration of FA (total 10mM) was also studied and 88% of CFA conversion with 77% FA decomposition was obtained. Concerning IBP, significant adsorption of IBP on TiO_2 supported NPs catalyst was observed during initial hour of reaction (Fig 2). Better result for IBP conversion was obtained with 10% Fe-0.5% Pd /Ƴ-Al_2O_3 catalyst but with low decomposition of FA. 30% Magnetite-Pd/Ƴ-Al_2O_3 catalyst was also tested in IBP degradation reaction using 40mM FA. Further studies will be focused on optimization of FA conc. in IBP degradation reaction and study of mineralization.



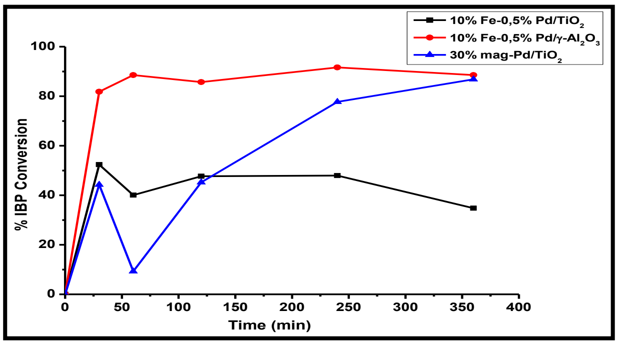


Fig 29: CFA decomposition with FA conc.5-

Fig 2: IBP conversion using different catalyst

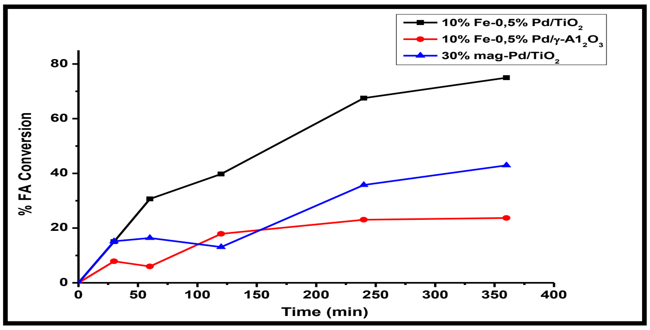


Fig 3: FA decomposition using different catalyst

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(58) Acute Inhibition Effects of Anaerobic Effluents Including Antibiotics on Aerobic Mixed Culture

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Abstract

Antibiotics used for treatment and protection in human health, veterinary and agriculture are considered as an important problem because of increasing population and developing technologies. They enter the ecosystem by both industrial and domestical wastewaters and accumulate in receiving environments. The aim of this study is to evaluate anaerobic-aerobic wastewater treatment strategy as an option for wastewaters generating from antibiotic production streams. ISO 8192 method is used to assess acute inhibitory effects of anaerobic effluents of this kind of wastewater. The results revealed that anaerobic treatment effluent could include antibiotic mother compounds with transformation products but they do not affect negatively aerobic mixed culture. So, anaerobic-aerobic treatment strategy is a good option for pharmaceutical industry wastewater coming from antibiotic production stream.

Keywords

Anaerobic effluent; antibiotic; activated sludge; ISO8192; inhibition

Introduction

Antibiotics are biologically active and persistent substances, which have been recognized as a continuing threat to environmental stability. Approximately 100,000 tonnes of antibiotics per year are produced and consumed in the world (Wise, 2002). Among those antibiotics, sulfamethoxazole (S), erythromycin (E) and tetracycline (T) are the most widely used ones (Cetecioglu, 2013). Also the action mechanisms of these antibiotics are bacteriostatic.

The purpose of this study is to help understanding an anaerobic-aerobic treatment system strategy to proper for treatment of pharmaceutical industrial wastewater generating form antibiotic production stream. For this purpose, effluents of two lab-scale anaerobic sequencing batch reactors (ASBRs), which were fed by ES and ET with synthetic wastewater was used as test materials in acute test by described in ISO 8192.

Materials and Methods

During this study, effluents of two lab-scale ASBRs was used. These ASBRs have 1,25 L active volume and are operated in a daily –fill-and-draw- mode by using synthetic substrate mixture. The F/M ratio was 0,4 mg COD/mg MLVSS and activated sludge concentration in each reactor was 3,000 mg/l. While one ASBR was exposed to erythromycin and tetracycline (ET Reactor), the other was exposed to erythromycin and sulfamethoxazole (ES Reactor) in a stepwise manner.

ISO 8192 method is used for aerobic inhibition tests to assess the dual inhibitory effect of three antibiotics. All experiments were run under 22±2 °C and pH is set to 7,5±0,5. The activated sludge was obtained from the aeration of a sewage treatment plant and fed with synthetic municipal wastewater, which is also described in ISO 8192 (1999) method and applied as the same as another study (Cetecioglu, 2013). The treated wastewaters from different operational phases of ASBRs were fed to the acute respirometric inhibition set with different concentrations to determine the half lethal concentration (EC50) for each sample in 30th min and 180th min.

Results and Discussion

While acute effects of antibiotics on activated sludge systems have been assessed, there is only one study in the literature to show short-term inhibition/toxicity effect on anaerobically treated pharmaceutical wastewater. According to the results obtained from this study were given in Table 1. Antibiotic concentrations of ASBRs in each phase and their acute inhibition effects in terms of EC_{50} concentrations were represented.

Table 1. Antibiotic concentrations of ET and ES reactor effluents and their EC_{50} concentrations within each phase

	ET_ASBR Reactor Effluent Concentration (μg/L)		30 min_EC 50 (μg/L)		180 min_EC 50 (μg/L)		ES_ASBR Reactor Effluent Concentration (μg/L)		30 min_EC 50 (μg/L)		180 min_EC 50 (μg/L)	
	E	T	E	T	E	T	E	S	E	S	E	S
1. Phase	50	60	185	529	540	529	50	300	20184	2018416	250	6567
2. Phase	170	170	4	196	200	196	160	4200	253	6645	157	1543
3. Phase	470	460	3	41	51	41	400	4000	14	198	95	585
4. Phase	460	450	NA	NA	42	14	360	8300	11	138	6	569
5. Phase	970	950	3	14	14	8	850	8300	ND	6	6	61
6. Phase	950	900	1	8	8	4	800	14000	ND	4	4	40
7. Phase	1450	1400	1	4	4	3	1360	13500	ND	4	2	1
8. Phase	1430	1380	1	3	3	1	1300	18300	ND	2	ND	2
9. Phase	1800	1750	ND	ND	2	ND	1820	18500	ND	1	ND	2
10. Phase	2320	2240	ND	ND	1	ND	2400	23800	ND	ND	ND	ND

As seen in Table 1, the effluents of ET reactor were more inhibitory than ES reactor. Synergistic effect of the erythromycin increased with tetracycline. In a similar study carried out by Cetecioglu (2013) showed that also dual effect of ST was more inhibitory than triple effect of ETS. So it is obvious that tetracycline has a negative effect on aerobic system than other compound in a synergistic composition. Also when compared the results, their single and joint effects on anaerobic systems, single effect of these selected antibiotics are higher than their dual and triple effects (Cetecioglu et al., 2012; Ozbayram, 2012).

According to the results, it can be concluded that anaerobic treatment can be an option as pre-treatment method for pharmaceutical industrial wastewaters including antibiotics prior to aerobic treatment. Despite activated sludge system is inhibited by low concentration of antibiotic mixture, while it could tolerate the higher concentration of the same mixtures after an anaerobic pre-treatment (Cetecioglu, 2013). In the future, a lab scale anaerobic-aerobic system could be operated to improve this approach and also as a second step of scale-up. Yet, it should be noted that ISO 8192 procedure only provides an index value as in many other similar procedures. In the future, a lab scale anaerobic-aerobic system could be operated to improve this approach and also as a second step of scale-up.

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(59) Benzothiazoles/Benzotriazoles In Wastewater: Constructed Wetlands As Emerging Treatment Technology?

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Abstract

This paper addresses the issues of using constructed wetlands for the treatment of wastewater containing benzothiazoles and benzotriazoles. The application of these substances, their occurrence in the environment and the treatment in activated sludge systems is discussed. Constructed wetlands were found to be an attractive alternative to activated sludge systems in terms of their efficiency in removing the discussed substances. However, the limited information on the fate and removal of benzothiazoles and benzotriazoles in constructed wetlands necessitates further research.

Keywords
activated sludge, constructed wetlands, benzotriazoles, benzothiazoles, wastewater,

INTRODUCTION

Benzotriazoles and benzothiazoles are high production volume chemicals that are widely used in various industrial processes and in households (Matamoros et. al., 2010; Weiss and Reemtsma, 2005). The substances belonging to the group of benzothiazoles are used as vulcanization accelerators in rubber production, as antifungal agents in paper and leather manufacturing (Matamoros et. al., 2010). 2-(mercapto)benzothiazole (MBT) serves as a biocorrosion inhibitor in various industries (Reemtsma et al., 1995). Benzotriazoles due to their complexing properties are used as corrosion inhibitors (Ding et al., 2010; Giger et. al., 2006, Weiss et. al, 2006). In households, benzotriazoles are used as components of dishwasher detergents (Ding et al., 2010; Giger et al., 2006). Benzotriazoles have been classified as being toxic to aquatic organisms, potentially carcinogenic and showing estrogenic activities (Giger, 2006; Matamoros et al., 2010). Removal efficiency for some of these compounds in conventional activated sludge system ranged from 0 to 74% for benzotriazoles and 5 to 28% for benzothiazoles (Kloepfer et al., 2005; Voutsa et al., 2006; Felis et al., 2010).

REMOVAL AND FATE OF BENZOTHIAZOLES AND BENZOTRIAZOLES IN CONSTRUCTED WETLANDS

To the best knowledge, there are only several articles that address the issue of the removal and fate of benozthiazoles and benzotriazoles in constructed wetlands (CWs). Castro et al. (2005) in a review dedicated to alternative treatment methods for aircraft deicing fluid waste stated that CWs have the potential for the removal of benzotriazoles especially by the vegetation-induced processes. This statement was, however, not supported by data for CWs at any scale. Bester and Schäfer (2009) used laboratory-scale activated soil filter planted with common reed to study the removal of several micropollutants from storm- and wastewater. This system was operated as continuous downflow CW. The findings of Bester and Schäfer (2009) proved that high removal efficiency (98%) for MBT was possible in this type of CW and was attributed to sorption by peat present in the CW (Bester and Schäfer, 2009). Matamoros et al. (2010) studied the removal of benzothiazoles and benzotriazoles in two CWs used either for secondary or tertiary treatment. The tertiary treatment system was a surface flow CW with a hydraulic retention time of 720 h and 616 PE. The secondary treatment system was a pilot-scale vertical downflow system with unsaturated bed and hydraulic retention time of 6 h and 2.4 PE. The authors found that the efficiency of the surface-flow CW was considerably affected by seasonality. The observed warm-weather removal was much higher for benzothiazole and benzotriazole (approx. 80% and 50%, respectively) than the removal characteristic for the cold weather, which was negative or equal to 0%. This observation may correspond to the enhanced photodegradation of the compounds studied, but even more to the stimulation of biodegradation and plant uptake during summer season. The removal efficiency of the selected benzothiazoles and benzotriazoles was invariably higher in vertical flow CW and was within 80-90%. The data for vertical flow CW was given only for the warm season (Matamoros et al., 2010).

CONCLUSIONS

Constructed wetlands due to combination of photodegradation, plant uptake and biodegradation can be a competitive solution to removing benzothiazoles and benzotriazoles from wastewater. It is unclear, which of the proposed removal processes plays a major role in the elimination of the substances of interest. The available yet limited data indicates that vertical flow systems with unsaturated bed, which stimulate aerobic processes, are the most efficient in the removal of benzothiazoles and benzotriazoles. This observation allows hypothesis that biodegradation and plants uptake rather than photodegradation by sunlight are responsible for the removal of these substances. This is because the wastewater in vertical flow CWs is present on the surface of the bed only for a short time as compared to the flow within the bed, thus the contact time of wastewater with sunlight is brief. Further research on the fate and removal of benzothiazoles and benzotriazoles in CWs is required. This research need has been addressed by the authors of this paper by establishing microcosm experiment using vertical downflow columns with the aim of studying the removal and fate of benzothiazoles and benzotriazoles form simulated domestic wastewater spiked with single-component solutions of each substance. The implications of the ongoing experiment (currently at an early stage) will be further discussed during the poster presentation.

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(60) Metabolism of Sulfamethoxazol in *Brassicaceae*

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Abstract

Sulfamethoxazol is an antibiotic that belongs to the group of sulfonamides. It is frequently used in human and veterinary medication and remains one of the most frequently found antimicrobial agents in wastewater and even ground waters. With its poor elimination rates in traditional wastewater treatment processes, the remediation of contaminated wastewaters with the use of plants seems to be a promising and cost effective option. In this pilot study we could show uptake and metabolism of Sulfamethoxazol into a root cell culture of *A. rusticana* and in *B. juncea*, a plant species frequently used in phytoremediation.

Keywords

Sulfamethoxazol; Phytoremediation; LC-MS

INTRODUCTION

During recent years the appearance of pharmaceutical compounds in the environment has drawn the attention of authorities and the scientific community to the insufficient waste water treatment process for novel pollutants. All of these compounds have in common an initial purpose to have an impact on living organisms. Belonging to the group of sulphonamides Sulfamethoxazol is an antibiotic widely used in human and veterinary medication. Its mode of action is based on the inhibition of folic acid synthesis in bacteria. In human body a large portion of SMX undergoes metabolisation, resulting in a number of metabolites that are excreted via the urine. Additionally 15-25 % percent of the drug leave the body unaltered.

As a polar compound, SMX shows only low absorption rates in sewage sludge. Together with its poor biological and photochemical degradation, the elimination of SMX during the wastewater treatment process only reaches 0-30 % in most of the cases.

Plants are capable of taking up and metabolising organic compounds from soil or water. In accordance to the mammalian metabolisation, the detoxification of xenobiotics in plant often is referred to as the green liver concept.

MATERILAS AND METHODS

Root cell culture

A hairy root culture of horseradish (*A. rusticana* L.) that was transformed by *Agrobacterium rhizogenes* strain A4 as previously described by Nepovim and coworkers (2004) was used. Cells were grown in Erlenmeyer flasks in 100 ml full-strength MS medium containing thiamine and inositol for 10 days. Sulfamethoxazol was added to the nutrient solution to set up a final concentration of 50, 10 and 1 µM in three biological replicates. Cells were harvested after six days, dried on lint tissue paper, immediately frozen in liquid nitrogen, and stored at −80°C for LC-MS analysis. Additionally medium samples were taken for SMX analysis.

Cultivation of *B. juncea*

Brassica plants were grown in perlite and MS-Medium under greenhouse conditions for seven weeks. SMX was added to the growth medium to the final concentrations of 10 and 50 µM. Plant samples were taken after 24, 48 and 120 hours after SMX exposure. Roots and leaves were separated and stored at -80°C for further analysis.

LC-MS Analysis

LC–MS analysis was carried out on a HPLC system (Varian ProStar 210) coupled to an ion trap mass spectrometer (Varian 500-MS), operated in the positive ion mode as described elsewhere (Huber et al. 2012). The HPLC eluent was introduced to the mass spectrometer using a pneumatically assisted electrospray source. The interface was adjusted to the following conditions: capillary voltage, 54 V; needle voltage, 4250 V; sprayshield voltage, 600 V; nebulizer gas pressure, 50 psi; drying gas pressure, 30 psi; drying gas temperature, 300°C. A 5-µl aliquot of each sample was directly injected into the HPLC system. MS/ MS spectra were obtained by collision-induced dissociation using helium as the collision gas.

The HPLC conditions were as follows: the column was a Phenomenex HYDRO-RP column (C18, polar endcapped; particle size 5 µm; 4.6×200 mm ID). SMX and its metabolites were separated using a linear gradient of eluents: buffer A (H_2O, 0.1% formic acid) and buffer B (acetonitrile, 0.1% formic acid). The flow rate was 0.3 ml/min. All solvents used for LC–MS were of the highest grade available, filtered and degassed before use.

RESULTS

SMX could be detected within the root and leave tissues of *B. junceae* as well as in the hairy root cells of *A. rusticana*. During MS/MS fragmentation SMX showed a base peak of m/z 156,2 at a retention time of 5,88 minutes. Further analysis a *Full Scan* measurement revealed another signal at 5,0 minutes with a m/z of $(M+H)^+$ 416 or m/z $(M+Na)^+$ 438 respectively. During MS/MS fragmentation of m/z $(M+H)^+$ a neutral loss of m/z 162, characteristic for glucose conjugates was observed.

Further fragmentation (MS^3) resulted in exactly the same fragmentation pattern as recorded for the SMX molecule itself, which clearly indicated the formation of a Sulfamethoxazol-Glucose conjugate. Interestingly in the growth medium at a retention time of 4.4 minutes another metabolite was observed with the same fragmentation properties as the Sulfamethoxazol but which could not be identified till now. A third, yet unidentified, SMX-metabolite was found exclusively in the leaves of *B. juncea* which eluted with a retention time of 6.8 minutes.

DISCUSSION

Based on these first experiments it could be shown that plants are able to uptake and metabolize Sulfamethoxazol from the growth medium. The strong similarities between the mammalian and the plant detoxification system became obvious. The plant derived SMX-Glucose conjugate parallels the most dominant metabolite in humans which is a SMX-N1-glucuronide which is excreted via urine. As plants do not have this option for excretion questions about the fate of the glycosylated metabolite within the plant arise, even though a conjugation with glucose points to the direction of eliminating the compound from the cytosol or the even more desirable formation of so called bound residues. To further identify the two unknown SMX metabolites as well as the identification of the enzyme systems that are involved will contribute to a better understanding of how plants can help to preserve our water resources for future generations.

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(61) The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in municipal waste water in Novi Sad

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Abstract

The main goal of this study was to determine fourteen analgesics/anti-inflammatories (ketoprofen, naproxen, ibuprofen, diclofenac, indomethacine, acetaminophen, salicylic acid, phenazone, propyphenazone, piroxicam, tenoxicam, meloxicam, oxycodone, codeine) in municipal waste water collected in Novi Sad. Compounds were identified and quantified using ultra-high performance liquid chromatography coupled to mass spectrometry with hybrid triple quadrupole - linear ion trap (UPLC–QqLIT–MS/MS) after solid – phase extraction (SPE).

Eleven compounds of 14 drugs were found in the analysed municipal waste water. According to the level of occurrence of target compounds found in this study the analysed analgesics/anti-inflammatories could be order as follows: ibuprofen (20.1 µg/L) > acetaminophen (15.7 µg/L) > diclofenac (1.4 µg/L) > codeine (1.0 µg/L) > ketoprofen (0.3 µg/L) > naproxen = salicylic acid (0.2 µg/L) > propyphenazone (0.1 µg/L) > phenazone (0.02 µg/L) > meloxicam (0.005 µg/L).

The obtained data will be discussed to the relevant data available literatures for municipal waste waters. The intention will be paid on diclofenac as a pharmaceutical added on watch list of EU priority compounds to be monitored.

Keywords: municipal waste water, Novi Sad, analgesics/anti-inflammatories, UPLC–QqLIT–MS/MS

INTRODUCTION

In recent years, pharmaceutical active compounds (PhACs) have provoked increasing concern, particularly as no legal requirements have been set for discharge into surface water bodies of these ubiquitous, persistent and biologically active substances (Petrović *et al*. 2014).

A significant portion of pharmaceutical wastes in wastewater is composed of analgesic/anti-inflammatory drugs which are used as pain relievers and inflammation reducers. Both groups of chemicals are extensively used without prescription with an estimated annual consumption of several hundred tons in developed countries (Daughton & Ternes 1999). There are more than 30 million people using nonsteroidal anti-inflammatory drugs (NSAIDs) every day. For example, in 2010, 28 tons of ibuprofen were used in Serbia populated with 7.5 million of inhabitants (Radonjić & Šipetić 2010), making ibuprofen the most consumed pharmaceutical.

Wastewater treatment plants (WWTPs) are not specifically designed to deal with highly polar micro pollutants, like anti-inflammatory and analgesic drugs. In surface water, concentrations of analgesics/anti-inflammatories lie between 0.001 and 4.11 µg/L (Boyd *et al.* 2003; Carballa *et al*. 2004), where in WWTP effluents the range is between 0.002 and 33.9 µg/L. Much lower levels in surface water than WWTP effluent is not only due to dilution effect, but also to the potential elimination by natural pathways such as hydrolysis, sorption, biodegradation and photolysis.

The main goal of this study was to determine fourteen analgesics/anti-inflammatories (ketoprofen, naproxen, ibuprofen, diclofenac, indomethacine, acetaminophen, salicylic acid, phenazone, propyphenazone, piroxicam, tenoxicam, meloxicam, oxycodone, codeine) in municipal waste water collected in Novi Sad.

2. MATERIALS AND METHODS

2.1 Sample

Sampling was performed in spring 2012. The analyzed sample of wastewater was prepared by mixing of grab samples collected during three consecutive days. The sampling was ensured by public water company “Vode Vojvodine”. Manual sampling was performed by trained inspectors, which are authorized for official control of contaminants in these types of samples. Briefly, each day five grab samples of equal volume (200 mL for effluent) were taken discontinuously at constant intervals over a period of 2 hours and blended.

Individual wastewater samples were collected in 500 mL amber PET bottles, previously rinsed with ultrapure water. Collected samples were kept at 4 °C until arrival to the laboratory, where they were mixed and the composite sample was processed.

2.2 Sample preparation

Procedures for the sample preparation for instrumental analysis were described in detail previously (Gros *et al*. 2009). It was based on solid phase extraction using Oasis HLB (60 mg, 3 mL, Waters Corporation, Milford, MA, U.S.A.).

2.3 Instrumental analysis

Instrumental analysis of all samples was done by high performance liquid chromatography (Waters Acquity Ultra-Performance ™) coupled to mass spectrometry with hybrid triple quadrupole - linear ion trap (5500 QTRAP mass spectrometer equipped with a turbo Ion Spray source (Applied Biosystems-Sciex, Foster City, CA, USA)) (UPLC–QqLIT–MS/MS) using a method previously developed validated by Gros *et al*. (2012).

2.4 Quality control

Calibration curves were generated using linear regression analysis and showed good fits (r^2>0.9900) over the established concentration points ranging from 0.1 to 50 or 100 µg/L depending of the compound. Quantification of target analytes, based on peak area, was performed by the internal standard approach (using of the isotopically labeled internal standards). Method detection limit (MDL) was determined as the minimum detectable amount of analyte with a signal-to-noise ratio of 3 (Table 1). Extraction recoveries for target compounds were determined by spiking samples of wastewater (n=3) at 100 ng/L (Table 1). Recovery (in %) was determined by comparing the concentrations obtained after the whole SPE procedure, calculated by internal standard calibration, with the initial spiking levels.

Table 1. Target compounds, optimized MS/MS parameters, cooresponding internal standard and the performance of the analytical method: limit of detection (LOD), limit of quantification (LOQ) and recoveries obtained for target compounds.

PhACs	Cooresponding internal standard	Precursor ion (m/z)	Q1[a]	Q3[b]	LOD(LOQ) (ng/L)	%Recoveries (%RSD) (n=3)
Codeine	Carbamazepine-d_3	300 $[M+H]^+$	152	115	8.8 (28.0)	100 (±10.9)
Oxycodone		316 $[M+H]^+$	298	241	17.1 (50.0)	112 (±5.8)
Propyphenazone	Phenazone-d_3	231 $[M+H]^+$	189	56	1.3 (4.5)	116 (±5.8)
Phenazone		189$[M+H]^+$	77	56	2.0 (6.5)	91 (±6.0)
Acetaminophen	Acetaminophen-d_3	150 $[M-H]^-$	107	-	6.0 (20.0)	139 (±7.3)
Salicylic acid		137$[M-H]^-$	93	66	4.2 (13.0)	137 (±6.0)
Tenoxicam	Meloxicam-d_3	336$[M-H]^-$	152	272	1.8 (6.0)	65 (±5.5)
Piroxicam		330$[M-H]^-$	146	266	2.0 (6.5)	76 (±3.2)
Meloxicam		350$[M-H]^-$	146	286	0.5 (±1.5)	107 (±9.8)

Naproxen	Ibuprofen-d_3	$229[M-H]^-$	170	185	3.5 (11.5)	104 (±14.6)
Ketoprofen		$229[M-H]^-$	209	-	9.0 (30.0)	108 (±14.6)
Ibuprofen		$205[M-H]^-$	161	-	1.1 (3.8)	174 (±3.5)
Diclofenac		$294[M-H]^-$	250	214	5.2 (17.1)	57 (±4.2)
Idomethacine	Idomethacine-d_3	$356[M-H]^-$	312	297	4.9 (16.4)	79 (±12.9)

[a]Quantification; [b]Confirmation

RESULTS AND DISCUSSION

In this study, eleven compounds of 14 drugs were found in the analysed municipal waste water. According to the level of occurrence of target compounds found in this study the analysed analgesics/anti-inflammatories could be order as follows: ibuprofen (20130 ng/L) > acetaminophen (15719 ng/L) > diclofenac (1338 ng/L) > codeine (1017 ng/L) > ketoprofen (247 ng/L) > naproxen = salicylic acid (208 ng/L) > propyphenazone (100 ng/L) > phenazone (13.5 ng/L) > meloxicam (5 ng/L).

The comparison of the data for selected analgesics/anti-inflammatories in municipal wastewater of Novi Sad with the relevant ones found in the literature is presented in Table 2. Rather high concentration of ibuprofen, acetaminophen, diclofenac and codeine were found in effluent discharged in Danube within Novi Sad, while the detected levels for naproxen, ketoprofen and salicylic acid were remarkably lower. Furthermore, it could be seen that there are contradictory results observed for diclofenac removal in different studies: whereas some treatments achieved removal rates up to 80% (Behera *et al*. 2011, Table 2), there were cases with insignificant removal or even with no removal at all (Clara *et al*. 2005).

Table 2. Country-wise occurrence of selected analgesics/anti-inflammatories in municipal waste water

PhACs	Influent (ng/L)	Effluent (ng/L)	Removal efficiency, %	Country
Ibuprofen		20130	-	Serbia (this study)
	3600	24	99	Sweden (Zorita *et al*. 2009)
		11000	-	China (Yang *et al*. 2011)
	39800	<LOQ	100	Spain (Gracia-Lor *et al*. 2012)
Naproxen		208		Serbia (this study)
	2560	146	94	Sweden (Zorita *et al*. 2009)
	7200			Spain (Jelić *et al*. 2011)
	3580	720	80	Spain (Gracia-Lor *et al*. 2012)
Diclofenac		1338		Serbia (this study)
	122	255	-109[a]	Sweden (Zorita *et al*. 2009)
		220	-	China (Yang *et al.* 2011)
	1500		-	Spain (Jelić *et al*. 2011)
	1490	740	50	Spain (Gracia-Lor *et al*. 2012)
	240	50	79	Korea (Behera *et al*. 2011)
	1400	1300	7	Austria (Clara *et al*. 2005)
Acetaminophen		15719	-	Serbia (this study)
		80000	-	China (Yang *et al.* 2011)
	201000	n.d.	100	Spain (Gracia-Lor *et al*. 2012)
Codeine		1017	-	Serbia (this study)
	152			Spain (Dolar *et al*. 2012)
Ketoprofen		247	-	Serbia (this study)

	2300		-	Spain (Jelić *et al*. 2011)
	1170	620	53	Spain (Gracia-Lor *et al*. 2012)
Salicylic acid		204	-	Serbia (this study)
	277000	236000	15	Spain (Gracia-Lor *et al*. 2012)

[a] increase of the effluent concentration relative to the influent concentration

CONCLUSIONS

The study revealed the presence of 11 of 14 used analgesics/anti-inflammatories in the municipal waste water collected in Novi Sad. The highest concentrations of detected analgesics/anti-inflammatories were found for: ibuprofen (20.1 µg/L), acetaminophen (15.7 µg/L), diclofenac (1.4 µg/L) and codeine (1.0 µg/L). High concentrations of these pharmaceuticals in municipal waste water is primarily associated with their high usage by the citizens of the Novi Sad.

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(62) Degradation of PCB-7 in the UV, UV/H_2O_2, O_3 and UV/O_3 processes

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Abstract

This paper deals with the problem of degradation of PCB-7, substance belonging to the group of polychlorinated biphenyls, in the UV, UV/H_2O_2, O_3 and UV/O_3 processes.The quantum yields of the PCB-7 photodegradation in aqueous solution was established to be 0.02. The estimated second-order rate constants of PCB-7 with OH* radicals was equal to 4.99×10^6 L mol^{-1} s^{-1}. For PCB-7, the determined rate constant with ozone was equal to 1.15×10^6 L mol^{-1} s^{-1}.

Keywords

degradation, kinetic constants, ozone, PCB-7, quantum yields, UV

INTRODUCTION

The term "polychlorinated biphenyls (PCBs)" refers to biphenyl derivatives, in which some (or all) of the hydrogen atoms have been substituted by atoms of chlorine. As a result of chemical synthesis, it is possible to obtain 209 congeners of PCBs. However, commercial preparations were composed of mixtures containing 60-90 congeners (Field and Sierra-Alvarez, 2008). In 2001, according to arrangements of Stockholm Convention, the production of PCBs was prohibited. However, PCBs are still used in closed electrical systems and they are still detected in different environmental compartments. Because of their properties, e.g. hydrophobicity, low biodegradability,chemical and thermal stability, they were classified as the mostpersistent pollutants in the environment (Patureau and Trably, 2006). In the literature, oxidation processes are mentioned as an effective tool to remove persistent pollutants from the environment. Therefore, in this study the degradation of PCB-7 in the UV, UV/H_2O_2, O_3 and UV/O_3 processes was examined.

MATERIALS AND METHODS

All the experiments were performed in deionized water (Milli-Q-purification system Millipore Corp.) containing the analytical standard of PCB-7 (Sigma Aldrich). The concentrations of PCB-7 during all the processes were confirmed by a high-performance liquid chromatograph coupled with UV detector. All the experiments (UV, UV/H_2O_2, O_3 and UV/O_3) were carried out in a 350-mL glass reactor (VitaTech, Germany) equipped with a polychromatic medium-pressure mercury lamp. A detailed description of the photo-reactor was presented in the previous publication (Felis et al., 2011). The lamp irradiance (E_0) was determined using actinometric investigation and it was equal to 6.19×10^{-6} Einstein L^{-1} s^{-1}. The O_3 and UV/O_3 processes were conducted as homogeneous ozonolysis processes, according to the procedure described by Huber (2004).

RESULTS

Preliminary tests

PCB-7 is a substance with hydrophobic properties that *may be adsorbed* on glass elements of the UV-reactor. In order to determine a mass loss of PCB-7 caused by sorption on the glass elements, the preliminary investigation was performed. A solution of PCB-7 (C_0 =7.85 ± 0.17 mg L^{-1}) was introduced to the reaction chamber of the UV reactor (UV lamp was turned off) and the mass loss of PCB-7 was measured every 5 min. The experiment lasted for 30 min. After 30 min of the process, the PCB-7 concentration in the solution was equal to 5.36 mg L^{-1}, which means that 2.49 mg L^{-1} (≈0.87 mg) has been adsorbed on the elements of the UV-reactor.

UV- and UV/H_2O_2-processes

The average initial concentration of PCB-7, during its direct photolysis, was equal to 9.89 ± 0.17 mg L^{-1}.

After 5 min of the process, its concentration in the reaction solution was determined to be 4.65 ± 0.63 mg L^{-1}. It corresponds to PCB-7 removal at the level of 53%. After 60 min of the irradiation, the concentration of PCB-7 was below LOQ (< 0.5 mg L^{-1}). It means that over 94% of the substance was eliminated from the reaction solution. Based on the results which were obtained during PCB-7 direct photolysis and also taking into account the adsorption level of PCB-7, the quantum yield of the PCB-7 photochemical decay (Φ) was calculated. The calculated value of the Φ parameter was equal to 0.02.

The UV/H_2O_2 experiments were performed at initial concentrations of PCB-7 and H_2O_2 equal to 10.37 mg L^{-1} and 100 mg L^{-1}, respectively. After 5 min of the UV/H_2O_2 process, the concentration of PCB-7 in reaction solution decreased to a value of 4.86 ± 0.47 mg L^{-1}, which corresponds to the removal of this compound at the level of 53%. After 30 min of the process, PCB-7 was still present in the reaction solution (C_i = 0.92 ± 0.02 mg L^{-1}) and its elimination was approximately 90%. Only after 60 min of the treatment, the concentration of PCB-7 was below LOQ. Comparing the results obtained during the UV/H_2O_2 process to the results obtained during the UV process, it can be concluded that the addition of H_2O_2 caused only slight increase of efficiency of PCB-7 decay. According to the procedure described in the previous publication (Felis et al., 2011), the second-order rate constant of PCB-7 with hydroxyl radicals (k_{OH}) was calculated. The value of k_{OH} was calculated to be 4.99 x 10^7 L mol^{-1} s^{-1}. The calculated for PCB-7 value of k_{OH} is *at the same order of magnitude as* k_{OH} values determined for other organic compounds containing atoms of chlorine in their structures (e.g. chloroform) (von Gunten, 2003).

O_3- and UV/O_3 – processes

Homogeneous ozonolysis of PCB-7 was carried out at the following ozone doses: 0.4 mg L^{-1}, 0.8 mg L^{-1} and 1.3 mg L^{-1}. The initial concentrations of PCB-7 were equal to: 3.0 ± 0.80mg L^{-1}, 3.23 ± 0.01 mg L^{-1} and 4.30 ± 0.02 mg L^{-1}, respectively. The elimination of PCB-7 was dependent on the ozone dose. The reactions of PCB-7 oxidation by means of O_3 occurred very rapidly – after 1 min of the process, and its removal was equal to 15%, 17% and 33%, respectively (proportional to the applied ozone dose). In the UV/O_3 system, the PCB-7 oxidation was followed by the reaction with hydroxyl radicals, molecular ozone and direct photolysis. The PCB-7 decomposition efficiency was also dependent on the initial ozone doses. For example, the following doses of ozone: 0.4 mg L^{-1}, 0.8 mg L^{-1} and 1.3 mg L^{-1}, after 30 min of the UV/O_3 process, caused the removal of PCB-7 from the reaction solution at the level of: 81%, 87% and 91%, respectively. Second-order rate constant for the reaction of PCB-7 with ozone (k_{O3}) was determined using competition kinetic model described by Huber (2004). Phenol was used as a reference substance. The calculated value of k_{O3} for PCB-7 was equal to 1.15 x 10^6 L mol^{-1} s^{-1}. It means that PCB-7 is susceptible to degradation by molecular ozone.

CONCLUSIONS

The estimated value of quantum yield (Φ=0.02) and the values of k_{OH} (4.99 x 10^7 L mol^{-1} s^{-1}) and k_{O3} (1.15 x 10^6 L mol^{-1} s^{-1}) were relatively high. It can be concluded that PCB-7 is susceptible to degradation in the UV, UV/H_2O_2, O_3 and UV/O_3 processes. The obtain data indicated that the above-mentioned processes may play an important role during the removal of PCB-7 from the aquatic environment

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(63) Risk assessment modelling of N_2O production for eco-activated sludge process optimization

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Abstract: There is a significant gap in the water sector for assessing the risk of nitrous oxide (N_2O) production in wastewater treatment plants (WWTPs) as operators look to optimize plant performance for cost savings and for overall eco-friendly operations. Therefore, a knowledge-based risk assessment model and modelling approach has been developed to provide a qualitative means of benchmarking WWTP design and control strategies for potential N_2O production along with traditional effluent quality and operational cost criteria. This risk assessment modelling approach leverages the knowledge gained in recent years with regard to the mechanisms, environmental conditions, and process parameters impacting N_2O production and emissions and then implements it in a rule-based system. The N_2O risk assessment model was linked to the Benchmark Simulation Model No. 2 platform to evaluate the tool's overall benchmarking potential for two different aeration control strategies. The risk model was found to be a promising benchmarking tool as it showed how risk of N_2O production can increase significantly through simple operational changes. In this paper a risk model validation case study is also included using data from a measurement campaign conducted in Florence, Italy.

Keywords: Eco, nitrous oxide, risk assessment modelling

INTRODUCTION

A tool is needed in the water sector to assess the risk of nitrous oxide (N_2O) production in activated sludge systems as wastewater treatment plant (WWTP) operators move towards energy neutrality and more eco-friendly operations through activated sludge process optimization. In light of this gap and the high global warming potential of N_2O emissions, a considerable amount of research focus has been placed on modelling and measuring N_2O production and emissions in both lab-scale and full-scale biological wastewater treatment reactors. Therefore, a significant amount of knowledge has been gained with regard to mechanisms, environmental conditions, and process parameters impacting N_2O production and emissions (Kampschreur et al., 2009; Foley et al., 2010; Ahn et al., 2010; Chandran et al., 2011; GWRC, 2011). Proposed herein is a knowledge-based risk assessment modelling approach leveraging this knowledge to provide a qualitative means of benchmarking WWTP design and control strategies for potential N_2O production, along with traditional effluent quality and operational cost criteria. The general modelling approach is consistent with that of Comas et al. (2008) for diagnosing the risk of microbiology related solids separation problems, such as filamentous bulking, foaming, and rising sludge, resulting from various activated sludge control strategies. In this study, two aeration control strategies are evaluated to demonstrate the potential of the N_2O risk assessment modelling approach. Also included is a risk model validation case study using data from a measurement campaign conducted in Florence, Italy (to be included in full paper).

METHODS

A knowledge base for the N_2O risk model was compiled (Table 1), and then represented in IF / THEN fuzzy logic rule-based system to qualitatively quantify risk on a scale of 0 to 1, through fuzzification and defuzzification (Comas et al., 2008). One particular rule based on heuristic knowledge on nitrite´s effect on N_2O production, synthesized by experts at a GHG State-of-the-Science Workshop held by the Global Water Research Coalition in Montreal (GWRC, 2011), was implemented for one of the activated sludge reactors to demonstrate the proof of concept of the N_2O risk model. Activated Sludge Model (ASM) output data was used from a modified Benchmark Simulation Model No. 2 (BSM2), with two-step nitrification and four-step denitrification (Corominas et al., 2012), to compare risk of N_2O production from nitrite concentrations in Activated Sludge Unit No. 4 (ASU4) for two different dissolved oxygen (DO) control scenarios, along with the Operational Cost Index (OCI), which includes energy costs, and Effluent Quality Index (EQI) per Nopens et al. (2010): Scenario 1 - DO set point is **2mg/l**, and Scenario 2 – DO setpoint is **1.3mg/l**. Time under high risk was considered as time steps having a risk of 0.8 or higher.

RESULTS AND CONCLUSIONS

Table 2 summarizes the results for the two different DO control scenarios. As anticipated the lower DO control resulted in cost savings based upon the OCI; however, the EQI decreased slightly and the time under high N_2O risk more than tripled, indicating the potential of total GHG emissions increasing given that N_2O is 300 times more potent than CO_2 in terms of global warming potential. Figures 1 and 2 show the dynamic N_2O risk results for Scenarios 1 and 2, respectively, graphically supporting the Table 2 summary and showing N_2O risk due to nitrite risk increase significantly through the simulation period. Also shown are N_2O risk results for the low DO and AOR risk parameters from Table 1 and how they change slightly with the corresponding change in DO control. An N_2O risk model validation case study using the data collected from a measurement campaign in Florence, Italy will also be highlighted along with a more comprehensive implementation of the knowledge base rules using the BSM2 platform for all five activated sludge reactors. As demonstrated in Table 2 and Figures 1 and 2, the qualitative N_2O production risk data, provided in addition to the EQI and OCI criteria, will allow for a more informed decision support in process optimization and can lead to more Eco-WWTP operations.

Table 1 - AS N2O Risk Model Knowledge Base

Process/ Condition	Operational Parameter / Condition	ASM Variable		Risk Classification			Mechanism	References for Operational Risk Parameter Identification	References for Parameter Values
				Low	Medium	High			
Denitrification	high NO_2	NO_2	range	<0.2	0.2 - 0.5	>0.5	- Heterotrophic denitrification - AOB denitrification	Kampschreur et al. 2009; Foley et al., 2010; Ahn et al., 2010; GWRC, 2011	GWRC, 2011
			units		mg/L				
	pH	pH	range	≥7	6.5	<6.5	Heterotrophic denitrification	Pan et al., 2012	Pan et al., 2012
			units		unitless				
	low COD/N	COD/N	range	5	4	3.5	Heterotrophic denitrification	Kampschreur et al. 2009; Foley et al., 2010; Ahn et al., 2010;	Itokawa et al., 2001
			units		ratio				
	high DO	DO	range	<0.1	0.1 - 0.35	>0.35	Heterotrophic denitrification	Kampschreur et al. 2009	Design practice for proper denitrification
			units		mg/L				
Nitrification	high NO_2	NO2	range	<0.2	0.2 - 0.5	>0.5	AOB denitrification	Kampschreur et al. 2009; Foley et al., 2010; Ahn et al., 2010; GWRC, 2011	GWRC, 2011
			units		mg/L				
	low DO	DO	range	> 1.5	0.4 - 1.5	< 0.4	AOB denitrification	Kampschreur et al. 2010	Tallec et al., 2008
			units		mg/L				
	Non-limiting DO and NH4, AOR	DO	range	< 1.8	2.15	> 2.5	AOB nitrification - NOH/NH2OH	Ahn et al., 2010, Chandran et al., 2011, Law et al., 2012	Law et al., 2012
			units		O2 mg/L				
Internal Recycle	Internal Recycle Rate	XQ	range	>10	5 -10	<5	AOB denitrification	Foley et al., 2010	Foley et al., 2010
			units		XQ				
Anoxic/Oxic transitions	Anoxic/Oxic transitions	Delta DO between reactors	range	≤0.5	1.25	≥2	AOB nitrification	Yu et al., 2010; Chandran et al., 2011	Yu et al., 2010 (transition form 0 to 4 mg/L created sharp spike)
			units		delta mg/L				
Rapid Process Changes	Spikes in NH4, flow, swings in COD:N	Delta	range	<20	30	>50	- Heterotrophic denitrification - AOB denitrification - AOB nitrification	Kampschreur et al. 2009; Foley et al., 2010	arbitrary
			units		%				

Table 2 – Summary of Scenario Benchmarking Results for N_2O Risk due to Nitrite in Reactor ASU4

	Scenario1 DO_2	Scenario2 DO_1.3
Time Under High N_2O Risk (%)	10	30
EQI (kg poll·d^{-1})	5612	5694
OCI (-)	10537	10023

Figure 30 – Scenario 1 Dynamic N_2O Risk Results for Reactor ASU4

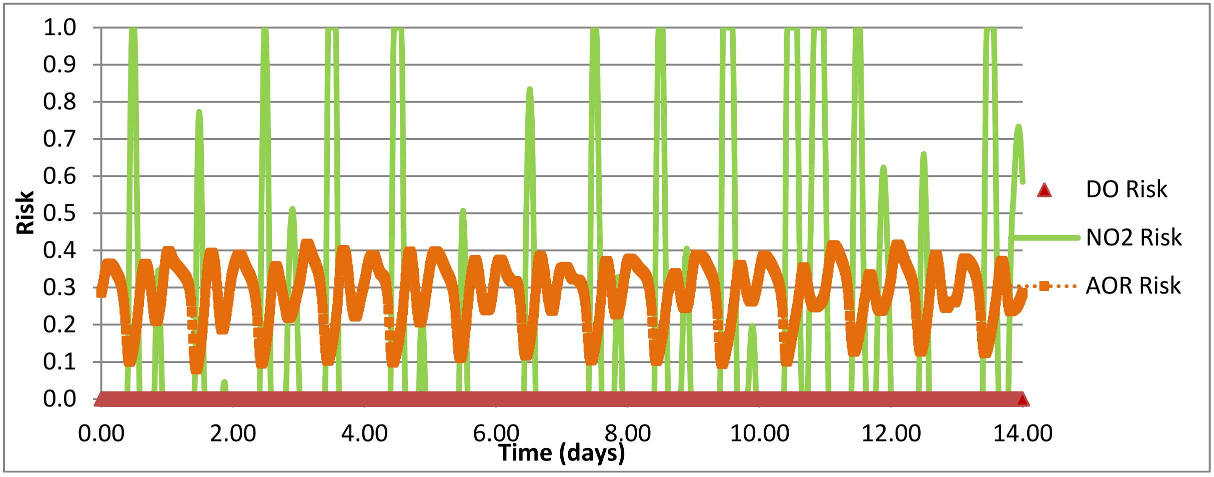
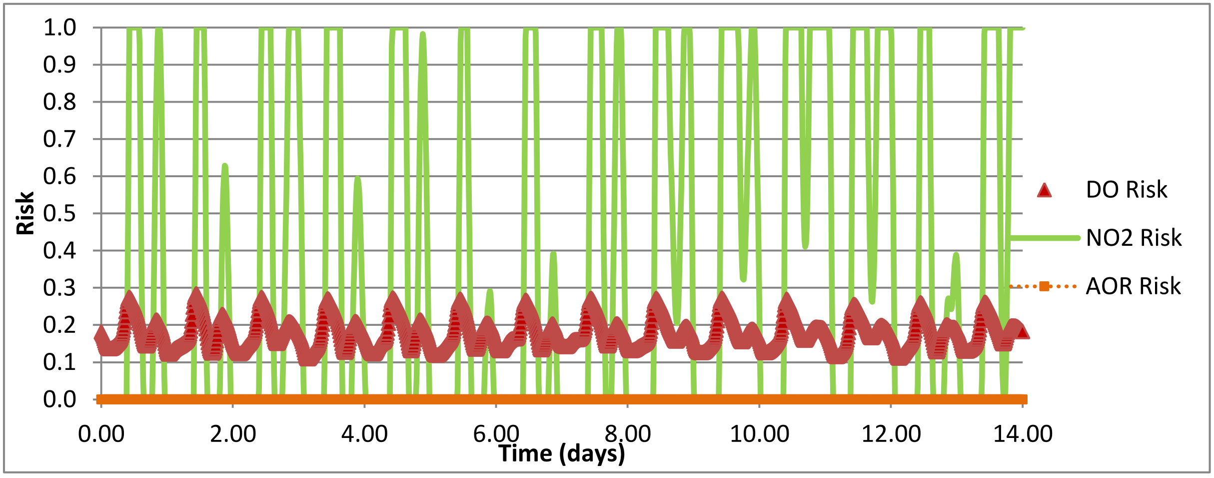


Figure 31 - Scenario 2 Dynamic N_2O Risk Results for Reactor ASU4



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(64) Network of Atmospheric Methane

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Abstract

We structured atmospheric methane sources and sinks into a well-organized network of 49 nodes and 302 links. In the network, reactions (including substrates and products) are considered as *nodes* and their pathways as *links*. Our directed network keeps sources and sinks independent of each other such that changes in the number or type of methane sources does not affect the findings related to sinks. Tracking the structure of methane sources and sinks not only provides valuable, and perhaps universal, information about the network structure, but also can lead to a better understanding of the dynamic processes that generate the network. Additionally, this network model may represent a common blueprint for the reactions (sources and sinks) of other greenhouse gases.

Keywords
Methane; source and sink; network

METHANE IN THE ATMOSPHERE

Atmospheric methane (CH_4) accounts for about 15–20% of overall global warming from greenhouse gases (second only to carbon dioxide), and has a global warming potential that is 20–30 times greater than that of carbon dioxide (CO_2).[1] The most abundant reactive trace gas in the troposphere, CH_4 has an important effect on both tropospheric and stratospheric chemistry [2] and has an atmospheric life of 8–12 years.[3,4] Of the approximately 600 million metric tons of CH_4 emitted each year,[5] about 40% comes from natural sources and about 60% from anthropogenic sources.[2,6] Methane sinks are classified into three broad pathways: tropospheric oxidation, stratospheric loss, and soil microbial reactions.

METHANE SOURCES AND SINKS

Drawing on existing literature,[1,3,6,7-10] we structured atmospheric methane sources and sinks into a well-organized small world network of 49 nodes and 302 links (including 18 reversible links), as listed in Table 1. Methane sources are not a complete network because the sources are parallel and not interconnected; thus, we used an integrated network of both sources and sinks. Methane sources are classified as anthropogenic (reactions 1–10) and natural (reactions 11–19). Major sources of methane include ruminants (reaction 7), fuel burning (reaction 4) and wetlands (reaction 11), all of which contribute more than 80 Tg CH_4/yr. Minor contributors ($<$ 30 Tg CH_4/yr) include reactions 1, 2, 8, 10, and 12–19.[2] The CH_4 produced from these sources eventually enters one of three pathways: 87% enters the troposphere, 7% enters the stratosphere, and 6% enters the soil.[6,10]

Methane that enters the soil pathway sink is degraded by microbes and is ultimately broken down to CO_2 through reactions 20–23. This is an independent pathway inside the methane sources and sinks network. The substrates and products of the soil pathway (NADH, NAD^+, and H^+ in nodes 20 and 23) are not included in the network analysis because these coenzymes/protons are ubiquitous in microbial metabolism. Similarly, O_2 and H_2O in the reactions (such as reactions 39, 40, and 47) are also ubiquitous in the atmosphere. For example, O_2 comes from and releases to the atmosphere, which has a stable O_2 content of 21%. Most CH_4 sinks involve photocatalytic reactions (reactions 24–40) through the troposphere route; a few occur at the remote stratosphere level (reactions 46–47). The two pathways are related through several reactions (e.g., reactions 42-43 and 48-49).

FORMULATION OF METHANE NETWORK

Since most CH_4 sink reactions are irreversible, we used a directed approach (e.g., A only to B) in our network analysis. We analyzed the incoming and outgoing networks separately, as has been done in the analysis of microbial metabolisms.[11] Each reaction in our network analysis is treated as an individual node; for example, reaction 1 in Table 1 is actually node 1 in our network map. Because of the complexity of microbial biochemical reactions, we list only the main substrates and products in these reactions (reactions 20–23). All outgoing/incoming reactions listed in Table 1.

For the directed CH_4 network of sources and sinks, we analyzed outgoing and incoming structures. For example, reaction 24 ($CH_4 + {}^{\cdot}OH \rightarrow CH_3{}^{\cdot} + H_2O$, Table 1) is the first reaction in the tropospheric pathway, leading directly to outgoing reaction 25 ($CH_3{}^{\cdot} + O_2 \rightarrow CH_3O_2{}^{\cdot}$); the radical $CH_3{}^{\cdot}$ is the product of reaction 24 and the substrate for reaction 25. However, the directed nature of the network prevents the product of reaction 25 from being used as the substrate of reaction 24. Also, because some nodes have more links than others, we assigned a weighted ratio (number of connections for each node divided by total network connections) to each node.[12-13] Finally, we compared the results between weighted and unweighted network nodes.

Using a small world model, we analyzed the weighted and directed network of methane sources and sinks. By analyzing the characteristic path length, clustering coefficient, and degree distribution, we obtained insights into the methane network. First, we discovered that only a few key nodes serve as hubs or limiting reactions. This makes the network highly efficient; when key hub reactions experience interruptions, pathways to other nodes can be accessed to complete the methane degradation process.

Table 1. Network nodes of methane sources

Reaction number	Reaction equation	Reaction number	Reaction equation
Sources			
1	Sewage fermentation → CH_4	11	Wetlands → CH_4
2	Animal wastes → CH_4	12	Lakes → CH_4
3	Landfills → CH_4	13	Ocean → CH_4
4	Fuel burning → CH_4	14	Forest (plants) → CH_4
5	Biomass burning → CH_4	15	Tundra → CH_4
6	Rice paddies → CH_4	16	Termites → CH_4
7	Ruminants → CH_4	17	Gas hydrates → CH_4
8	Lignite mining → CH_4	18	Volcanic mud → CH_4
9	Coal mining → CH_4	19	Geothermal → CH_4
10	Industrial loss → CH_4		
Sinks			
20	$CH_4 + O_2 + NADH + H^+ \rightarrow CH_3OH + H_2O + NAD^+$	35[a]	$NO_2 \rightarrow NO + O^{\cdot}\ ({}^3P)$
21	$CH_3OH \rightarrow CH_2O$	36	$NO + O_3 \rightarrow NO_2 + O_2$
22	$CH_2O \rightarrow HCOOH$	37[b]	$O^{\cdot}\ ({}^3P) + O_2 \rightarrow O_3$
23	$HCOOH + NAD^+ \rightarrow CO_2 + NADH + H^+$	38[a]	$O_3 \rightarrow O^{\cdot}\ ({}^1D) + O_2$
24	$CH_4 + {}^{\cdot}OH \rightarrow CH_3{}^{\cdot} + H_2O$	39[a]	$O_2 \rightarrow O^{\cdot}\ ({}^3P) + O^{\cdot}\ ({}^3P)$
25[b]	$CH_3{}^{\cdot} + O_2 \rightarrow CH_3O_2{}^{\cdot}$	40	$O^{\cdot}\ ({}^1D) + H_2O \rightarrow 2\ {}^{\cdot}OH$
26	$CH_3O_2{}^{\cdot} + NO \rightarrow CH_3O^{\cdot} + NO_2$	41	$O^{\cdot}\ ({}^1D) + H_2 \rightarrow H^{\cdot} + {}^{\cdot}OH$
27	$CH_3O^{\cdot} + O_2 \rightarrow CH_2O + HO_2{}^{\cdot}$	42	$CH_3O_2{}^{\cdot} + HO_2{}^{\cdot} \rightarrow CH_3O_2H + O_2$

28	$CH_2O + {}^{\cdot}OH \rightarrow HCO^{\cdot} + H_2O$	43[a]	$CH_3O_2H \rightarrow CH_3O^{\cdot} + {}^{\cdot}OH$
29	$HCO^{\cdot} + O_2 \rightarrow HO_2^{\cdot} + CO$	44	$CH_3O_2H + {}^{\cdot}OH \rightarrow CH_3O_2^{\cdot} + H_2O$
30	$CO + {}^{\cdot}OH \rightarrow H^{\cdot} + CO_2$	45	$CH_3O_2H \rightarrow CH_2O + H_2O$
31[b]	$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$	46	$CH_4 + Cl^{\cdot} \rightarrow CH_3^{\cdot} + HCl$
32[a]	$CH_2O \rightarrow HCO^{\cdot} + H^{\cdot}$	47	$HCl + HOCl \rightarrow Cl_2 + H_2O$
33[a]	$CH_2O \rightarrow H_2 + CO$	48	$CH_4 + O^{\cdot}(^1D) \rightarrow CH_3^{\cdot} + OH^{\cdot}$
34	$HO_2^{\cdot} + NO \rightarrow NO_2 + {}^{\cdot}OH$	49	$HCl + {}^{\cdot}OH \rightarrow Cl^{\cdot} + H_2O$

[a]photochemical reactions. [b]termolecular reactions. Node 45: omits ${}^{\cdot}OH$ in both sides of substrate and product.

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(65) Energy Management – A new challenge for a river basin management company

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Abstract

This contribution to the conference presents the actual energy management activities of Wupperverband as well as the perspective possibilities and tasks. In future Wupperverband will increase the decentralized and independent energy production to make itself autonomous of the volatile prices of electric energy und other fossil raw materials.

Keywords:
River Basin Management, Energy Management, Wastewater treatment plant, Renewable Energy,

In Germany about 10,200 sewage plants consume more than 4,400 GWh per year or 0.7 % of the total national power consumption. The main portion with about 86 % of the consumption is caused by about 2,000 sewage plants with a size larger than 10,000 population equivalents (pe).

Energy management is a new challenge for a river basin management company. Besides the given duties as a river basin manager new structures and goals have to be introduced. The paper focuses on the energy related activities in the catchment area.

Wupperverband -as an river basin management company in the catchment area of the river Wupper- operates 12 dams, 11 wastewater treatment plants, a sludge incineration plant and additional facilities, e.g. storm water retention tanks and rain basins. Wupperverband is engaged to ensure sustainable environmental protection within the catchment area of the river Wupper. In fulfilling its tasks in the field of water management – in particular the purification of sewage water, operation of reservoirs, maintenance of ecological waterways and drinking water supply – the main focus is to provide optimal utilisation for humans and the environment.

Fulfilling these tasks needs an amount of electric and thermal power. The overall electric power consumption of the river association amounts to 40 GWh with an average consumption of 33 kWh/pe on the waste water treatment plants. In addition to the electric power consumption Wupperverband needs around 45 GWh heat which is mainly generated by the heat of the CHPs and additionally by fossil oil and gas.

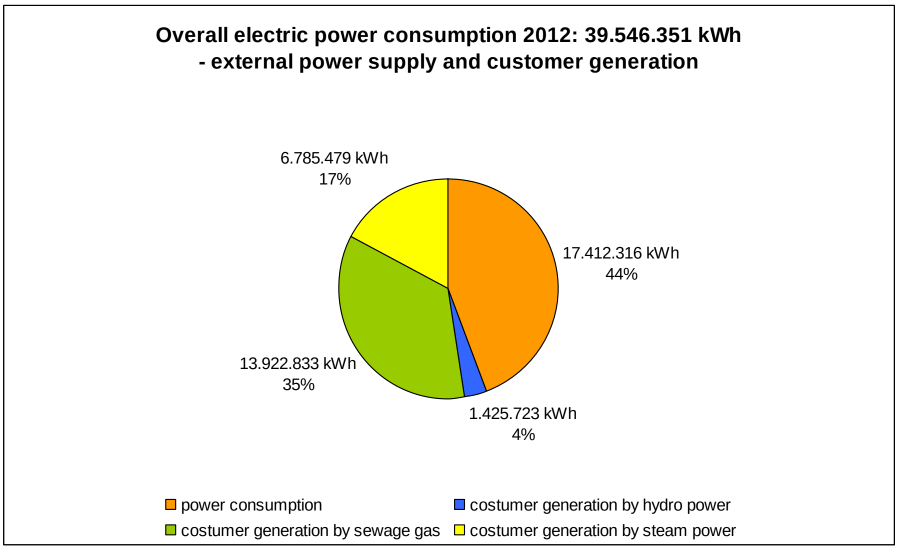

Figure 1. External power supply and customer generation 2012

Due to the structure of the river Wupper catchment Wupperverband is the main producer of renewable energy in the region (28 GWh in 2012).

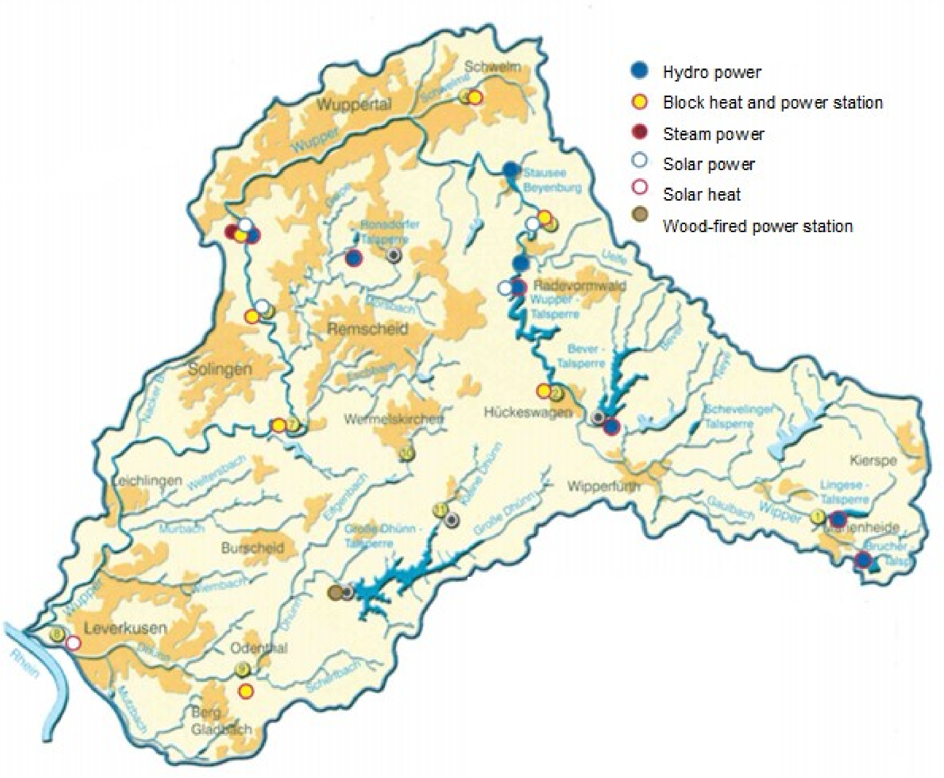

Figure 2. Renewable energy by the river basin management company Wupperverband

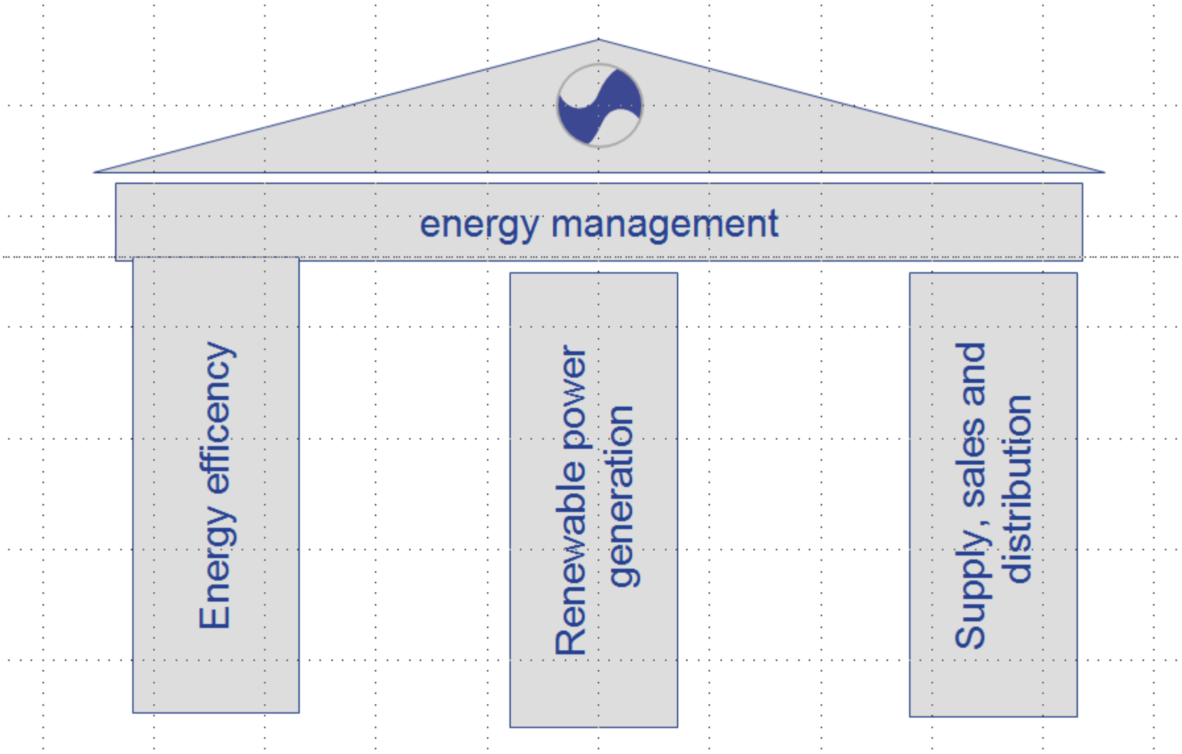

Figure 3. Three pillar strategy of energy management

The medium-term objective is to produce more electric power than needed for its task fulfilments by 2020. Cost wise there is a need to scope with energy related questions. The energy costs of the Wupperverband are the main costs of operation. The focus by this paper is the concept of energy management of Wupperverband as a river basin management company and the development of this concept for the challenges in future. In the end it comes to a three pillar strategy of energy management. The essential task of energy management is to increase the efficiency of the plants in the context of the continuous improvement process. Mainly efficient oxygen enrichment, sewage dewatering and the energy consumption of pump operation. With changing energy markets the question of load management becomes a new important topic in water management.

After putting the efficiency measures into action, the next step is to cover the required energy by customer generation. The essential possibilities consist in increasing the amount of sewage gas and a more efficient utilisation of this gas. Mainly co-digestion seems to be a successful way of increasing the amount of gas on a waste water treatment plant.

In addition to the - for a water management company - conventional possibilities of using water-power, combined heat and power plants, the structure of Wupperverband offers prospects of using steam power, wood and solar energy. During times of high electrical energy consumption there is a gap between consumption and generation because of missing storage infrastructure which has to be buffered by the national grid. Besides the classic purchase of energy the market-orientated sales of the surplus electrical power is one of the main task for the association in future. A fairly complicated german energy law needs a continuous analysis of this topic to find out what could be relevant for an water management company. All this will be ecological but it is also important for economic reasons to follow the innovative and decentralized energy concept up to the future. Treating wastewater treatment plants as an energetic island wouldn't be an effective way, but in content of a local energy infrastructure is will become an important part.

(66) Comprehensive Life Cycle Inventories for the construction of sewer systems and wastewater treatment plants

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Abstract

Many Life Cycle Assessment studies applied to wastewater treatment simply include the operation of wastewater treatment plants (WWTPs) and neglect the environmental load of the construction and demolition phases. Depending on the goal of the study the system boundaries should also include the construction of the sewer systems (SS). This has not probably been conducted for the limited availability of comprehensive Life Cycle Inventories of sewer systems construction and wastewater treatment plants (including equipment). The aim of this paper is to describe our recent developments in construction inventories. First, an approach to efficiently obtain the inventory of WWTPs construction and second, a flexible tool to facilitate SS construction inventories will be presented. The results suggest that both the construction of sewer systems and the inclusion of the equipment play a significant role when evaluating the impact of urban wastewater systems.

Keywords
Wastewater, construction, sewer systems, life cycle inventories, wastewater treatment plants

MOTIVATION

Many Life Cycle Assessment studies applied to wastewater treatment include only the operation of wastewater treatment plants (WWTPs) and neglect the environmental load of the construction and demolition phases (Corominas et al., 2013). Depending on the goal of the study, system boundaries should consider the whole urban wastewater system (UWS) and therefore also include the construction of the sewer systems. Frischknecht et al. (2007) stated that construction works contribute significantly to UWS impacts, particularly due to the construction of sewer system infrastructure (confirmed by the findings of Roux et al. (2011)) and the diluted pollutant content of domestic wastewater. Limited studies such as that by Foley et al., (2010) provide rigorous inventories for WWTPs operation, even though the inventories for WWTPs construction are not as rigorous as those for plant operation and are based on previous studies. Besides, these construction inventories do not include the equipment nor sewer systems information. Inventory descriptions do not allow the analysis of impact studies for individual unit processes within the plant but they have to be performed for the whole WWTP as a unique unit.

Construction inventories are not systematically included in LCA studies due to the limited availability of guidelines and generic comprehensive Life Cycle Inventories for the construction of sewer systems and wastewater treatment plants including plant equipment. The aim of this paper is to describe advances in construction inventories for use in wastewater treatment plant Life Cycle Assessments, including an approach to efficiently obtain the inventory for UWS construction together with a flexible tool to facilitate the development of inventories of sewer systems.

APPROACH TO EFFICIENTLY OBTAIN THE INVENTORY FOR UWS CONSTRUCTION

***Concept and description of the approach*.** The most comprehensive source of information for the construction phase of a WWTP is included in the design phase of a project, specifically in the budgeting documentation where all operations and material needed for its construction are listed. GIS or sewer system plans could offer a complete source of information with regards to the sewer systems construction.

The proposed systematic procedure involves the following steps: (i) firstly, it is necessary to identify all the unit operations and items of the construction budget or databases; (ii) these items must be identified and related to the items of the database used to create building budgets (e.g. ITEC database, a public database used for engineers and architects in Catalonia, www.itec.cat), which include information about the required mass or volume of materials and energy used per unit of each item; (iii) the material and energy used are calculated, by relating the first and second phases; and (iv), the equivalent material should be identified in a LCI database (e.g. Ecoinvent).

Although there is a part of the construction budget specific for equipment, a list of the equipment normally used for the maintenance plan is more reliable. To facilitate the inventory of the equipment it is first necessary to classify all the equipment in different groups. Secondly, information about the material composition, weight and energy used for the manufacture of each group of machines must be searched in the Environmental Product Declarations (EPD's) of these products or information obtained directly from the manufacturers. Thirdly, the equivalent material must be searched in a LCI database (e.g. Ecoinvent).

Comparison between environmental impacts of civil works vs. installed equipment at a WWTP. A comparison of the environmental impacts between the civil works and equipment installed in the Girona WWTP was performed. The Girona WWTP has a capacity of 55,000 m^3/day and consists of an activated sludge system with biological nitrogen removal. Sludge treatment is based on anaerobic digestion with biogas production which is used for electricity production. This WWTP was constructed to replace an aging plant, although some parts of the previous plant were reused. Information about the civil works was primarily taken from the construction budget while some approximations were made for the reused components of the previous WWTP.

As can be seen in Table 1, after introducing the inventory data into the SimaPro 8 software and using the CML I-A baseline and a functional unit of 1 plant, the equipment has a significant impact with respect to the civil works for the abiotic depletion and toxicity categories (around 50%), while the global warming impact of equipment is only around 10% of the civil works impact. These results only consider new equipment installed in the plant and the impacts will therefore increase when the maintenance and replacement of the equipment during the life of the plant will be taken into account.

FLEXIBLE TOOL FOR SEWER SYSTEM INVENTORIES

Concept and description of the tool. The construction phase of sewer systems can be divided into four different steps: (i) Trench excavation, (ii) laying of pipelines and the construction of other infrastructure such as manholes and pumping stations, (iii) trench refilling and surface operations, and (iv) disposing of excess soil and materials. A spreadsheet tool has been developed to facilitate the inventory of materials and energy for the construction of sewer systems. The inputs of the tool enable the user to consider all the critical aspects which have to be included in these steps such location and type of soil to be excavated, need for cleaning the area or not, the shape of the trench and the need for shoring, traffic present, size and materials of piping and distances to suppliers and landfill sites, each of which are specific to the case study. The developed tool, then, based on empirical relationships used by construction consultancies, provides the most important characteristics of the trench (depth, width, volume to be excavated, etc.) and also the quantities of the used materials and energy. Thus, this flexible tool facilitates the construction inventory phase since performs in a single phase the second and third steps of the above systematic approach.

***Comparison of different sewer system configurations*.**

In order to illustrate the usefulness of the tool, the inventory data for two different sewer systems were obtained. The first sewer system has 1 km and is located in an urban zone with traffic in the upper part of the trench, is installed in a rectangular trench in a compact soil and the pipe material is a PVC tube of 40 cm of diameter. The second sewer system is 1 km long and is located in a non-urban zone, is installed in a trapezoidal trench in a soft soil and the tube is made of reinforced concrete of 40 cm of diameter. The distances to landfill and suppliers are the same in both cases. After introducing these data into the spreadsheet tool, the inventory shown in Table 2 was obtained. It can be seen that the type of materials used and the mass for each material differs a lot between the two cases. As an example, the type of soil has an influence in the excavation. For this reason the second case needs less diesel to excavate more volume of soil due to the shape of the trench (1694 m^3 in the first case and 1727 m^3 in the second one). The location also has its importance since in a non-urban area the excess excavated soil can be normally distributed around the work and thus, it is not necessary to transport it to a landfill. Also, in an urban area, it is more usual to have traffic in the upper part, so that there is a need to place the tube deeper and to install a layer of asphalt. In relation with the tube material there are also a lot of differences between PVC and reinforced concrete.

TAKE-HOME MESSAGE

This study presents a comprehensive approach to carry out Life Cycle Inventories in urban wastewater systems. A comprehensive approach is presented to obtain the inventory of the used materials and energy for WWTPs construction and equipment, while a flexible tool can be used to facilitate the inventory phases for SS construction. This study is illustrated with two examples that conclude that in WWTPs construction, it is important to consider not only the civil works but also the equipment used. Also, in sewer systems it is important to consider not only the tube material but also aspects such as distances, type of soil, location, etc that can influence the resources used. For this reason it could be useful to carry out such studies comparing different options with the proposed tool before starting construction works.

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TABLES AND FIGURES

Table 15. Energy and material comparison between civil works and equipment for the construction of a WWTP and comparison of its potential environmental.

Resource/material	**Unit**	**Civil works**	**Equipment**
Energy	MJ	21063871	5363369
Concrete	Kg	45965593	0
Steel	Kg	1966139*	90378**
Synthetic rubber	Kg	128901	3563
Mortar	Kg	553200	0
PVC	Kg	15226	202
Cast iron	Kg	32731	47169
Bricks and tiles	Kg	287399	0
Wood	Kg	341359	307
Gravel	Kg	5345837	0
Aluminum	Kg	788	4598
Copper	Kg	0	3574
Other materials	Kg	1070384	11095
IMPACT CATEGORY			
Abiotic Depletion	%	100	47,15
Global warming	%	100	9,84
Human toxicity	%	100	53,99

*78,5% reinforcing steel; 0,5% Chromium steel; 21% Low-alloyed steel.

** 80% Chromium steel; 20% Low-alloyed steel.

Table 16. Inventory results for two sewer system examples.

Construction phase	Material	Unit	Sewer system 1	Sewer system 2
Excavation (I)	Diesel burned	MJ	77697	66829
Tube placement (II)	Diesel burned	MJ	28648	123749
	Water	Kg	152700	116700
	Polyurethane mastic	Kg	42	0
	PVC	Kg	4170	0
	Reinforcing steel	Kg	0	18540
	Concrete	Kg	0	185350
	Synthetic rubber	Kg	0	1520
	Transport	Tkm	105,3	5135
Refilling and surface works (III)	Diesel burned	MJ	108100	101297
	Granite sand	Kg	1357172	1876921
	Water	Kg	78417	77164
	Arid	Kg	252120	0
	Bitumen	Kg	11880	0
	Transport	Tkm	98776	122000
Deposition (IV)	Diesel burned	MJ	0	82181
	Water	Kg	0	64391
	Transport	Tkm	101640	0

(67) Environmental analysis of five odour treatment technologies under life cycle assessment perspective

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Abstract

Odour abatement technologies are widely implemented nowadays due to the increasing concern about atmospheric pollution. In this work, biofiltration, biotrickling filtration, activated carbon filtration, chemical scrubbing and biotrickling filtration coupled with activated carbon filtration were evaluated using the life cycle assessment methodology. An emission of 50,000 $m^3 \cdot h^{-1}$ from a wastewater treatment plant was selected as the model malodorous emission. The comparative analysis showed that biological treatments entailed lower impacts than their physical/chemical counterparts. Specifically, activated carbon filtration showed significant impacts due to its production process whereas sodium hypochlorite production was the main contributor to environmental impacts in chemical scrubbing. According to the normalized impact index, freshwater eutrophication, human toxicity, and freshwater and marine ecotoxicity presented the largest contributions, biofiltration emerging as the most recommendable technology.

Keywords

Activated carbon; biofiltration; chemical scrubbing; Life Cycle Assessment (LCA)

INTRODUCTION

Public concern about atmospheric pollution has significantly increased over the past years based on its detrimental effects on human health and the environment. For this reason and with the aim of complying with odour regulations, odour abatement technologies are widely studied, including physical/chemical and biological treatments. Estrada et al. (2011) analyzed six of these technologies by means of the Icheme Metrics and the results showed that biological treatments exhibited a superior performance than physical/chemical technologies from an economic and environmental viewpoint. In this work, a comprehensive Life Cycle Analysis (LCA) was applied in order to determine the environmental impacts of five odour abatement technologies at full-scale.

MATERIALS AND METHODS

Air emissions of 50,000 $m^3 \cdot h^{-1}$ from a wastewater treatment plant with 30 volatile organic compounds (VOCs), H_2S (20.9 mg/m^3) and methyl mercaptan at trace level concentrations were selected as model malodorous emissions (Zarra et al., 2008). Five full-scale technologies were assessed: biofilter (BF), biotrickling filter (BTF), activated carbon filtration (AC), chemical scrubbing (CS) and BTF coupled with AC (BTF+AC). Three different methodologies were applied in the LCA. Firstly, the Cumulative Energy Demand (CED), which considers direct and indirect energy use. Secondly, the malodorous air was evaluated with the methodology reported by the Centre of Environmental Science of Leiden University (CML, 2001). Finally, the impact categories evaluated in the ReCiPe Midpoint Method, v1.05 (H) were normalized and considered for a comprehensive assessment. The software SimaPro 7.3.2 was used for the analysis.

RESULTS AND DISCUSSION

The impact associated to each technology was divided in different issues: direct emissions; energy use;

chemicals consumption; production and final disposal of the packing material; transport and infrastructure material. Results showed that biological treatments presented the best environmental performance regardless of the impact category assessed. Impact normalization allows us to compare all environmental impacts using the same scale and obtaining a unique value per scenario. The factors reported by the ReCiPe methodology have been used for obtaining a normalized impact index for the technologies. BF was the most beneficial technology in terms of the normalized impact index, followed by BTF (Figure 1). The main difference among biological technologies was the impact associated to the preparation of NaOH solution added during biotrickling filtration to maintain constant pH values, which caused a higher impact in BTFs. CS presented the highest normalized impact index mainly due to the use of NaOCl solution. On the other hand, the impacts associated to AC were attributed to the manufacture of activated carbon, which is replaced every 6 months. Although the global impact of BTF+AC included the impacts associated to 2 different technologies, the lifetime of 2 years considered for the activated carbon used in this case led to a normalized index similar to the one obtained for AC. Among the impact categories evaluated using ReCiPe methodology, freshwater eutrophication, human toxicity and freshwater and marine ecotoxicity were the most relevant categories contributing to the global impact.

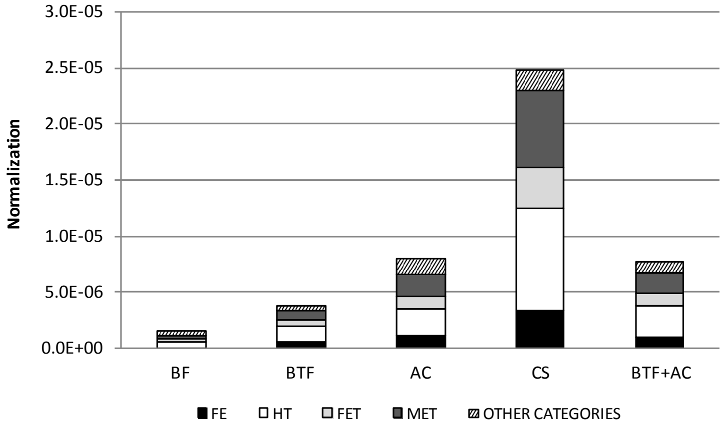

Figure 1. Normalized index for BF, BTF, AC, CS and BTF+AC (FE: freshwater eutrophication; HT: human toxicity; FET: freshwater ecotoxicity; MET: marine ecotoxicity)

The CED and malodorous air methods constitute also a valuable tool for the analysis of the environmental performance of odor abatement technologies. Biological techniques were the most effective options in terms of CED. For malodorous air, direct emissions caused the highest environmental impacts and consequently the use of technologies decreased the impact when compared with the non-treatment scenario. In conclusion, biological treatments were the most environmentally friendly option from a global perspective, whereas packing material and chemical use must be carefully considered in the operation of physical/chemical treatments.

ACKNOWLEDGEMENTS

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(68) The Relevance of Direct Greenhouse Gases Emissions on the Environmental Assessment of WWTPs

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Abstract

There is a remarkable controversy among the scientific community regarding the quantification and relevance of diffuse greenhouse gases emissions in wastewater treatment plants. This study attempts to evaluate the importance of this type of direct emissions when calculating the global environmental impact of a wastewater treatment facility. Sampling campaigns for greenhouse gases were performed on two different facilities from Atlantic and Mediterranean regions of Spain. The results showed a large contribution in the impact categories under assessment, reaching 57% of the total global warming potential impact for one of the wastewater treatment plants. Another objective of the work was to confirm the influence of different climate conditions on the performance of wastewater treatment systems.

Keywords
Greenhouse Gases (GHG); Life Cycle Assessment (LCA); Wastewater Treatment Plant

INTRODUCTION

It is widely known that Wastewater Treatment Plants (WWTPs) are a source of diffuse Greenhouse Gases (GHG) emissions. Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are the main GHG associated towastewater treatment. While the emissions of CO_2 and CH_4 have already been quantified, there is still a gap in the determination of N_2O emissions. The International Panel on Climate Change (IPPC) estimates that N_2O emissions for advanced centralized WWTPs accounted for 0.035% of the total nitrogen load. However,other authors highlighted that the IPCC guidelines underestimate the emissions of CH_4 and N_2O(Foley et al., 2010). This work tries to demonstrate the importance of the GHG direct emissions on the environmental assessment of a WWTP. For this purpose, two complete sampling campaigns including GHG emissions were carried out on two different WWTPs:Betanzos (Northwest Spain, Atlantic region) and Calafell(Northeast Spain, Mediterranean region). Data obtained was used to study the relevance of these GHG emissions on the final environmental impact of the plants, applying the Life Cycle Assessment (LCA) methodology.

MATERIALS AND METHODS

Sampling campaigns performed in July 2013 for both WWTPs included measurements in the different units of water and sludge lines (Table 17). The equipment used for the GHG measurement was based on infrared radiation absorption. Apart from GHG direct emissions, conventional physical-chemical parameters were assessed for the sampling points.

Table 17.GHG sampling campaign results per Functional Unit (1 m^3 of treated water)

	Betanzos WWTP		*Calafell WWTP*	
Treatment Unit	**CH_4 (mg/m^3)**	**N_2O (mg/m^3)**	**CH_4 (mg/m^3)**	**N_2O (mg/m^3)**
Pretreatment	546.73	11.84	-	-
Primary Settler	(-)[a]	-	49.17	n.d
Biological Reactor	1,202.73	426.34	379.0	n.d
Secondary Settler	n.d	146.01	n.d	n.d
Sludge Thickener	1,193.86	n.d	8.74	n.d

Homogenizer	749.46	n.d	-	-
Sludge Filter	184.16	27.18	570.29	n.d
Sludge Silo	1,001.32	n.d	-	-

-n.d: not detected. -a: The type of treatment unit was not present on the corresponding WWTP

A volume-based functional unit, one cubic meter of treated water, was considered as the most suitable option for the analysis. Concerning system boundaries, the study considers the environmental impact associated with the construction and operation of the WWTP, the direct GHG emissions, the final discharge of the effluent and the sludge management. Impact Categories under analysis were: Acidification (AC), eutrophication (EU), freshwater ecotoxicity (FE), global warming potential (GWP), ozone layer depletion (OD) and photochemical oxidation (PO).

RESULTS AND CONCLUSIONS

The inclusion of the GHG direct emissions increased the impact in the following categories: GWP, PO and FE. There are large differences in the relevance of GHG contribution between both case studies mainly because the absence of N_2O emissions in Calafell WWTP (Table 17). Further researchwill be carried out to determine if these variations are linked either to the type of technology (i.e. Betanzos has a Carrousel biological reactor while Calafell has a Plug flow system) or to other parameters such as climate. Results pointed out inFigure 32for GWP impact category, show an increase of circa 280 kg CO_2eq/m^3 in the case of Betanzos WWTP and 40 kg CO_2eq/m^3 in the case of Calafell WWTP, being the contribution to GWP51.2% and 15.1% respectively, and meaningfully important enough to need to be taken into account for the assessment.

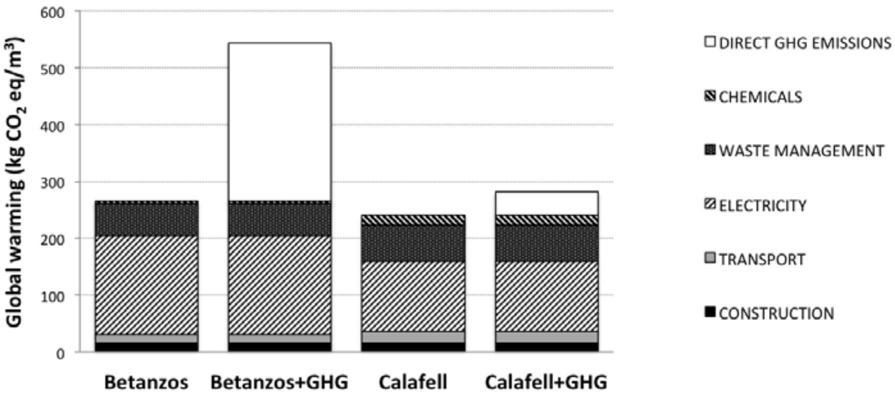

Figure 32. Global Warming Potential for both case studies with and without GHG direct emissions

By calculating the normalized impact index for both WWTPs under study, the resulting global impact of the treatment is $1.68 \cdot 10^{-10}$ for Betanzos WWTP and $1.3 \cdot 10^{-10}$ for Calafell WWTP. Anefficiency rate that expresses the total normalized impact per kg PO_4^{-3}eq removed was calculated. The performance of Betanzos WWTP resulted $7.58 \cdot 10^{-12}$ per kg PO_4^{-3}eq removed while CalafellWWTP obtained $2.02 \cdot 10^{-12}$ per kg PO_4^{-3}eq removed. As found in previous studies, the Atlantic region WWTP showed lower efficiency due to the dilution factor existing in its effluent (Rodriguez-Garcia et al., 2011).

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(69) Water quality history of the Guarapiranga Reservoir (São Paulo, Brazil): analysis of management tools

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Abstract

We examined a historical data series (1978-2010) of 9 parameters (faecal coliforms, pH, biochemical oxygen demand, total nitrogen, total phosphorous, temperature, turbidity, total solid residue and dissolved oxygen) collected at Guarapiranga Reservoir, São Paulo, Brazil, and verified the historical degradation of water and the effectiveness of two alternative tools used to monitor the quality trends: the Water Quality Index (IQA), officially adopted in Brazil, and a multiproxy approach based on a principal component analysis (PCA). Although a continuous and progressive degradation of the water quality was observed through the last three decades, the classification of waters by the IQA maintained relatively stable in the classes “excelent”, “good” and “acceptable”. On the other hand, the PCA was a more effective and informative tool to assess the degradation trends. We concluded that IQA was subjected to the eclipse effect and that the PCA is the better multiproxy tool for water quality management. Moreover, distinct factors influenced the water quality in each region of the reservoir in time and space, which denotes the temporal and spatial heterogeneity of the watershed. Thus, management actions must take into account the peculiar environmental traits of each region in order to maximize the efficiency of recovery and conservation of the water quality.

Keywords
Water quality; reservoir management; multiproxy analysis; anthropogenic impacts.

INTRODUCTION

The Metropolitan Region of São Paulo (MRSP), southeast Brazil, is the biggest urban agglomeration in South America, with 19.6 million residents dispersed in 39 cities, being the most economically developed region in Brazil. As consequence, the enormous demand for water supply creates the controversial situation of water availability per capita similar to arid regions. The Guarapiranga is the second more important reservoir in a system of 23 reservoirs that supply the MRSP and produces 14,000 L s^{-1} of water for 3.8 million people (São Paulo, 2008). Despite its strategic importance, the water quality of Guarapiranga has continuously declined as response to diverse anthropogenic impacts caused mainly by unplanned urban growth (Whately & Cunha, 2006; Fontana et al., 2014).

CETESB (Environmental Company of São Paulo State) monitors bimonthly the water quality of Guarapiranga since 1978, by collecting superficial samples in 3 fixed points (Figure 1). The company annually releases a comprehensive report of many parameters (more than 70) and water quality indexes for an overview about conformities and nonconformities in accordance to the Brazilian guidelines (Resolution CONAMA 357/05). However, there is a lack of closer analysis of the main parameters that influence the water quality and what they can reveal. Therefore, we explored the whole historical series of data to provide a more precise interpretation about the water quality trends along time and to verify the efficiency of the Water Quality Index (IQA) used by CETESB as a management tool for water monitoring.

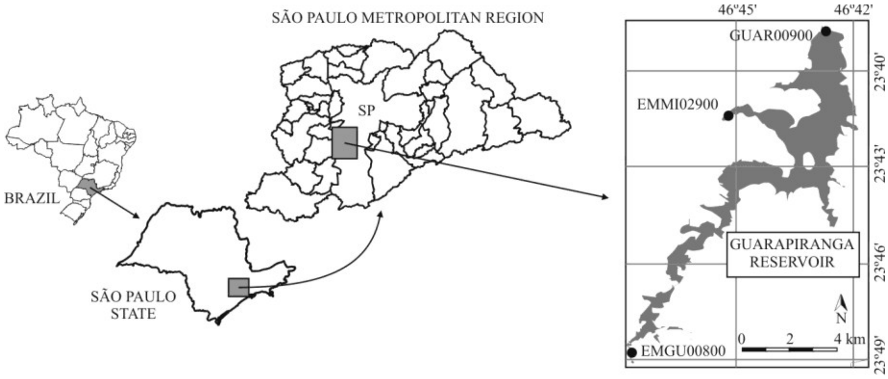

Figure 1. Location map of Guarapiranga Reservoir and fixed monitoring points. The point GUAR00900 is located at the dam.

MATERIALS AND METHODS

We selected all the data from CETESB's annual reports (1978-2010), considering only the 9 parameters that are used to calculate IQA: faecal coliforms, pH, biochemical oxygen demand, total nitrogen, total phosphorous, temperature, turbidity, total solid residue and dissolved oxygen. The IQA was adapted by CETESB from a study conducted in the 1970's by the National Sanitation Foundation (USA) for water supply monitoring. It is the result of the weighted product of the 9 parameters as follows (CETESB, 2003):

$$IQA = \prod q_i^{w_i} \qquad \text{(Eq. 1)}$$

In the Equation 1, *IQA* means Water Quality Index (ranges from 0 to 100), q_i means the quality of the parameter obtained in an average curve as function of concentration (ranges from 0 to 100) and w_i means the weigh of the parameter given as the proportion of its importance for water quality, previously determined by experts. The IQA is divided in 5 quality categories that help managers to plan actions to recover and/or conserve the water resource: "Excellent", "Good", "Acceptable", "Bad" and "Very Bad".

Considering that none of the data fitted the normal distribution (Shapiro-Wilk W test, $p<0.01$), the averages were compared using the Kruskal-Wallis non-parametric test. A principal component analysis (PCA) was executed with the main parameters to assess the water quality historical trends as a multiproxy tool alternative to the IQA. The data were previously transformed by $\log(x)+1$ and the analyses were performed using the software PAST version 2.17c (Hammer et al., 2001).

RESULTS AND DISCUSSION

Water Quality Index (IQA)

The best IQA average was observed for the point GUAR00900. However, 97% and 94% of the results of dissolved oxygen and total phosphorous concentrations, respectively, exceeded the legal limits when the waters were classified as "excellent" (Table 1). We found the same situation for faecal coliforms and dissolved oxygen concentrations in the points EMGU00800 and EMMI02900 when the waters were classified as "good". These results indicate that the IQA is subjected to the eclipse effect which occurs when many environmental parameters are aggregated in a single value and the negative impact of one parameter is attenuated by the stability of other (Silva & Jardim, 2006). This undesirable condition can potentially distort the interpretation about the water quality trends as it gives the illusory impression of relative stability, which in its turn can delay the implementation of actions to recover the water resources, substantially increasing costs and time.

The IQA remarkably declined in the point EMMI02900 in 1995 (Figure 2), when the direct discharge of untreated sewage dramatically increased because of new irregular settlements ("favelas") without an adequate sanitary system. All the parameters that indicate untreated sewage contamination presented averages significantly different before and after 1995 ($p<0,01$) (Table 3). In this case, the IQA oscillated in the class "good" before 1995 and changed the oscillation range to the limit between the classes "good" and "acceptable" after 1995. Although the proportion of nonconformities of faecal coliforms, $BOD_{5,20}$ and total phosphorous doubled after 1995, the relative stability in a "positive" class may induce managers to implement minor recovery actions.

Table 1. Percentage of times that the parameters exceeded the Brazilian guidelines when the waters were classified as "excellent", "good" and "satisfatory" (IQA). FC: faecal coliforms; DO: dissolved oxygen; $BOD_{5,20}$: biochemical oxygen demand; P: total phosporous.

Point	IQA	pH	FC	DO	$BOD_{5,20}$	P	Turbidity
EMGU00800	excellent	13 *(n=8)*	13 *(n=8)*	88 *(n=8)*	0 *(n=2)*	0 *(n=6)*	0 *(n=8)*
	good	18 *(n=206)*	67 *(n=206)*	75 *(n=206)*	44 *(n=135)*	13 *(n=196)*	6 *(n=206)*
	satisfatory	41 *(n=17)*	88 *(n=17)*	12 *(n=17)*	62 *(n=13)*	59 *(n=17)*	59 *(n=17)*
GUAR00900	excellent	1 *(n=116)*	1 *(n=98)*	97 *(n=116)*	39 *(n=82)*	94 *(n=106)*	4 *(n=116)*
	good	7 *(n=123)*	30 *(n=120)*	82 *(n=123)*	56 *(n=98)*	96 *(n=116)*	9 *(n=122)*
	satisfatory	0 *(n=1)*	0 *(n=1)*	0 *(n=1)*	0 *(n=0)*	100 *(n=1)*	0 *(n=1)*
EMMI02900	excellent	0 *(n=1)*	0 *(n=1)*	0 *(n=1)*	0 *(n=0)*	0 *(n=1)*	0 *(n=1)*
	good	2 *(n=168)*	56 *(n=168)*	92 *(n=168)*	43 *(n=148)*	36 *(n=167)*	1 *(n=168)*
	satisfatory	2 *(n=65)*	92 *(n=65)*	34 *(n=65)*	92 *(n=59)*	86 *(n=64)*	67 *(n=65)*

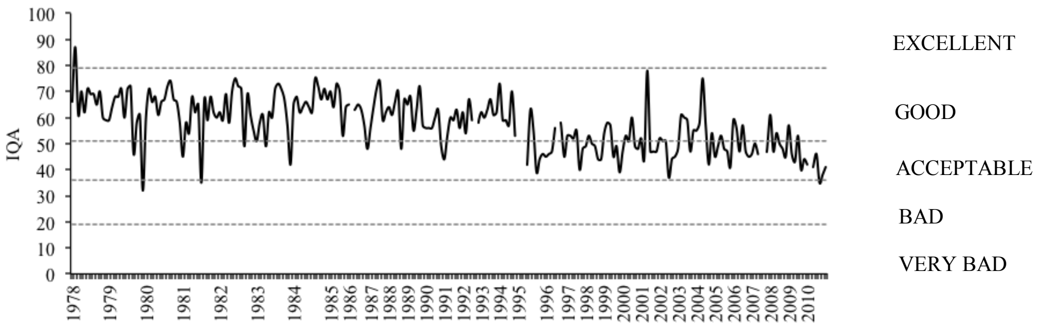

Figure 2. Historical data series of the Water Quality Index (IQA) in Guarapiranga Reservoir (EMMI02900).

Table 3. Averages and standard deviations of variables used to calculate the IQA before and after 1995 in Guarapiranga Reservoir (EMMI02900). All averages are significantly different ($p<0,01$).

Parameters	Before 1995	After 1995
Dissolved oxygen (mg O_2 L^{-1})	6.7 ± 1.2	4.7 ± 1.3
Biochemical oxygen demand (mg O_2 L^{-1})	2.7 ± 2.5	5.7 ± 6.5
Faecal coliforms (MPN 100 ml^{-1})	7570 ± 36985	28480 ± 403010
Total nitrogen (mg L^{-1})	2.4 ± 12.1	4.3 ± 2.9
Total phosphorous (mg L^{-1})	0.01 ± 0.12	0.28 ± 0.98
Total solid residues (mg L^{-1})	113.6 ± 110.7	134.3 ± 35.2

Multiproxy Analisys (PCA)

Considering the three decennial series (1978-1987, 1988-1997 and 1998-2010), the water quality continuously decreased in the point EMMI02900 (Figure 3), where the proportion of nonconformities of faecal coliforms concentration has changed from 46% in 1978-1987 to 87,5% in 1988-1997 and to 96% in 1998-2010. On the other hand, the water quality has somewhat decreased in the points EMGU00800 and GUAR00900, notwithstanding the continuous increasing of faecal coliforms concentration and the slight eutrophication in the first and second point, respectively. In fact, the use and occupation of landscape in these two points has not significantly changed in the last 30 years whereas a phenomenon of urban invasion of unplanned and irregular settlements (favelas) took place in the 1990's in the watershed nearby the point EMMI02900.

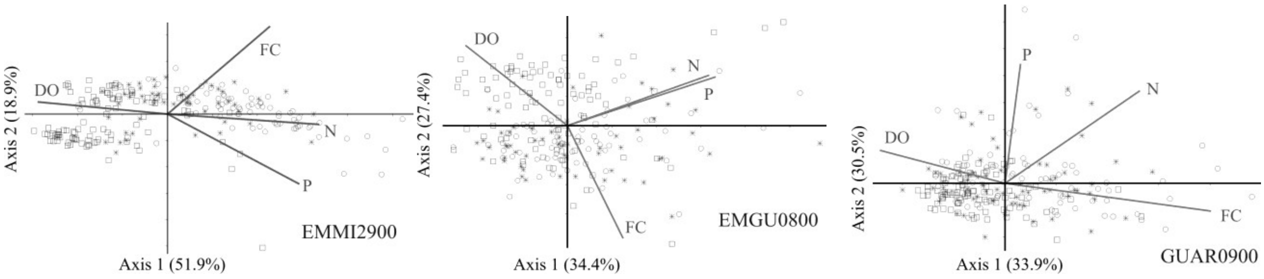

Figure 3. PCA scatterplots for the 3 monitoring points in Guarapiranga Reservoir. Squares: 1978-1987; Stars: 1988-1997; Circles: 1998-2010.

CONCLUSION

In spite of the utility of environmental indexes for management that take incorporate diverse variables, we observed that the IQA is not an efficient tool. It was frequently subjected to the eclipse effect and classified the water as "good" whereas important parameters for water quality such as faecal coliforms, $BOD_{5,20}$, total nitrogen and total phosphorous concentrations indicates significant degradation of the reservoir. The PCA is a more effective and informative alternative for management purposes.

Distinct factors influenced the water quality in each region of the reservoir along time and space, which denotes the temporal and spatial heterogeneity of the watershed. Thus, the control of the landscape use and occupation, diffuse sources of pollution, sewage treatment and reforestation of the riparian zones must take into account the peculiar environmental traits of each region in order to maximize the efficiency of recovery and conservation of the water quality.

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(70) Water Footprint Assessment for the Alcohol Production Industry

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Abstract

Many severe water-supply related problems affect industry and agriculture and become more visible in periods of extreme events like droughts and flooding with major environmental, social and economical impacts. Water footprint (WF) represents one of the useful instruments for water management in general, by considering water consumption volumes by source and polluted volumes by type of pollution. All components of a total water footprint are specified geographically and temporally, this instrument having applications in integrated water resources management, industry, agriculture, urban water supply, energy sector, transport, trade, etc.

This study is the first assessment that considers the water footprint approach in a maize based ethyl alcohol production facility by using the specific WF methodology and the CROPWAT model. For this case study, based on actual data provided by the industry, the calculated supply chain water footprint accounts for 98.6%, while the operational water use represents only 1.4% of the total water footprint. The operational water footprint is entirely *blue water*, used in the production processes, mainly for cooling. The *green* and *grey* water footprints are associated with the supply chain, being divided into 94% and respectively 6%.

The total water footprint of the studied beverage is 5620 L of water per 1L alcohol, being distributed in 93% *green* water, 5.6% *grey* water and only 1.4% *blue* water. A set of sustainable practices in the field of the ethyl alcohol production industry was proposed by taking into consideration: pollution prevention and control practices, economical issues and social aspects (for both maize growing and ethyl alcohol production).

Keywords
Alcohol industry; sustainable production, water footprint

INTRODUCTION

Businesses have became more aware of the water-related risks in their production, facilities and/or supply chain and have started to consider the water accounting tools useful for identifying the "*hotspots*", managing the social and environmental impacts, improving the operational efficiency and communicating the performances with stakeholders (Ene et al., 2013).

The water footprint of a product is the volume of freshwater used to produce the product, measured over the full supply chain. It is a multidimensional indicator, showing water consumption volumes by source and polluted volumes by type of pollution; all components of a total water footprint are specified geographically and temporally. The *blue water footprint* refers to consumption of surface and groundwater resources (denoted as *blue water*) along the supply chain of a product. The *green water footprint* refers to consumption of rainwater (commonly denoted as *green water*) as long as it does not become run-off. The *grey water footprint* refers to the pollution potential and is defined as the volume of freshwater (*grey water*) that is required to assimilate the load of pollutants given natural background concentrations and existing ambient water quality standards (Hoekstra et al., 2011).

By measuring water consumption over the full supply chain, the water footprint offers a wider perspective than the classical measure of water withdrawal, on how a consumer or a producer relates to the freshwater system (Teodosiu et al., 2012). It furthermore includes the *indirect* use of water (the water use in a producer's supply chain) as well as the *direct* water use (Ene et al., 2012).

The main objective of this study is to evaluate a water-intensive industry (alcohol production industry) from the water footprint perspective. The case study approached is developed onto an alcohol-production facility for which all water footprint components have been calculated for both direct and indirect water uses. After the description of the technological processes involved in the alcohol production, the water footprint has been calculated and assessed by identifying the *blue*, *green* and *grey* water components. The specifications of the water footprints related to both operational and supply chain within the business have been performed, and according to the results, recommendations for an efficient use of water resources in the alcohol industry have been developed.

This study is the first assessment that considers the water footprint approach in a maize based ethyl alcohol production facility. The weighted global average water footprint of maize has been assessed and ranges between 566 and 2537 m^3/t (Gerbens-Leenes and Hoekstra, 2012). However, in our case study, the inputs needed to calculate the water footprint for the maize production and for the production of ethyl alcohol from maize was performed based on data obtained from the alcohol production facility.

METHODOLOGY AND DATA ACQUISITION

Data acquisition was based on the records of county administration organizations, from the alcohol production industry database, as well as on the selected references specified in the text. Water footprint accounting was carried out based on the approach presented in the Water Footprint Manual (Hoekstra et al., 2009, 2011).

The water footprint of crops was calculated according to the methodology developed by Hoekstra and Chapagain (2008). The total crop water requirement, effective rainfall and irrigation requirements were estimated using the CROPWAT model (Allen et al., 1998; FAO, 2004). The evaluation of the *green*, *blue* and *grey* water footprints for growing a crop requires a substantial volume of data as presented in this study.

The **climatic parameters** have been obtained from the National Institute of Meteorology and Hydrology (NIMH, 2010), for the three closest and most representative meteorological stations for Botosani County, situated near the considered crop producing region, for the period of 2005-2008, a period containing years with different precipitation regimes. The data have been used as input in the CROPWAT 8.0 model.

Data on **crop parameters** such as the duration of maize growing stages, sowing and harvesting periods and crop coefficients are sourced from Allen et al. (1998), Chapagain and Hoekstra (2004) and FAO (2004).

In this study, nitrogen (N) fertilizer has been chosen as an indicator of the impact of its use in the production system. The total volume of **dilution water required** per ton of nitrogen has been calculated by considering the volume of N leached (t/t) and the maximum allowable concentration in the water bodies.

Description of the technological processes

For this study a large-size company from Botosani County which produces ethyl alcohol from maize was selected. The company produces ten months a year, 24/24 hr, 7/7 days in continuous flow. The production capacity of the company reaches 145.000 L ethyl alcohol /month (14,500 hL/y).

RESULTS AND DISCUSSION

Water footprints accounting is essential for the product and business transparency, which is requested nowadays by consumers. Since 70 percent of the world water use is located in the agricultural sector, which is part of the supply chain of many industries, the water footprint of a business that has agricultural products as input is likely to be dominated by the supply chain water footprint. The contribution of the operational water footprint is relatively small in such a case.

However, in our case study, the inputs needed to calculate the water footprint for the maize production and for the production of ethyl alcohol from maize was performed based on real data obtained from the alcohol production facility, representing the reality of the production system.

The total average water footprint for maize production was calculated using the CROPWAT software, and found to be 1680 m^3/t, with the maximum value in 2007 for both *green* and *grey* water footprints, with 2094 m^3/t and respectively 140 m^3/t.

The specifications of the water footprints related to both operational and supply chain within the ethyl alcohol production facility have been performed and according to the results, recommendations for an efficient use of water resources in the alcohol industry have been developed. The general results of the study are the following:

- The total water footprint of the business, after summing up the *indirect* water use in the supply chain and the *direct* water use in the operational stage, exceeds 8,000,000 m^3/y.
- The largest part of the product water footprint comes from the field, not the factory. As expected for any business that has agricultural products as input, the supply chain water footprint accounts for 98.6% while the operational water use forms only 1.4% of the total water footprint.
- The total water footprint of the studied beverage is 5620 L of water per 1L alcohol, being distributed in 93% *green* water, 5.6% *grey* water and only 1.4% *blue* water (Fig. 1).

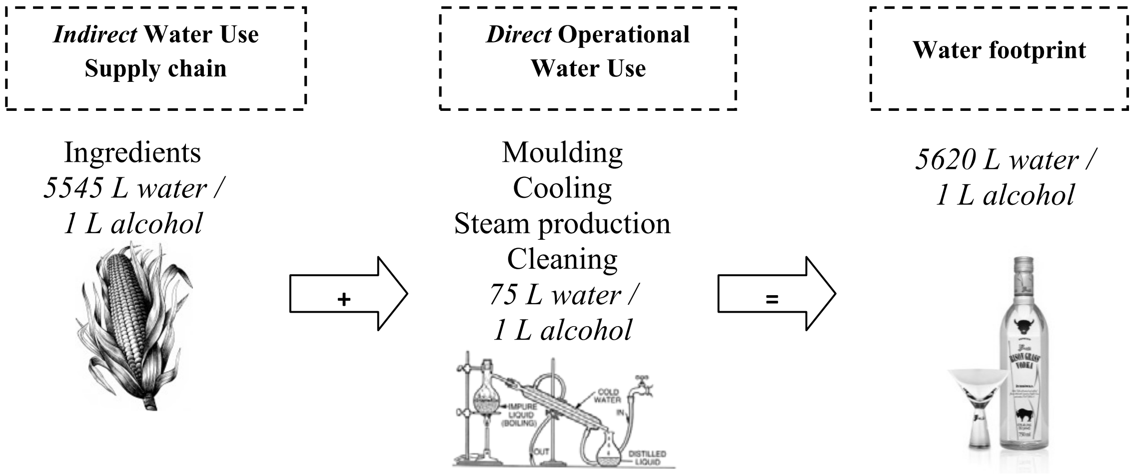

Figure 1. Indirect and Direct Water Footprint Components for alcohol production

- The operational water footprint is entirely *blue* water, used in the production processes, mainly for cooling. The *green* and *grey* water footprints are associated with the supply chain, being divided into 94% and respectively 6% (Fig. 2).

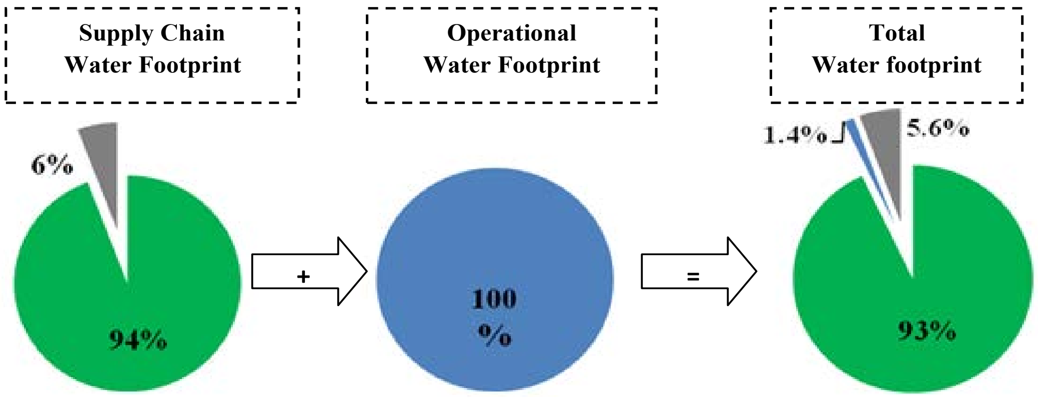

Figure 2. Water Footprint Components of 1 L ethyl alcohol production

The consideration of sustainable practices in the field of the ethyl alcohol production industry refer usually to the components of sustainability addressed at the level of economically feasible, environmentally-friendly technology and socially equitable processes (for both maize growing and ethyl alcohol production). Such practices may contribute to savings in water, energy, raw materials, diminished emissions and waste generation and a more efficient use of personnel time, with benefits for the decrease of business costs, the increase of profit and competitiveness.

The water footprint accounting helps companies in providing a good overview of the water use in the value chain. In addition, it provides strategic information needed for the understanding and assessing the water-related risks and vulnerabilities.

ACKNOWLEDGEMENTS

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(71) Effect of constant voltage on denitrification in bio-electrochemical systems

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Abstract
This study aimed to evaluate the denitrification efficiencies of using different types of bio-electrochemical systems (BESs) operated with constant voltage. An open type BES (O-BES) and a cell type BES (C-BES) obtained nitrate removal efficiencies of 22.7 ± 4.5% and 21.0 ± 3.6% at a fixed voltage of 2.0 V, and the operating HRTs were 4.6 h and 6.1 h, respectively. As a result, the O-BES achieved a higher efficiency than the C-BES because the O-BES operated on a higher current.

Keywords
Bio-cathode; Bio-electrochemical systems; Cell voltages; Denitrification; Wastewater treatment

INTRODUCTION

Denitrification in bio-electrochemical systems (BESs) is a process where nitrates are reduced to nitrogen gas using electrons obtained from electrodes by applying a voltage or current to the electrodes. Recently, BESs have been studied with a focus on the economical aspects and towards the optimization of denitrification (Wang et al., 2003, Wan et al., 2009). This study aimed to evaluate denitrification efficiencies in wastewater with constant voltage conditions.

MATERIALS AND METHODS

The denitrification efficiencies of two types of reactors were compared. The first was a cell type BES (C-BES), which consisted of an abiotic anode and a biotic cathode with an inner baffle. Another was an open type BES (O-BES), composed of two rectangle reactors with a separator, and the water surface was exposed to the air. Constant voltage conditions were maintained using a Potentiostate (WMPG 1000, WonA Tech, Korea), and synthetic wastewater was made from KNO_3 with an M9 medium according to Claweart *et al.* (2007). The average influent NO_3^--N concentration was 103.3 mg/L.

RESULTS and DISCUSSIONS

An O-BES and a C-BES were operated with constant voltages of 1.5 V and 2.0 V with a hydraulic retention time (HRT) of 4.7 hours. The percentages of nitrates removed were 11.7 ± 3.15% in O-BES and 16.6 ± 5.04% in C-BES at a cell voltage of 1.5 V. When the cell voltage was increased to 2.0 V, the average nitrate removal efficiency of the O-BES and the C-BES increased to 22.7 ± 4.6% and 21.0 ± 3.6%, respectively. The average current was 34.4 ± 3.3 mA in the O-BES and 6.7 ± 0.4 mA in the C-BES at 2.0 V. For O-BES and C-BES, the denitrification rate was 180.8 ± 44.8 $g/m^3/d$ and 83.4 ±17.2 $g/m^3/d$, respectively, at 2.0V. The O-BES achieved a higher current than the C-BES, so that the efficiency of the O-BES was higher. However, the reactors were not operated over 2.0 V due to the potential damage to the graphite felt electrodes. These results were a little different when compared to those of Kim *et al*. (2012). Kim *et al*. (2012) determined that the optimum condition was 1.5 V for the denitrification, since the reactor was operated from 0.7 V to 2.0 V.

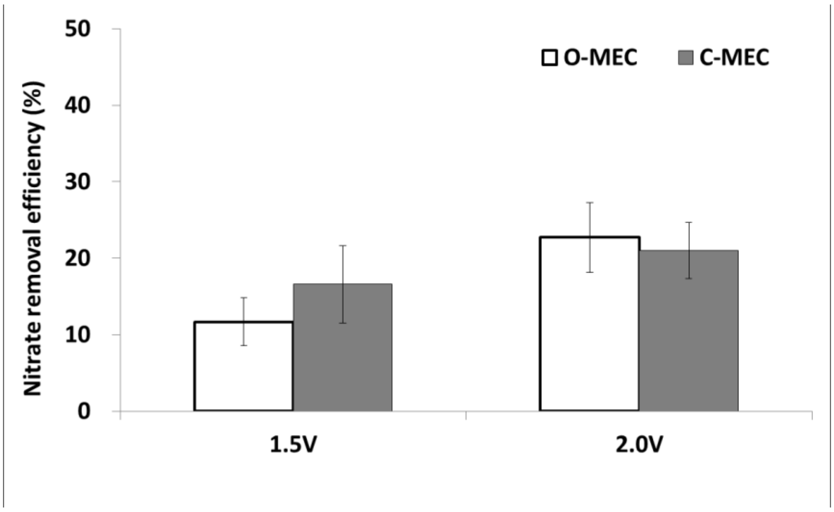

Figure 1. Comparison of the nitrate removal efficiencies in C-BES and O-BES at different cell voltages.

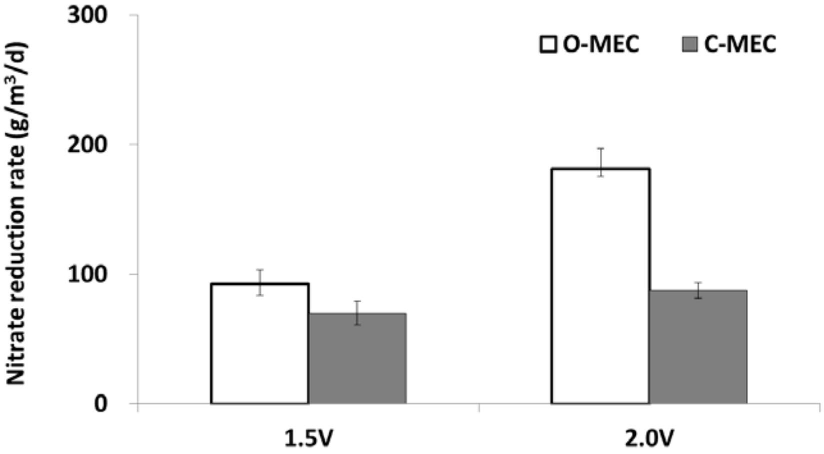

Figure 2. Comparison of the nitrate reduction rates.

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(72) Can competition for electrons increase the potential for N_2O emissions during denitrification?

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Abstract

The competition for electrons has been recently demonstrated to affect the reduction rates of the nitrogen oxides in a methanol enriched denitrifying community. The aim of this study was to test if electron competition also occurred when other substrates were used for denitrification and if that could have an effect on the potential nitrous oxide (N_2O) production and subsequent consumption. A denitrifying culture was developed in a sequencing batch reactor using nitrate as electron acceptor and a combination of acetate, ethanol and methanol as carbon sources. Four sets of batch tests were conducted using acetate, ethanol, methanol and a combination of the three carbon sources respectively. For each set the effect of nitrate, nitrite and nitrous oxide in each other reduction rates when present individually or in combination was assessed. Results show that reduction rates are affected by the type of substrate added, probably due to different microbial populations specialized with consuming a particular substrate. Also, N_2O reduction rate is the most reduced under the different electron competition scenarios tested, which results in an N_2O accumulation in some cases.

Keywords
denitrification; electron competition; nitrous oxide; carbon sources; reduction rates.

INTRODUCTION

Nitrous oxide (N_2O) is one of the most potent greenhouse gases and its high increase rate at around 0.31% per year has attracted the interest of the research community to study its sources and sinks. Heterotrophic denitrification is one of the key processes in biological nitrogen removal during wastewater treatment which produces N_2O as an intermediate product (Lu and Chandran, 2010). Several factors have been shown to affect N_2O accumulation and subsequent emissions during denitrification, such as pH (Pan, Ye, et al., 2012), sludge retention time (SRT) (Hanaki, Hong, et al., 1992), dissolved oxygen (DO) (Park, Inamori, et al., 2000), types of organic carbon source (Lu and Chandran, 2010) and COD/N ratio and nitrite/Free nitrous acid accumulation (R.von Schulthess, D.Wild, 1995; Zhou et al., 2008). A recent study conducted with a methanol denitrifying culture showed that electron competition had an effect on the reduction rates of the different nitrogen oxides. Although N_2O did not accumulate in the majority of their experiments, they suggested that electron competition, even under non-limiting substrate conditions could lead to N_2O accumulation (Pan et al., 2013).

The aim of this study was to investigate the impact of electron competition on N_2O accumulation in a denitrifying culture developed with three carbon sources: acetate, ethanol and methanol. The effect of each carbon source to the different nitrogen oxides reduction rates was also assessed and compared.

MATERIALS AND METHODS

A cylindrical 6L SBR was inoculated with activated sludge from Girona's wastewater treatment plant (WWTP). It was operated in a 6h cycle, consisting of anoxic feed (4min) where 1L of synthetic WW was added, anoxic phase (5h), aerobic mix (15min), settle (20min) and decant (20min). The synthetic feed contained 300ppm COD (equally divided between acetate, ethanol and methanol) and 90 mg $N\text{-}NO_3^-$. The sludge retention time (SRT) was 15 days. Nitrate and COD were completely removed at the end of the anoxic phase. The pH was controlled at 7.5±0.4 using 0.6M hydrochloric acid.

Four sets of experiments were conducted. The first three were carried out using three different carbon sources separately (acetate, ethanol and methanol) and in the last set a combination of the three was used. Each set was comprised of 6 batch tests where different electron acceptors were added as shown in table 1. All the batch tests were conducted taken the sludge from the SBR at the end of the anoxic phase to ensure that nitrate, nitrite and COD were removed completely. The sludge was pretreated with one hour aeration to oxidize any internal COD that could be remaining, washed with a phosphate buffer solution (PBS), bubbled with nitrogen gas for 30 min to ensure anaerobic conditions, and placed in a sealed batch reactor. pH was adjusted to 7.5±0.1 adding 0,6M HCl or 0,5M NaOH. Anoxic conditions were controlled during all the experiments. All the experiments were carried out in triplicates. In each batch, a concentration of 100 mg COD/L and 20 mg N-NOx was initially added as a pulse. Dissolved N_2O was monitored with an online N_2O microsensor (Unisense A/S) and samples for the analysis of nitrate, nitrite and acetate were taken across the experiment and analyzed using ion chromatography and gas chromatography respectively.

Table 1. Batch tests conducted for each set of experiments.

Batch test type	*A*	*B*	*C*	*D*	*E*	*F*
Electron acceptors used	NO_3^-	NO_2^-	N_2O	NO_3^- N_2O	NO_2^- N_2O	NO_3^- NO_2^-

RESULTS AND DISCUSSION

Effect of substrate on nitrogen oxides reduction and N_2O accumulation

Figure 1 shows the nitrate, nitrite and nitrous oxide reduction rates obtained during the different batch tests conducted with acetate, ethanol, methanol and a combination of the three respectively. The reduction rates obtained for each nitrogen oxide differed depending on the carbon source added. The lowest rates were obtained when methanol was used as the only carbon source. Nitrate reduction rate was similar when acetate and ethanol were used independently. However, in the case of ethanol, some nitrite accumulated during nitrate reduction due to the lower nitrite reduction rate compared with the rate for nitrate reduction (figure 1B). N_2O reduction presented the highest rate when ethanol was used as the only substrate. These differences are likely due to the mixed microbial community present in the SBR. Although the same COD concentration was added for each of the substrates, it is possible that acetate and ethanol were preferred against methanol, growing in the SBR more microorganisms able to consume these two substrates. With all the substrates, nitrous oxide reduction rate was always higher than the nitrate or nitrite reduction rates when a single electron acceptor was used (Figure 1, tests A, B, C).

Effect of electron competition on nitrogen oxides reduction and N_2O accumulation

Six different combinations of electron acceptors were studied (see Table 1). Nitrate, nitrite and nitrous oxide reduction rates differed depending on which electron acceptor was added. When comparing the reduction rates obtained when using a single substrate, it can be observed that nitrous oxide reduction rates decreased when more than one electron acceptor was added (Figure 1, tests D, E, F). Interestingly in these tests, the reduction observed for nitrate and nitrite reduction rates was less dramatic. This observation not only suggests the occurrence of a competition for electrons but also a preference in electron flow when this competition occurs, giving priority to the reduction of nitrate/nitrite rather than N_2O. This prioritization on the reduction of different electron acceptors is probably related to the bioenergetics of denitrifying bacteria that will give priority to those processes with more energy production. If we take into account that 80% of the ATP is generated during the reduction of nitrate to nitrous oxide, the lack of further reducing the N_2O to N_2 will make very little difference to the overall energy production on this group of microorganisms, originating a net accumulation of N_2O under certain conditions (Richardson, Felgate, et al., 2009).

Nitrous oxide accumulated in some cases as its reduction rate was more affected by the electron competition. This accumulation is remarkable in the F type of batch tests when the carbon source used was acetate (batch tests with ethanol and methanol are ongoing experiments and data will be provided in the full paper).

There was not N_2O accumulation when a combination of the three carbon sources was added. These batch tests explain the behavior inside the SBR where N2O accumulation was never detected.

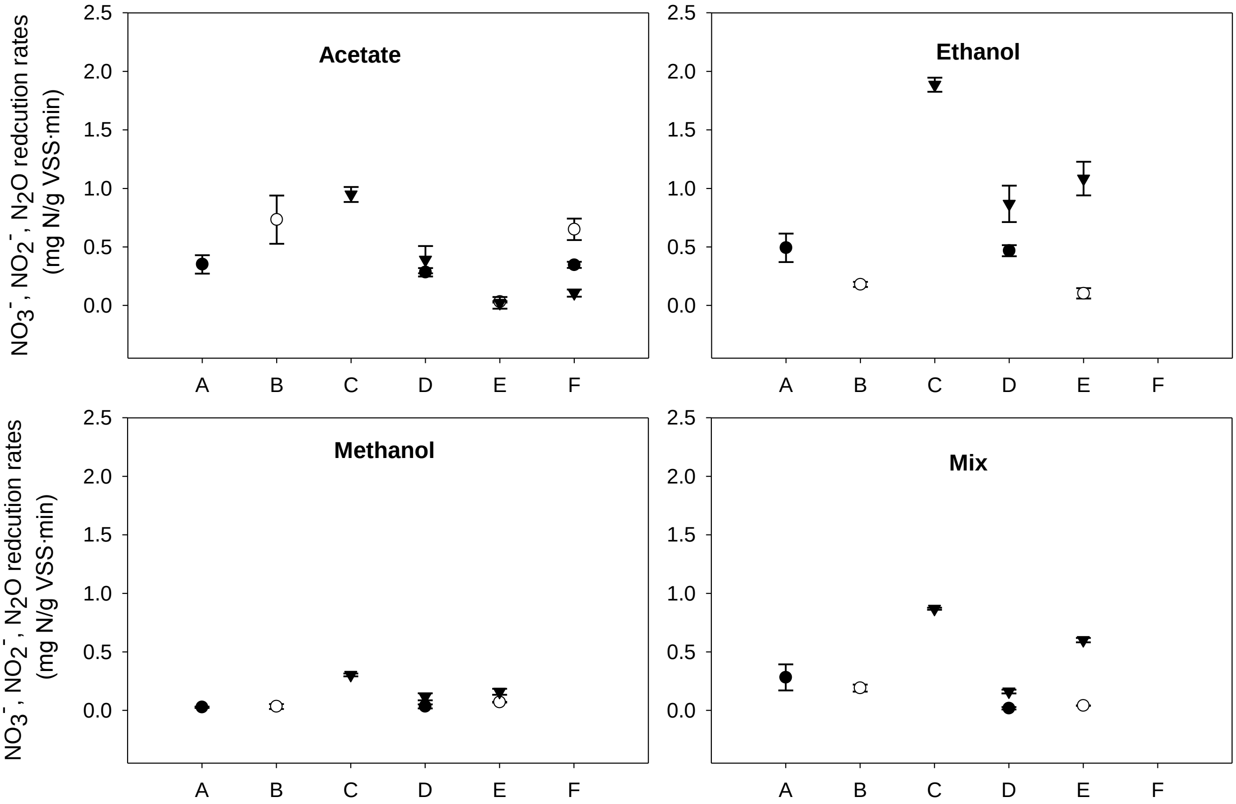

Figure 1. Nitrate, nitrite and nitrous oxide net reduction rates using acetate or ethanol or methanol or the combination of the three carbon sources with error bars showing the standard deviation associated (● NO_3^-, ○NO_2^-, and ▼N_2O).

CONCLUSIONS

- The N_2O reduction rate is the highest one compared to nitrate and nitrite reduction rates when a single nitrogen oxide is added.
- Acetate and ethanol are the substrates providing higher reduction rates. This suggests presence of different groups of bacteria specialized in consuming each of the substrates.
- N_2O reduction rate is the most affected when a competition for electrons exists. In some cases, this competition can increase the potential of nitrous oxide accumulation and lead to incomplete denitrification resulting in the release of N_2O as the end-product of the process.

Acknowledgements

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(73) Leachate Remediation at Closed Solid Waste Landfill using Permeable Reactive Barrier with Vegetation

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Abstract

This research was conducted to investigate leachate treatment efficiencies by using permeable reactive barrier (PRB) with guinea grass (Panicum maximum TD 58). Pilot scale PRB was examined at hydraulic loading rate of 0.028 m^3/m^2d and hydraulic retention time of 10 d. Two different types of media in PRB were used i.e. system 1: clay and sand mixture of 40:60 %w/w and system 2: clay, ferric chloride sludge and sand mixture of 30:10:60 %w/w. The results showed that the performance of system 2 was better in terms of pollutant removal efficiencies. Average BOD, COD and TKN removals were 76.1, 68.5 and 73.5% respectively. Greenhouse gas (GHG) emissions during the treatment of PRB were 8.2-52.1 $mgCH_4/m^2.d$, 69.1-601.8 $mgCO_2/m^2.d$ and 0.04-0.99 $mgN_2O/m^2.d$. The use of system 2 with vegetation resulted in lower GHG emissions. The results show that PRB with vegetation could be effectively used to remediate leachate from close landfill site.

Keywords
Leachate treatment; permeable reactive barrier; site remediation; vegetation

INTRODUCTION

Leachate is a highly concentrated wastewater generated as by-product from municipal solid waste landfill. It poses a threat to the environment in terms of air, surface water and ground water pollution. Conventional leachate treatment systems available in developing countries are generally low-cost technologies such as stabilization pond, aerated lagoon or land treatment. Nevertheless, those treatment technologies are usually implemented only during the operation stage of solid waste disposal site. After site closure, most of the treatment systems are not well operated or poorly maintained due to lack of post-closure operation and maintenance cost. The control of leachate migration off the site after landfill closure is not an easy task because of high variations of leachate quantity and characteristics with time. Subsurface flow constructed wetland which utilizes coarse media with high permeability and vegetation has been proven to be an efficient treatment method for landfill leachate treatment (Chiemchaisri et al., 2009). Its main treatment functions include biological treatment using attached growth on the media and plant root and plant uptake of nutrients. Meanwhile, permeable reactive barrier (PRB) technology using low permeable media like clay and sand mixture has been also successfully applied for reducing groundwater pollution from solid waste disposal site (Dong et al., 2009). PRB utilizes reactive media to prevent contaminated water pollutants by physical, chemical and/or biological processes. The treatment processes can include precipitation, sorption, oxidation/reduction, fixation or degradation to remove the contaminants from the water (McMahon et al., 1999). This research is carried out to investigate the possibility of utilizing PRB containing high permeable reactive media and plant as an in-situ pollution control technology for close landfills. The concept is to construct PRB surrounding the waste disposal area so that infiltrated leachate can be treated until it is safe for discharge off-site. It is also anticipated that vegetation could also enhance the performance of PRB by improving soil porosity and oxygen diffusion for the microbial activities. In our previous investigations, vegetation has provided positive effect on leachate treatment in soil-plant system while also helped reducing greenhouse gas emission during it treatment (Suwunpukdee et al., 2013).

MATERIALS AND METHODS

Two pilot-scale permeable reactive barrier (PRB) units of 1 m width, 2 m length, and 1 m depth, as the schematic shown in Fig. 1, were used. The inlet and outlet zones of the experimental unit were filled with 30-60 mm gravel of 0.80 m depth. PRB media made of clay: sand mixture at 40:60 (%w/w) was provided in system 1 and clay: ferric chloride sludge: sand mixture at 30:10:60 (%w/w) was provided in system 2. Clay was obtained from local soil and ferric chloride sludge was brought from sludge storage pond of an advanced leachate treatment system at the same solid waste disposal site. The main purpose for introduction of ferric chloride sludge in reactive media was to investigate its effect on suppression of methane production during the treatment (Sylvia and Schnell, 2000). Guinea grass (Panicum maximum TD 58) was used as vegetation in both units with an initial plant density of 20 rhizomes/m^2. Leachate was fed into the system at a hydraulic loading rate (HLR) of 0.028 m^3/m^2.d, equivalent to a hydraulic retention time (HRT) of 10 d.

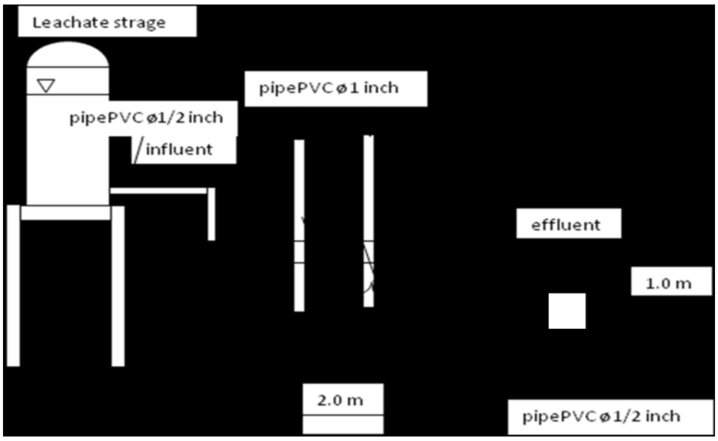

Figure 1. Schematic of pilot-scale permeable reactive barrier (PRB) with vegetation

The characteristics of leachate are shown in Table 1. The water qualities were monitored over 257 days for pH, EC, BOD, COD, SS, TDS, NH_4^+, TKN, NO_2^-, NO_3^- and TP. Soil samples in the media were analyzed for pH, EC, organic carbon, NH_4^+-N, NO_3^--N, TKN and TP. The growth of plant was determined in terms of height, number of leaves and shoots and total dry weight.

Table 1. Characteristics of leachate used in this study.

Parameter	Range	Average±SD
pH	7.5-8.8	8.3±0.4
EC (ds/m)	11.5-25.9	19.2 ± 4.3
BOD (mg/l)	704-1,434	922±211
COD (mg/l)	2,200-3,145	2,694±480
SS (mg/l)	230-810	575±192
TDS (mg/l)	8,140-13,520	10,610±1,240
NH_3-N (mg/l)	56.7-179	102±33
TKN (mg/l)	112-296	191±47
NO^-_2 (mg/l)	0.1-1.3	0.4±0.4
NO^-_3 (mg/l)	0.2-3.5	1.2±1.1
TP (mg/l)	4.8-11.6	5.2±2.3

During the treatment, GHG emission was also evaluated using close flux chamber technique. The gas emission was conducted over bare soil and soil with plant for comparison. Methane and carbon dioxide and nitrous oxide was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Treatment performance of the PRB system

Table 2 shows average effluent qualities from the pilot-scale PBR. Moderate organic and nutrient (N,P) removals of about 50-80% were achieved. The removal rates of pollutants were different between the experimental units using different media. The removals were higher in the experimental unit in which ferric sludge were added into clay: sand mixture. On average, BOD, COD and TKN removals were 76.1%, 68.5% and 73.5% respectively meanwhile those of clay: sand mixture alone were 69.5%, 63.3% and 66.9%. Moderate dissolved solids removals in terms of EC (48.4%) and salinity (54.1%) was also observed in PRB system suggesting the removal of salts through precipitation either in media or plant root zone. The enhanced treatment in ferric chloride sludge amended media was possible due to organic adsorption onto sludge particles and Fenton-like chemical reaction between hydrogen peroxide and ferric ions could take place in the ferric chloride amended media and helped improving organic removals. The presence of ferric chloride could yield an improvement of organic (COD) removal organics through the reaction of the iron salt (Fe^{3+}) with H_2O_2 to produces hydroperoxyl radical ($HO_2^{\cdot}$) (Amuda, 2006). Moreover, vegetation could also help improving organic and TKN removal possibly through enhancement of oxygen transfer into the soil by plant root system which subsequently promoted aerobic biodegradation by soil microorganisms.

Table 2. Effluent characteristics and steady state removal efficiencies.

Parameter	system 1 (clay: sand)			system 2 (clay: sludge: sand)			% removal (system 1)	% removal (system 2)
	port 1	port 2	Eff.	port 1	port 2	Eff.		
pH	7.86	7.76	7.71	8.22	8.07	7.79	-	-
EC (ds/m)	13.8	11.5	10.9	13.1	10.9	9.9	43.3	48.4
BOD (mg/l)	577	399	281	544	342	221	69.5	76.1
COD (mg/l)	1,824	1,331	989	1,630	1,196	849	63.3	68.5
SS (mg/l)	-	-	150	-	-	114	73.9	80.2
TDS (mg/l)	-	-	5,475	-	-	4,887	48.4	53.9
NH_3-N (mg/l)	55	52	31	50	45	28	69.5	73.4
TKN (mg/l)	147	112	63	134	92	51	66.9	73.5
NO^-_2 (mg/l)	0.2	0.15	0.05	0.2	0.16	0.04	-	-
NO^-_3 (mg/l)	0.9	0.5	0.24	0.86	0.66	0.21	-	-
TP (mg/l)	3.30	3.03	1.44	3.51	3.17	1.36	71.7	74.4

Growth of plant in the PRB system

During the operation of PRB system, the growth of plant (Guinea grass or *Panicum maximum TD* 58) was also studied. It was found that the growth of plant in system 2 was better than system 1. The provision of ferric chloride sludge in PRB media did not have negative impact on plant growth but on the other hand slightly promoted plant growth. The promotion of plant growth could be due to an improvement on physical properties of media for plant growth or the addition of ferric iron can also help in promoting photosynthesis mechanism of plant chlorophyll. Higher growth of plant in system 2 also promoted water removal through evapotranspiration resulting in lower effluent volume obtained from system 2 compared to system 1.

Greenhouse gas emission from the PRB system

Table 3 compares average methane, carbon dioxide and nitrous oxide emission rates from soil and soil-plant in PRB with different media. For all gases, the emission rates from bare soil were higher than soil-plant location indicating that the plant helped reducing greenhouse gas emission possibly due to improved oxygen transfer into their root system. The system 2 had lower emission rates than system 1 for all gases. These results suggested that an introduction of ferric chloride sludge into the media helped mitigating GHG emission during the treatment. Ferric chloride amended sludge media could promote the activity of Fe^{3+} reducing bacteria, resulting in a switch in electron flow from methanogenesis to Fe^{3+} reduction (Frenzel et al., 1999). Furthermore, plant–microbe interactions could lead to an efficient iron oxidation and reduction reaction in an oxidized rhizosphere environment (Roden and Wetzel, 1996).

Table 3. Emission rate of greenhouse gas from the PRB system.

System	location	Methane		Carbon dioxide		Nitrous oxide	
		range	average	Range	average	range	average
1	bare soil	16.3-52.6	31.2	215.7-570.2	380.7	0.21-0.69	0.42
	soil-plant	14.2-46.8	26.6	155.0-536.0	316.1	0.14-0.53	0.31
2	bare soil	11.3-41.7	22.6	112.5-508.9	293.6	0.07-0.43	0.21
	soil-plant	8.0-37.0	17.8	69.1-373.3	259.6	0.04-0.41	0.19

CONCLUSIONS

Permeable reactive barrier (PRB) with vegetation was successfully applied to remediate leachate from closed landfill site. Moderate removals of organic and nutrients was obtained during which highest removals of BOD, COD and TKN were 76.1%, 68.5% and 73.5%. Introduction of ferric chloride sludge into PRB media slightly improved the treatment performance of PRB while promoting plant growth. It also helped reducing greenhouse gas emission during the treatment. The growth of Guinea grass (*Panicum maximum TD 58*) in PRB system could be sustained in long term operation and it provided positive effect to the treatment and reducing greenhouse gas emission.

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(74) Ant colony optimization for improving the management of the first flush effect in urban wastewater systems

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Abstract

A new method to improve the real-time management of stormwater Retention Tanks (RT) and reduce first flush (FF) effect is proposed. The method is based on Ant-Colony-optimization algorithm (ACO) that develops the optimal sequence of discharging RT's during storm event without overflowing the treatment plant. The ACO works with a colony of virtual ants, iteratively searching for the best solution of sewage discharges from RT, based on an objective-cost function dependent on the specific unitary cost of the contaminants present in the stormwater. The ACO was successfully applied in a virtual case scenario and helped to increase both the volume of wastewater and amount of pollutants treated in a storm event. The developed ACO is highly modular and could be easily applied to real urban wastewater systems.

Keywords

First flush, combined sewers, urban wastewater system, Ant Colony Optimisation algorithm

INTRODUCTION

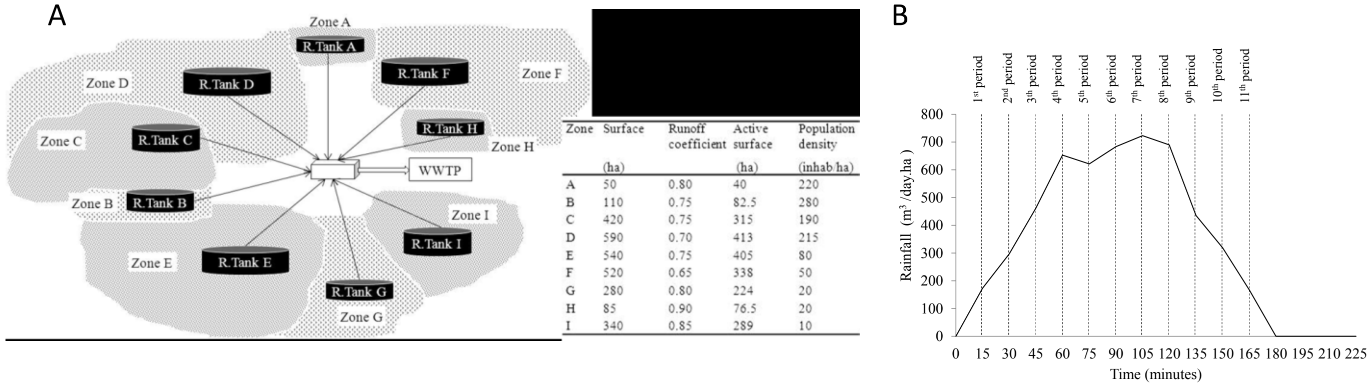
The first flush (FF) effect in combined sewer systems during storm events often causes overflows of the wastewater treatment facilities. The FF wastewater contains a greater fraction of washed-out contaminants compared to the remainder of the storm, reduces the efficiency of the wastewater treatment and also impacts the quality of the receiving waters due to the pollutants released (Gupta and Saul, 1996). FF are normally managed with the storage of the sewage runoff in Retention Tanks (RT), underground structures designed to contain and manage excess stormwater runoff to help prevent flooding. However, the management of RT and its load of pollutants is a complex task, especially when several tanks need to be simultaneously controlled under dynamic and often-unpredictable storms. To date, only a few number of artificial-intelligence tools have been applied to optimize the controlled-transfer of stormwater to the wastewater treatment plant (WWTP). For instance, Darsono and Labadie (2007) developed a hydraulic control with a system-wide regulation of in-line storage by a neural-optimal control algorithm. But alternative tools for RT+WWTP integrated management are still required.

In this work we propose a new approach to improve the management of pollutant loads in RT during a storm event by using an Ant-Colony-optimization algorithm (ACO). The ACO method aims to provide the optimal real-time discharge of a number of retention tanks (with multiple options, partial or total) during a storm event by maximizing the wastewater discharged (both in volume and contaminant loads) without exceeding the capacity of the WWTP downstream. The approach is inspired on the "multidimensional knapsack" computational problem and aims to develop an optimal sequence of emptying RT by working with a colony of virtual ants. The ants search for a solution iteratively, moving through a search space of solutions, consisting of RT and possible wastewater discharges. To drive the ants search, the ACO maximises an objective-cost function based on the specific unitary cost of the contaminants present in the stormwater.

MATERIAL AND METHODS

Case study

The ACO has been applied in a virtual case study simulating a benchmark municipality subjected to a storm pattern. The virtual city has a population of ≈330.000 inhabitants, 9 retention tanks and 1 WWTP, located equidistant from all the RT (Fig. 1). Each RT receives domestic wastewater and storm runoff from proportionally to its area. WW characteristics for dry weather conditions were adapted from Gernaey et al., (2005) and Gasperi et al., (2008). WW volume produced was 0.15m^3/inhabitant·day. WW pollutants considered were Suspended Solids (SS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), and Total Phosphorus (TP). The rainfall pattern was selected from the BSM1 model (Alex et al., 2008). A storm of 165 minutes, with a maximum value of 723.18 m^3 /day· ha. The rain event was divided in 11 periods of 15 min/period.



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Zone	Surface (ha)	Runoff coefficient	Active surface (ha)	Population density (inhab/ha)
A	50	0.80	40	220
B	110	0.75	82.5	280
C	420	0.75	315	190
D	590	0.70	413	215
E	540	0.75	405	80
F	520	0.65	338	50
G	280	0.80	224	20
H	85	0.90	76.5	20
I	340	0.85	289	10

Figure 1. A: scenario of the case study, and the characteristics of different areas; B: Rainfall dynamics proposed for the event to study.

First Flush management loop

The management loop, adapted from Verdaguer et al. (2012), was programmed in Java and included 4 steps:

1) Acquisition of data volume and pollutant concentrations in each RT in real time; 2) Acquisition data volume and pollutant loads admissible at the WWTP inflow in real time; 3) Run the ACO algorithm to achieve the optimal sequence of discharges from RT's. 4) Execute the RT discharges obtained from Step 3.

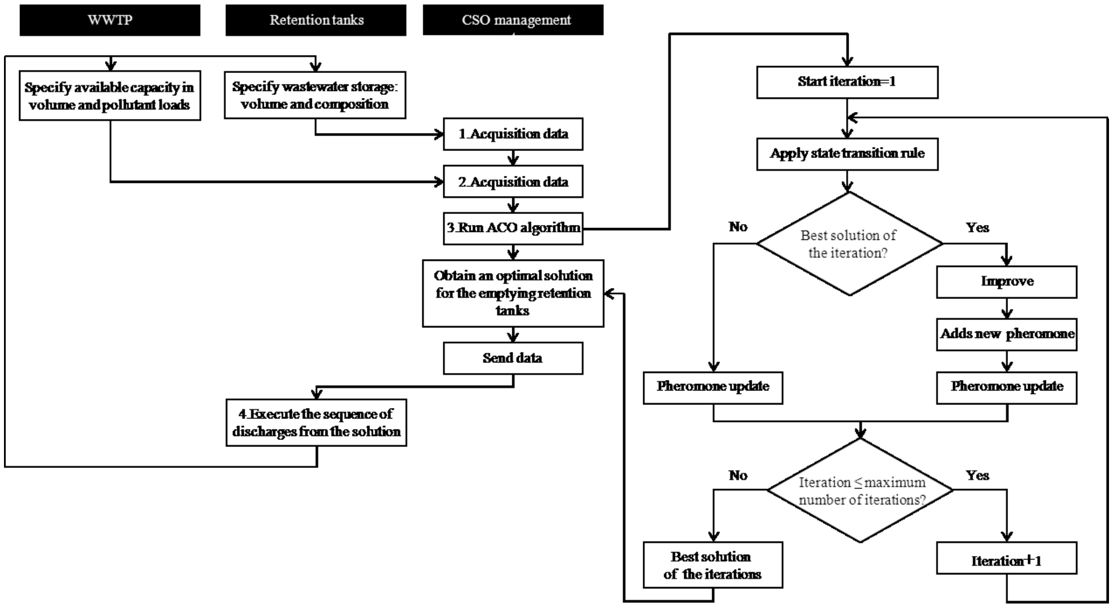


Figure 2. Procedure followed by the FF management system.

ACO algorithm

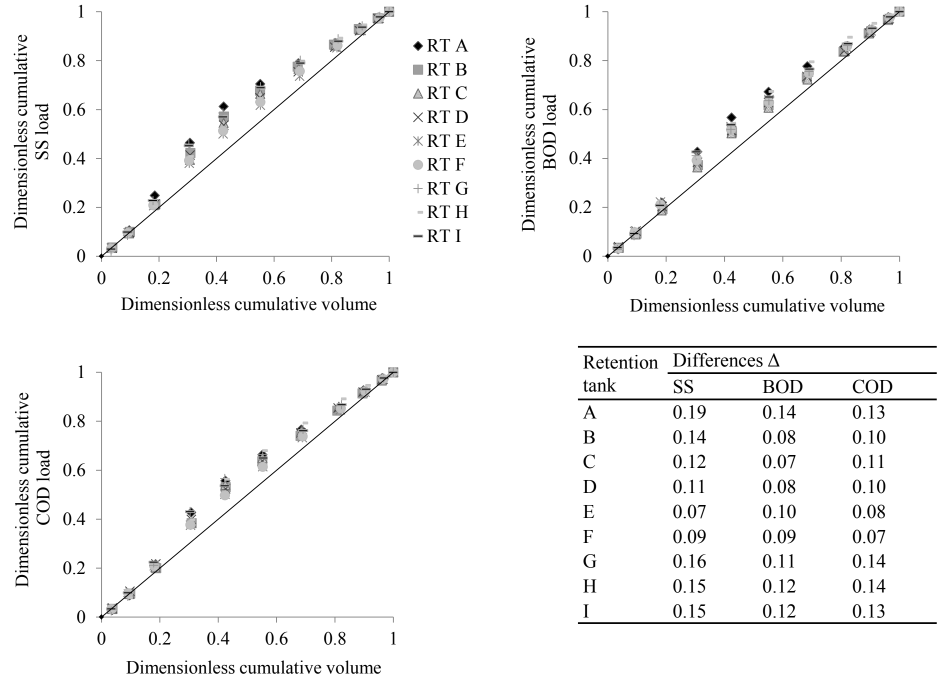
Step 3 consisted on the running of the ACO algorithm. To drive the ants' search, the algorithm maximises an objective-cost function based on the specific unitary cost of the contaminants present in the stormwater. The objective function to maximise (Verdaguer et al. 2012) is expressed in the following equation:

$$Z=\sum_{i=1}^{n}\sum_{j=0}^{l_i} y_i^j V_i^j \left(\nu + \psi K_i \sum_{r=1}^{5} C_i^r P^r T_i^r \right) \qquad \text{(eq.1)}$$

where **Z** is the global cost of discharges; **y_i^j** is a binary decision variable; **V_i^j** is the volume discharged from tank *i.*; ν is the unitary ww volumetric cost, 0.1314 €/m^3; **Ψ** is the constant of pollutant loads; **K_i** is a coefficient of WWTP saturation produced by the discharge **V_i^j**; **C_i^r** is the concentration of each pollutant in the RT; **r** is the set of pollutants (SS, BOD, COD, TKN, TP); **P^r** is the unitary cost for each pollutant (0.3980€/Kg SS, 0.5000€/Kg BOD, 1.1945€/Kg COD, 0.6145€/Kg TKN, 1.2092€/Kg TP); and **T_i^r** is a coefficient of excess pollutant relative to the initial conditions of ww before the rain event. All simulations included 10 algorithmic repetitions with 500 iterations and 100 ants per iteration. The results of the ACO-RT discharges were compared with results obtained using a process of Normalized RT Discharge (ND), proportional to the volume of wastewater stored in the tank.

RESULTS

Figure 3 shows the representation of the dimensionless cumulative loads SS, BOD, and COD versus the dimensionless cumulative volumes for the rain event studied. Each sequence of dots represents the evolution of the curve through the 11 periods of time for the wastewater stored in each RT. The sequences showing a deviation above the 45º line (which would indicate that the pollutants are uniformly distributed) indicated the occurrence of the first flush phenomenon (Periods 4 to 7). The maximum differences (Δ) between the dimensionless cumulative pollutant load and the dimensionless cumulative runoff along the rain event are indicative of the strength of the first flush (Lee et al., 2002). The Δ values in each RT, always below 0.2 (Table imbedded in Figure 3) reflect a moderate FF.



Retention tank	Differences Δ		
	SS	BOD	COD
A	0.19	0.14	0.13
B	0.14	0.08	0.10
C	0.12	0.07	0.11
D	0.11	0.08	0.10
E	0.07	0.10	0.08
F	0.09	0.09	0.07
G	0.16	0.11	0.14
H	0.15	0.12	0.14
I	0.15	0.12	0.13

Figure 3. Curves of dimensionless cumulative loads versus dimensionless cumulative volume corresponding to the 11 periods of the rain event studied.

The application of the ACO algorithm produced an increase both in the volume of wastewater and loads of contaminants successfully transferred to the WWTP. The WWTP was able to cope with 100% the discharged wastewater due to the moderate magnitude of the simulated storm. The ACO application produced a RT discharge pattern similar to the volume of WW stored in the system. (Figure 4.A). A maximum of 76.6% of the wastewater was discharged from the RT during Period 4. In the same way, the discharges of SS, BOD and COD from the RT to the WWTP showed a pattern similar to the profile of their storage (4.B to 4.D), with an increase from the 3rd to 4th periods because of the highest concentration of pollutant loads and a latter reduction related to its lower concentration in the latter collected rainwater.

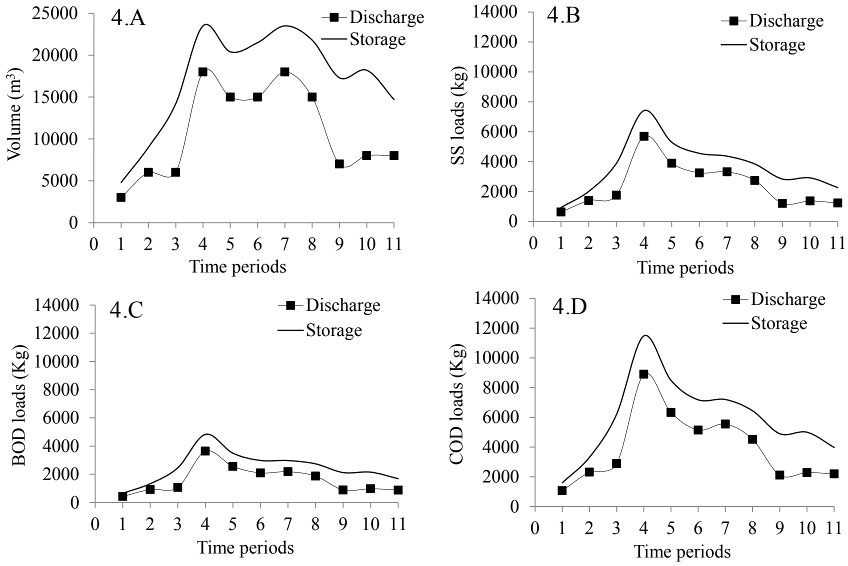


Figure 4. Profile of discharges obtained for volume and loads of the pollutants SS, BOD and COD using the ACO.

The algorithm tended to select discharges that involved higher volumes and higher pollutant loads but also more pollutants with higher values of the coefficient T_i^r. The comparison of the results achieved using the ACO vs ND showed an improvement in the pollutant loads treated. The amount of SS, COD, TKN and TP successfully sent to treatment increased by 6.25%, 7.43%, 7.26% and 12.46% respectively. On the other hand a reduction of the 2.48% of the BOD treated was also observed when using the ACO method.

CONCLUSIONS

An ACO algorithm has been successfully used to optimize the management of First Flush in stormwater retention tanks. The ACO allowed to dynamic optimal discharge of wastewater depending on its chemical characteristics (volume and pollutant concentrations). The ACO strengthens the discharge of higher volumes from the biggest RT and also containing higher pollutant concentrations. The proposed methodology permits the overall volume of discharges to achieve the maximum volume acceptable for the WWTP for all time periods. The developed method is highly modular and can be easily adapted to real urban wastewater systems.

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(75) Enhanced Acidification of Cattle Manure during Anaerobic Digestion

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Abstract

Hardly-biodegradable fractions can be problematic in anaerobic digestion systems when dealing with agricultural wastes such as manure. In this study, effects of sonication and 2 different hydrolytic enzyme mixtures on acidification of cattle manure were investigated in anaerobic batch digesters. The volatile fatty acids (VFA) concentrations showed that the addition of hydrolytic enzymes was superior to sonication and increased VFA production from 982 mg (as acetic acid)/L up to 4506 mg (as acetic acid)/L.

Keywords
Acidification; anaerobic digestion; cattle manure; pre-treatment

INTRODUCTION

Cattle manure can be asuitable substrate for anaerobic digestion due to its high organic matter content, however; lignin, hemi-cellulose and cellulose fractions can be problematic since they are hardly-biodegradable. In anaerobic digestion systems, hydrolysis of particulate organic matter to soluble substance is believed to be a rate-limiting step and therefore increasing the hydrolysis rate is important to achieve efficient biomass conversion (Romano et al., 2009). There are several pre-treatment methods that can be employed including thermal or alkali treatment, sonication, enzyme addition and mechanical shearing, where the effect of these methods depends on the biomass composition and operating conditions (Quiñones et al., 2012).In our study focusing on the anaerobic cattle manure digestion, effects of a commonly used veterinary antibiotic, oxytetracycline (OTC), on biogas production and microbial communities were investigated along with different operating conditions including total solids (TS) content and mixing rate (Ince et al., 2013; Turker et al., 2013). This particularstudy presented is aimed to investigate the effect of 2 pre-treatment methods, sonication and hydrolytic enzyme addition, on the acidification rate of unscreened raw cattle manure during anaerobic digestion.

MATERIALS & METHODS

4 batch anaerobic cattle manure digesters (D1, D2, D3 and D4) were operated for 120 hours at 37±1^{o}Cand continuously stirred at 100 rpm in an incubating shaker (Thermo Scientific MaxQ 4000 Benchtop Orbital Shaker, U.S.A.). TS content of manure slurries were adjusted to 6.0±0.2%in 300 mL active slurry volumes and pH was maintained at 5.5±0.1. The application of pre-treatment methods for the digesters is given in Table 1.

Table 1. Pre-treatment applications in the digesters**.**

Digester	Pre-treatment	Application
D1 (Control)	No pre-treatment	-
D2	Sonication	35 kHz for 30 minutes
D3	Enzyme addition	Hydrolytic enzyme tablet (Enzyme mixture A)
D4	Enzyme addition	Hydrolytic enzyme powder (Enzyme mixture B)

Sonication (30 minutes via 35 kHzTransonic ultrasonic bath, ELMA D-78224 Singen/Htw) was conducted prior to digestion and 2 different commercially available enzyme mixtures (Enzyme mixture A and

Enzyme mixture B, SEPT and PACK, respectively, ALFA Kimya, Istanbul) were pounded and then added in the amounts stated in the prospective.Samples were taken from the digesters every day to observe VFA productions. VFA concentrations were measured by Perkin Elmer Clarus 600 Gas Chromatograph equipped with a flame ionization detector (FID). The column used was Elite FFAP (30 m x 0.32 mm).

RESULTS &CONCLUSIONS

Total volatile fatty acids (VFA_{tot}) concentrations in the digesters can be seen in Figure 1. At the end of the digestion period, VFA_{tot} concentrations were 982 mg (as acetic acid)/L, 1637 mg (as acetic acid)/L, 4506 mg (as acetic acid)/L and 2644 mg (as acetic acid)/L in digesters D1, D2,D3 and D4, respectively. Although sonication had an affirmative effect on the acidification, its effect is comparatively lower when compared to enzyme addition. The highest VFA production was observed in D3, where hydrolytic enzyme mixture A was used.

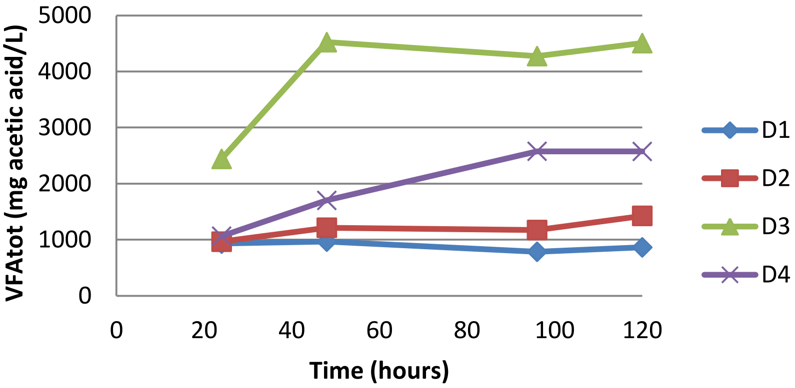

Figure 1. Total volatile fatty acids (VFA_{tot}) concentrations

In our previous studies, comparatively lower biogas yields (118-121 L/kg TVS) were obtained which could be attributed to hardly-biodegradable particulate matter content of cattle manure (Turker et al., 2013). The application of hydrolytic enzymesin anaerobic digestion systemstherefore can be an effective solution in order to enhance hydrolysis and acidification steps which can lead to higher biogas and methane yields. Although enzyme addition is thought to be an expensive solution, recent developments in environmental biotechnology has given rise to achieve more cost-efficient ways to use enzymes in such systems, which makes it a promising alternative solution for efficient anaerobic digestion performances.

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(76) Enzymatic Treatment of a Diclofenac Solution

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Abstract

Due to the persistent feature of some compounds commonly found in wastewaters, their treatment is very difficult through conventional processes. Therefore, alternatives, among which arises the enzymatic treatment, are continuously sought. The objective of this work is to analyze the feasibility of degradation of a widely used pharmaceutical compound, Diclofenac, using the enzyme Horseradish peroxidase as a catalyst of the reaction. Very promising results were obtained since there is no evidence of the use of this enzyme for the elimination of diclofenac compound. The influence of the initial concentration of enzyme and hydrogen peroxide in the removal efficiency is analyzed. A maximum value of removing close to 47% was reached when hydrogen peroxide and diclofenac were used in stoichiometric quantities.

Keywords

Diclofenac; enzymatic treatment; horseradish peroxidase; pharmaceutical compounds

INTRODUCTION

Pseudo-persistent contaminants in wastewater create a need to study different methods capable to degrade these contaminants in order to reduce its concentration in water sources and treatment plants, since they could generate some problems therein. The growing attention to the pharmaceutical compounds as potential pollutants leads to the need to study different methods to be able to remove them from these sources. One of the possible methods is the enzymatic elimination, which has proven to be very efficient in the removal of other recalcitrant contaminants, such as phenol (Pramparo, 2008; Gutiérrez, 2011).

In the last two decades, several processes have been implemented using different enzymes extracted from plants and microorganisms, such as peroxidases from various sources, including the horseradish peroxidase. Peroxidases are a type of enzymes that catalyze the oxidation of certain hydrogen donor's compounds, such as phenols and aromatic amines, by means of the hydrogen peroxide (H_2O_2) as a precursor of polymerization (Cánovas et al., 2003).

Among the different pharmaceutical compounds that can be found, there are substances in everyday use as antibiotics, hormones, pain relievers and anti-inflammatories (El-Ahmad & Mersch-Sundermann, 2000; Verlicchi et al., 2012). Different authors have reported the presence of these compounds in concentrations of µg/l in effluents from wastewater treatment plants (WWTP) and the environment, due to the persistence that exhibits these types of compounds (Kummerer et al., 1998; Cunningham et al., 2006). Because of the low efficiency of conventional processes used on the WWTP to treat this type of polluting compounds, usually physic-biologics, technologies using enzymes can be an interesting alternative. That is why this paper proposes the use of this technique to analyze the possible degradation of pharmaceutical compounds using enzymes. The objective of the present study is to analyze the feasibility of degradation of a non-steroidal anti-inflammatory, such as diclofenac, using the enzyme Horseradish peroxidase (HRP).

MATERIALS AND METHODS

Materials. Diclofenac was used in commercial presentation type ampoule of 3 ml containing 75 mg of sodium diclofenac per ampoule. Several dilutions of the compound were prepared in water and were measured for absorbance using a spectrophotometer UV, model Hach DR 5000. Using a scanning range of wavelength between 190 and 900 nm, it was determined that wavelength for maximum absorption of Diclofenac is 275 nm. This value was used to observe the behavior of the compound in the degradation process. The enzyme Horseradish peroxidase (HRP) was obtained from Sigma Aldrich (ref. P8250-50KU), with an activity of 181 U/mg according to the method of the pyrogallol. A stock solution was prepared in distilled water. The aliquots were stored at -4° C. The stock solution of hydrogen peroxide (H_2O_2) was prepared by dissolving the required amount of 30% hydrogen peroxide supplied by Bioquigen to obtain a final concentration of 100mM.

General Procedure. Different concentrations of H_2O_2, HRP and Diclofenac were analyzed. The different solutions of diclofenac were prepared by adding distilled water until obtaining the desired concentration. Both diclofenac and the solution of HRP were maintained within the reactor before adding the appropriate amount of hydrogen peroxide. Reaction time began when H_2O_2 was introduced into the reactor. In all experiments several liquid samples were taken (3 ml) to different reaction times to perform the analytical procedure.

RESULTS AND DISCUSSION

Analysis of the optimal Diclofenac concentration

Three different dilutions of diclofenac were prepared in 1, 2 and 3 L, to obtain a final concentration of 75, 37.5 and 25 mg/L respectively. A decrease in the absorbance value was obtained when the diclofenac concentration was diminished. This is related to the Beer-Lambert's law, in which absorbance is related with the concentration of the product, although it is proportional only to a certain extent. That is why, from the obtained results, it was decided to work with a Diclofenac concentration of 25 mg/L to have the absorbance value lower than 1.0 and ensure proportionality between concentration and absorbance.

Assay for the enzymatic elimination of Diclofenac

Various experiments were conducted to analyze if the enzyme Horseradish peroxidase is able to degrade or remove the selected compound. In the first instance, the influence of the hydrogen peroxide concentration was studied. The degradation test consisted of the measurement of the absorbance change of the solution at the time. To do this, 100 ml of Diclofenac with a concentration of 25 mg/L was placed in a batch reactor, continuously agitated with magnetic stirring at room temperature. The necessary amount of enzyme and hydrogen peroxide were added to the solution. Once hydrogen peroxide is added to the sample, reaction time starts and the value of absorbance at 275 nm it is regularly measured. The reaction is approximately evaluated over a period of time between 2 - 3 hours.

Analysis of the initial H_2O_2 concentration influence

Experiments to analyze the influence of the initial concentration of H_2O_2 were carried out in batch conditions. The concentration of HRP was maintained at $4.3 \bullet 10^{-4}$ mM in all cases. In every experiment, the solution changed color to yellow or orange, depending on the concentrations used, after the addition of H_2O_2. Darker solutions were obtained when more H_2O_2 was added to the sample, however, when excess of H_2O_2 was added, the solution had a final color a little clearer, as shown in Figure 1.

Figure 1. Observation of the colour produced in different reactions depending on the initial conditions used.

This fact is due to the amount of products formed in the reaction increased with an increase in the amount of H_2O_2 and, moreover, the inactivation of the enzyme causes lower levels of conversion and, therefore, fewer colors in the solution. This was evidenced with the occurrence of different peaks in the scanning of absorbance during the reaction. The results obtained from the removal of diclofenac for 4 different H_2O_2 initial concentrations are shown in Figure 2.

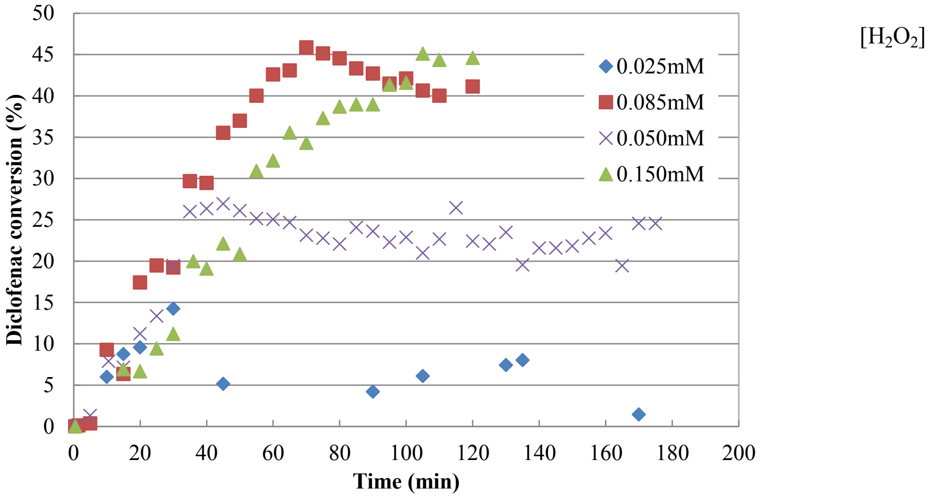

Figure 2. Influence of the initial H_2O_2 concentration. $[Diclofenac]_0$: 0.084 mM, $[HRP]_0$: $4.3•10^{-4}$ mM, pH 6 y T= 25°C.

As it can be observed in the figure, when a low concentration of H_2O_2 was applied, there was almost no reaction. As to the quantity of hydrogen peroxide was increasing, a greater removal of diclofenac was obtained, until it reached a maximum value of elimination or conversion. From this maximum value, when more H_2O_2 was added, higher performance in reaction was not obtained or, on the contrary, the amount of removed diclofenac decreased. This is due to the enzyme inhibition. For other compounds, it was determined that the optimum concentration of H_2O_2 to be used is an equimolar ratio with the compound to treat, for example, phenol (Pramparo, 2008). In this case, since the concentration of diclofenac is 0.084 mM it would be assumed that behavior should be similar. This is confirmed in Figure 2, where it can be observed that the maximum removal is obtained using an equivalent quantity of 0.085 mM of H_2O_2.

It was obtained around 47% of conversion of Diclofenac when using an equimolar ratio of H_2O_2. With an increase in the concentration of peroxide, the conversion of diclofenac decreased, as well as the reaction rate. More experiments are needed to determine a possible inactivation of the enzyme to increased levels of H_2O_2.

Analysis of the initial HRP concentration influence.

Several experiments were carried out to analyze the influence of the initial concentration of enzyme in the reaction. They used 6 different concentrations of HRP, varying between $4.3•10^{-5}$ mM to $8.6•10^{-4}$ mM. As it can be seen in Figure 3, as the initial concentration of HRP was increased, it increases the amount of removed diclofenac. When concentrations are used at less than $2.15•^{-4}$ mM a significant reaction is not evidenced, even after 180 minutes of reaction. However, with HRP concentrations greater than $3.23•10^{-4}$ mM, good percentages of elimination are obtained, reaching a maximum value of removal close to 47% using a concentration of HRP $8.6•10^{-4}$ mM.

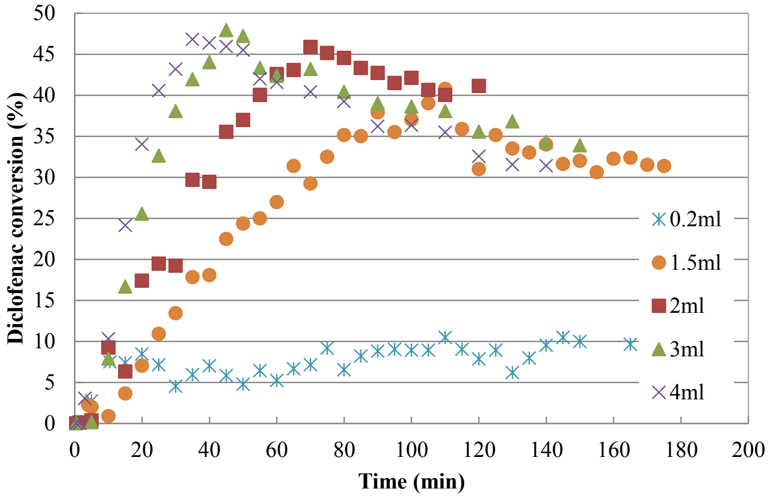

Figure 3. Influence of the initial HRP concentration. [Diclofenac]$_0$: 0.084 mM, $[H_2O_2]_0$: 0.085 mM, pH 6 y T= 25°C.

CONCLUSIONS

In the study of the enzymatic removal of diclofenac using HRP, high degrees of removal were obtained in most studied conditions. It was determined that the optimum concentration of work for diclofenac is 25 mg/L. The optimal initial concentration found to H_2O_2, for greater conversion of diclofenac, must be equal to 1 ratio between the molar concentration of diclofenac and that of H_2O_2. An excess of hydrogen peroxide in the reaction mixture may inhibit the catalytic action of the enzyme through its conversion to an inactive form, resulting in lower levels of conversion of diclofenac. The results obtained in this work are very promising due to the lack of evidence of the use of this technology for treating Diclofenac, which is often found in wastewaters and difficult to remove because of its high persistence.

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(77) The use of Oxygen Uptake Rate for the evaluation of a wastewater treatment plant efficiency

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Activated sludge processes are the most widely used wastewater treatment methods, which are based on the biodegradation of wastewater constituents by the microbial communities. The degradation and removal of organic substances is carried out by a large number of heterotrophic bacteria through aerobic processes, although nitrogen compounds removal is taken place in subsequent aerobic nitrification followed by anoxic denitrification steps. The aerobic process may be assessed by the utilization of a microorganim respiration technique, the measurement of the so called Oxygen Uptake Rate (OUR) parameter. The requirement for a wastewater treatment plant effluent to comply with stricter guidelines, results to significant efforts for the process appropriate adjustment and for its performance under optimised conditions. Towards that direction, OUR measurement is a useful tool for the evaluation of system's efficiency; in addition, oxygen uptake rate may provide useful information on the biodegradability potential of various influents, and the prediction of a wastewater treatment plant response during the addition of particular wastewaters. The aim of this study was the implementation of OUR technique for the evaluation of the performance of various municipal and industrial wastewater treatment plants.

A bench scale device was designed and constructed consisting in a batch reactor with a stirring system, placed in a constant temperature environment. Aeration was provided by a compressor and was measured by a dissolved oxygen sensor; the concentration of dissolved oxygen was continuously monitored and the oxygen uptake rate was calculated by the experimental data. Wastewater samples were collected from various locations of a municipal and a molasses wastewater treatment plant, and the oxygen uptake rate of an aerobic sludge sample was examined. The results showed that depending upon the wastewater sample origin, different respirographs could be deduced consisting in two distinctive areas: a higher one corresponding to easily biodegradable fraction of organics and a lower one corresponding to slowly biodegrading compounds or even to refractories. The presence of these compounds greatly affects their removal potential by the activated sludge and determines the biological process efficiency.

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(78) Chronic Effects of Antibiotic Combinations on Anaerobic Microbial Community

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Abstract

Anaerobic treatment methods can be an alternative application for treatment of pharmaceutical wastewaters, which has high organic content. Pharmaceuticals release through ecosystem and cause switching on microbial community structure and developing resistance genes. The aim of this study is to assess the effects of selected antibiotic mixtures on lab-scale anaerobic sequencing batch reactors in terms of microbial community structure. In this scope, four anaerobic sequencing batch reactors were operated by addition of different combinations of antibiotics (sulfamethoxazole, erythromycin and tetracycline) during six months. Bacteria, archaea and methanogens were quantified using quantitative PCR with specific primers. A decline characteristic was determined in bacterial, archaeal and methanogenic population during the operation period. Results indicating that, antibiotic addition has negative impact on microbial community structures of anaerobic reactors.

Keywords

Anaerobic reactor; antibiotic mixture; microbial community; pharmaceutical wastewater; q-pcr

1. INTRODUCTION

Antibiotics are chemotherapeutic agents that inhibit or abolish the growth mechanisms of microorganisms (Kümmerer, 2008). They are usually present as multi-component mixtures in environmental compartments. Moreover mixtures generally cause higher effects than individual compounds (Backhause et al., 2008). A considerable amount of antibiotics releases through ecosystem and causes changing on microbial community structure and developing resistance genes. One of the major sources of antibiotics in environment is the effluent of pharmaceutical production facilities (Larsson et al., 2007). Pharmaceutical industry generates wastewater with a high COD concentration (Zhou et al., 2006). Anaerobic treatment methods can be applied to this kind of wastewaters due to their high strength characteristics. The aim of this study is to evaluate the long-term effects of the selected antibiotic combinations on the lab-scale anaerobic reactors in terms of the bacterial and archaeal community dynamics. To achieve this goal, real-time quantitative polymerase chain reaction was applied to determine the changes of the amount of microbial groups.

2. MATERIAL AND METHODS

Five, 1,75 L-anaerobic sequencing batch reactors (ASBR) with 1,25 L-active volume were operated by addition of four different combinations of antibiotics (sulfamethoxazole, erythromycin and tetracycline). Reactors were abbreviated by ETS (erythromycin, tetracycline, and sulfamethoxazole), ET (erythromycin, tetracycline), ST (sulfamethoxazole and tetracycline), and ES (erythromycin and sulfamethoxazole) according to the antibiotic combination fed. A control reactor with no antibiotic addition was also operated for comparison with antibiotic fed reactors. Reactors were operated during 6 phases; each phase was operated 30 days. Antibiotic concentrations applied to the reactors are given in Table 1. The reactor was operated with a 24 h cycle (fill: 10 min, react: 22 h 45 min, settle: 1 h, decant: 5 min) at 35ºC with solids retention time of 30 days, hydraulic retention time of 2.7 days and MLVSS concentration of 12250 mg/L. Tested antibiotic concentrations are given at Table 1. Triple samples were taken on 10th, 20th, and 30th days of each operation. Genomic DNAs were extracted using GF-1 Bacterial DNA

Extraction Kit according to the manufacturer's instructions (GeneON, Germany). Bacteria, archaea and methanogens were quantified using quantitative PCR with specific primers Bac519f-917r, Arc349f-806r, and Met348f -786r, respectively. Statistical analyses were conducted by using Minitab program.

Table 1. Tested antibiotic concentrations.

	Tetracycline	Erytromycin	Sulfamethoxasole
Phase 1	5 mg/L	0,2 mg/L	0,2 mg/L
Phase 2	5 mg/L	0,5 mg/L	0,5 mg/L
Phase 3	10 mg/L	0,5 mg/L	0,5 mg/L
Phase 4	10 mg/L	1,0 mg/L	1,0 mg/L
Phase 5	15 mg/L	1,0 mg/L	1,0 mg/L
Phase 6	15 mg/L	1,5 mg/L	1,5 mg/L

3. RESULTS AND CONCLUSION

There was a significant change in the amount of these populations during operation period. The bacterial, archaeal, and methanogenic communities decreased over time with antibiotic concentration increased. While bacterial population started going up at 6th phase in erythromycin and tetracycline combination added reactor, only decreasing trend observed in the others. The number of archaea and methanogens went down over operation period. Minimum numbers of methanogenic and archaeal communities were measured in the samples taken from sulfamethoxazole and tetracycline combination added reactor at phase 6 (1,4E+05 and 1,5E+06, respectively. A decline characteristic was determined in methanogenic and archaeal population during the operation period. Similarly, Ahammad et al. (2013) reported that, wastewater from personal care products industy caused reduction on the number of methanogens. Moreover, in a study carried out by Cetecioglu and her collegues (2013), tetracycline had no significant effect on microbial community structure of the batch tests. In another study, Deng et al. (2012) reported that, microbial communities maintained system stability through adjusting bacterial, archaeal, and eukaryal compositions under high antibiotic concentrations. However, the results obtained from this study indicate that, antibiotic mixture addition has negative impact on microbial community structures of anaerobic reactors.

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(79) Two-Phase Microbial Removal of Hexavalent Chromium

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Abstract

The present study aims to the development of a novel two phase partition bioreactor (TPPB) for the microbial removal of Cr(VI) in synthetic wastewaters with extremely high chromium concentration (up to 1000 ppm). A TPPB could be either a two-phase liquid-liquid bioreactor (TPLLB) or a two-phase solid-liquid bioreactor (TPSLB) that allows maintaining a chromium concentration in the aqueous at levels that can be handled effectively by microbial reduction. As chromium is reduced, more chromium is released to the aqueous phase until eventually all the chromium is reduced to its nontoxic trivalent counterpart.

Preliminary studies focused on identifying the most effective and less toxic combination of organic solvent- extractant and the optimization of extraction conditions. In terms of organic solvents, hexane, heptane, chloroform, ethyl-acetate and kerosene were tested, whereas as extractants Aliquat 336, TOPO and TPB were used. Hexane, chloroform and ethyl-acetate were quite inhibitory on microbial growth and were excluded from our investigation. On the other hand, microorganisms exhibited tolerance to kerosene and heptane. So, the combination of kerosene and heptane with each of the extractants was investigated further. The combinations of kerosene/Aliquat 336 and heptane/Aliquat 336 proved to be the most effective for the extraction of Cr(VI) from aqueous solutions, but both formed a mesophase with the aqueous phase,. The problem was overcome for the combination of kerosene/Aliquat 336 by the addition of 1-hexanol, which had no toxic effect on microbial growth. Subsequently an enriched mixed microbial culture with high Cr(VI) reduction rate (15ppm/day) and high tolerance to the organic solvents was developed. The incubation of the acclimated culture with the mixture kerosene/ Aliquat 336/ 1-hexanol led to 100% mortality of microorganisms in the TPLLB during the second day of the bioreactor operation. It was proved that Aliquat 336 was the toxic substance that led to the toxicity of the mixture. The development of a solid-liquid two-phase bioreactor that employs an alkyl quaternary ammonium salt bentonite has on the other hand proved much more promising for the two-phase microbial reduction of hexavalent chromium. The key in this is the good reversible adsorption of the hexavalent chromium and the lack of toxicity.

Keywords: hexavalent chromium, microbial reduction, bioremediation, two-phase bioreactors

(80) Anaerobic digestion of halophyte plant biomass waste with an integrated wash pre-treatment for optimum biogas and nutrients recovery

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ABSTRACT

Salicornia bigelovii is a halophyte plant with great potential usage as sustainable feedstock for bioenergy generation since it can be cultivated without need for fresh water irrigation or arable land. Its oil-rich seeds are harvested for biofuel production with a major part of the plant remaining as biomass waste containing highly saline organic solids. The conversion of this biomass waste into biogas and nutrients through anaerobic digestion is proposed in integration a mild sea water extraction pre-treatment to both increase biodegradability and dilute salinity. When the biomass waste is given some contact time with sea water a large portion of COD becomes dissolved and biodegradable. In order to achieve maximum biogas conversion both dilution water and contact time at the pre-treatment are variable that need to be optimised as the former affects COD and salt influent concentration and the later the amount of biodegradable COD extracted. Experimental data combined with literature are used to optimise the process design in order to maximise methane production and waste stabilisation.

(81) Application of hollow fibre membrane MBR separation processes instead of GAC filtration in the physical-chemical industrial wastewater treatment

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Abstract

Nowadays, membrane technologies are becoming more frequently used for separation of wide varying mixtures result from a lot of industries and can compete successfully with traditional schemes. The aim of this paper was to analyse the use of ultra filtration with polypropylene hollow fibre membrane in the chemical physical systems instead of GAC filtration. A process data collection was performed and integrated with a characterization of the process effluents in terms of treatability and reusability. In order to evaluate properly the wastewater loading, an analysis course was set. The samples have been gathered for two years; instantaneous samples were drawn from the influent and treated wastewater. Based on daily average values, a general average has obtained. The experimental data were statistically analysed and the average values of the investigated parameters. It was found that ultrafiltration is a good process solution before discharge of the effluent.

(82) Characteristics of Ceramic Membrane Resistance in MBR Process

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Abstract

Ceramic membranes have been more useful than polymeric ones in membrane bioreactor (MBR) because of longer life and better physiochemical stability. In this study, flux and trans membrane pressure (TMP) were measured during the ceramic membrane filtration. In particular, the filtration resistance was evaluated as a function of membrane thickness. Silicon dioxide based tubular ceramic membranes with different thickness of 12, 7, 6.1 and 3 mm were submerged in the 5 liter of acryl reactor containing 2500mg/L mixed liquor suspended solid (MLSS). Filtration and backwashing were performed for 20 and 10 min, respectively. Reactor was operated for 100 min, and TMP was measured periodically while keeping flux constant. In experimental results, the filtration resistance decreased when the membrane thickness was lowered from 12 to 3 mm, the reduction in membrane thickness allows the effective use of air backwashing, which can save the energy and cost, eventually. Also the aeration can be done during air backwashing, simultaneously. The filtration resistance was nearly zero for the membrane with 3 mm thickness, and the effect of TMP was also negligible. Notably, the air backwashing was proven to be highly effective for ceramic membranes with lower thickness.

Keywords
Ceramic membrane; MBR; membrane resistance; backwashing

INTRODUCTION

Recently, proving the economic viability and functionality of membrane separations technology has been widely applied for the water treatment. With improved effluent quality standard, Membrane bioreactor (MBR) has become an option alternative to the activate sludge process (Pierre Le-Clech et al., 2006). Adding the membrane separation technology to conventional biological treatment process, this process possesses a number of advantages such as, effective separation of supernatant and solid phase, controlling sludge retention time (SRT) and stable effluent quality. However, the intrinsic membrane fouling and expensive physiochemical cleaning process applied to remove foulants are still persisting as the major issues. Due to longer life and better physiochemical stability, ceramic membranes have been considered as more useful than polymeric ones. Importantly, greater stability of ceramic membranes allows the use of air for backwashing. Thus, an evaluation of physical abilities of submerged ceramic membranes in MBR while operating periodic filtration and aeration is crucial. In the present study, an attempt has been to perform the aforementioned evaluation. By directly connecting filter and air pumps to the ceramic membranes, change in flux (J) and trans membrane pressure (TMP) can be measured. In particular, the change in filtration resistance (R_T) was evaluated as a function of membrane thickness.

EXPERIMENTAL METHODS

Silicon dioxide based tubular ceramic membranes with different thickness of 12, 7, 6.1 and 3 mm were obtained from Korea Ceramic Co., Ltd., Korea. The ceramic membranes were submerged in the 5 liter of acryl reactor containing 2500mg/L mixed liquor suspended solid (MLSS). Filtration and backwashing were performed for 20 and 10 min, respectively. Reactor was operated for 100 min, and TMP was measured periodically while keeping J constant.

R_T was calculated using the following equation (Ozako et al., 2001),

$$J = \frac{TMP}{\mu(R_T)} = \frac{TMP}{\mu(R_m + R_c + R_f)}$$

Where, R_m = intrinsic membrane resistance, μ = permeate viscosity, R_T = total resistance, R_c = cake layer resistance, R_f = fouling resistance.

RESULTS AND DISCUSSION

Fig.1 shows the changes in R_T as a function of membrane thickness. R_T was increased with increase in membrane thickness, irrespective of number filtration run. Profound increase in R_T was noticed for the membrane with 12 mm thickness as a function of increase in number filtration run. R_T for membrane with 3 mm thickness was zero, throughout the filtration process (100 min). As shown for membranes of other 3 mm thickness, the gradual increase in R_T at 0 min of consecutive filtration runs indicates the occurrence of fouling. Notably, the air backwashing was proven to be highly effective for membranes with lower thickness. Also it can be predicted when the TMP < 30 kPa, backwashing is sufficient enough to restore the filtration efficiency during the successive filtration runs, but when TMP > 30 kPa, chemical treatment is required to remove the foulants. These results show that considerable amount of energy can be conserved by using the combination of membranes with optimized thickness and air backwashing.

Table 1. Membrane specification and intrinsic membrane resistance(R_m)

	Size(H x D x T)	**Surface area(m^2)**	**Thickness**	**Mean intrinsic membrane resistance(R_m)**
#1	235 mm x 50 θ, 12 mm	0.037 m^2	12 mm	1.78E+11 m^{-1}
#2	241 mm x 50 θ, 7 mm	0.038 m^2	7 mm	1.37E+10 m^{-1}
#3	240 mm x 48.2 θ, 6.1 mm	0.0363 m^2	6.1 mm	5.47E+10 m^{-1}
#4	236 mm x 42 θ, 3 mm	0.0311 m^2	3 mm	1.34E+10 m^{-1}

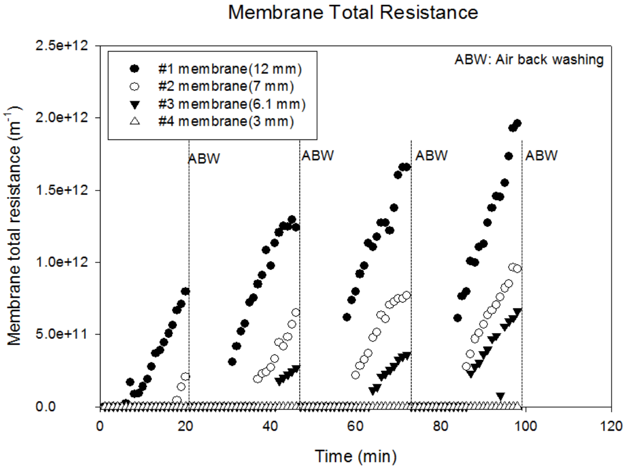

Figure 1. Changes in total membrane resistance (R_T) with respect to membrane thickness.

CONCLUSIONS

1) The filtration resistance decreased when the membrane thickness was lowered from 12 to 3 mm, the reduction in membrane thickness allows the effective use of air backwashing, which can save the energy and cost, eventually. Also the aeration can be done during air backwashing, simultaneously.

2) The filtration resistance was nearly zero for the membrane with 3 mm thickness, and the effect of TMP was also negligible.

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(83) Microbial Characterization and Quantitative Microbial Risk Assessment of Wastewater Reuse for Irrigation of Vegetables in Abu Dhabi

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Abstract

The use of treated wastewater for irrigation of edible crops presents an opportunity to enhance food security while overcoming water scarcityin the UAE. Owing to the lack of human-health risk studies, treated wastewater is currently only used for landscape irrigation. In this study, a comprehensive microbial diversity analysis and quantitative microbial risk assessment (QMRA) was carriedout using molecular biology tools. In contrast to previous QMRA studies, where common pathogens or indicators were directly targeted, this study focused on the analysis of the overall microbial community. The microbial diversity study using Illumina sequencing showed the presence of 21 untargeted pathogens at different stages of the treatment plant, including post-disinfection. The analysis showed that most Gram-positive pathogens increased significantly in relative abundance in post-disinfected samples, suggesting that chlorine-disinfection was not adequate in removing them. A QMRA model was constructed to estimate salmonella infection disease burden from consumption of treated wastewater-irrigated vegetables (lettuce, cabbage and cucumber). A quantitative-PCR (qPCR) was used to enumerate *Salmonella spp.* in post-disinfected samples. The median disease burden of all scenarios considered ranged from 1.8×10^{-5} to 6.1×10^{-3} DALYs pppy, which was above the acceptable disease burden threshold of 10^{-6} DALYs pppy recommended by the WHO.

Keywords

Wastewater, Illumina sequencing, QMRA, qPCR

MICROBIAL DIVERSITY

Prior studies have focused on detecting indicator organisms such as *Escherichia coli* and other pathogens from different stages of wastewater treatment to assess pathogen reduction[1]. In our work, in addition to targeting specific pathogen,*Salmonella spp.*, microbial community profiles from different stages of the treatment plant were also studied, using next generation sequencing (Illumina® sequencing). The raw Illumina sequencing results were clustered against the human pathogenic database [2], where 4225 sequences were found a match with 21 pathogens. The relative abundance revealed the effective reduction of Gram-negative pathogens, with the exception of *Vibrio cholera* and *Yersiniapestis*(results not shown). Conversely, the relative abundance of Gram-positive pathogens showed an increase in post-disinfected samples. The highest risk from Gram-positive pathogens was associated with*Mycobacterium tuberculosis* and *Bacillus anthracis*, which represented 2.84% and 9.3% of the overall pathogenic sequences, respectively (Figure 1). These pathogens were also significantly present in the post-disinfected samples, indicating inadequate efficiency of removal at the wastewater treatment plant.

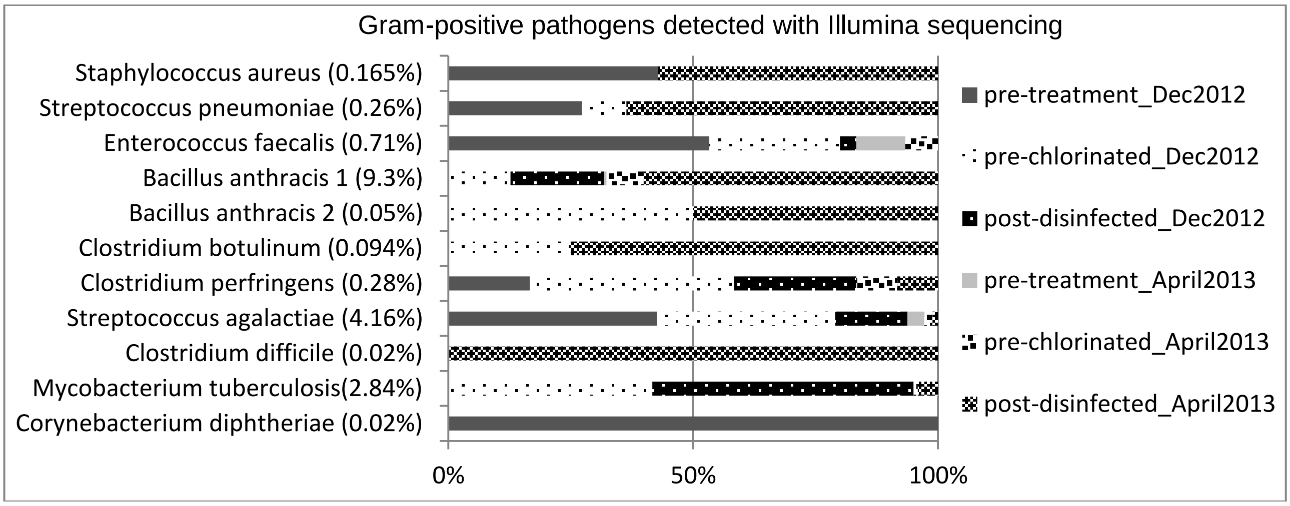

Figure 1.Relative abundance of Gram-positive pathogens detected with Illumina sequencing, out of a total of 4225 sequences that matched with 21 human pathogens.

QUANTIATIVE MICROBIAL RISK ASSESSMENT

A QMRA model was constructed to estimate the disease burden of salmonella infection from raw consumption of treated wastewater-irrigated vegetables (lettuce, cabbage and cucumber). Quantitative PCR (qPCR) was used to enumerate *Salmonella spp.* in post-disinfected samples. The results showed salmonella concentration ranging from 4-100 numbers/ml. Exposure models were developed and simulated with 10,000 iterations per simulation. The Monte Carlo analysis showed an elevated risk of disease burden(Figure 2), when compared with WHO's threshold value [3], which is 10^{-6}disability adjusted life years (DALYs) per person per year.

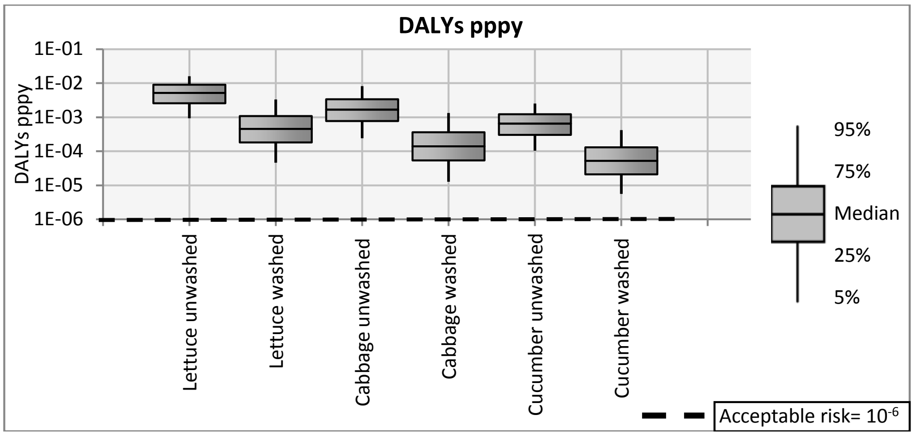

Figure 2.Annual disease burden (DALYspppy) of salmonella infection from raw consumption of vegetables irrigated with treated wastewater.

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(84) Zero Liquid Discharge Desalination: a demonstrated pilot application in Greece

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Abstract

Nowadays, the brine effluent from desalination plants is raising increasing concern. According to the United Nations, this is particular true for the Mediterranean Sea, with brine being recognized as one of the most critical threats to the sea life of the Mediterranean. In this paper, Zero Liquid Discharge (*ZLD*) is being suggested as a promising process for solving permanently this problem. A pilot application has been installed in Tinos Island, Greece and has been tested thoroughly in the context of the LIFE+ project with the acronym SOL-BRINE. This paper describes the design philosophy and contains evaluation data concerning the quality of the end-products. Finally, suggestions for the full-scale deployment of this innovative technology are provided.

Keywords

Desalination; Brine management; Renewable energy; Zero Liquid Discharge; Brine treatment.

INTRODUCTION

Balance between water demand and availability has reached a critical level, while water shortage problems are becoming increasingly acute in several areas across the world. This will be exacerbated significantly due to climate change. Europe has been recognized to be greatly affected by climate change with significant changes both in water resources availability and water rainfall patterns.

In order to address this challenge, more and more countries are turning to desalination for balancing existing or forthcoming gaps in water supply needs. Mediterranean countries and more importantly the Southern and Eastern Mediterranean Countries (SEMC) are emerging into a dynamic desalination market. Should all Mediterranean countries be seen as a whole, the total desalination capacity installed is estimated over 11.6 million m^3/day (Boyé, 208; Canovas 2012). Some of the major desalination producers are: Spain, Algeria, Israel, Turkey, Italy, Malta etc. They pump seawater from the Mediterranean Sea and through membrane treatment they produce potable water.

However, the desalination process involves the production of a huge amount of wastewater: 2 liters for every liter of potable water produced. This volume of wastewater poses a significant management problem, as well as critical pressures in the sea environment (for seashore desalination plants) and the underground aquifers (for inland desalination plants). The United Nations Environment Program (UNEP-MAP) has recognized the problem of brine disposal as one of the major threats to the Mediterranean Sea. More specifically, one of the most significant seagrasses of the Mediterranean Sea (Posidonia Oceanica), which is protected under the Barcelona Convention, has been identified to be highly vulnerable in salinity changes and as a result to brine exposure. The problems are becoming increasingly severe at cases where low circulation rates predominate.

THE SOL-BRINE SYSTEM

The SOL-BRINE project

In order to address this critical problem, a pilot system has been developed in the framework of a European project with the acronym SOL-BRINE.

SOL-BRINE is a LIFE+ Environmental Policy and Governance Project (LIFE09 ENV/GR/000299) co-funded by the European Community. The project was implemented in Tinos Island, Greece under the coordination of Tinos Municipality and the cooperation of the National Technical University of Athens and Culligan Hellas SA. Within the framework of the project, an energy autonomous brine treatment system has been developed for the total elimination of brine, according to the Zero Liquid Discharge (*ZLD*) principle. The system has been designed by the Unit of Environmental Science and Technology (UEST), which belongs to the school of Chemical Engineering of the National Technical University of Athens.

The SOL-BRINE concept

The overall scope was to develop an energy autonomous brine treatment system for the total elimination of the brine, so as to address effectively the complex issue of sustainable water management and desalination. The innovative features of the system include (Xevgenos et al, 2013):

- Total brine elimination. The system has been designed in line with the Zero Liquid Discharge principle;
- Water Recovery (>90%);
- Production of useful end-products. Through the operation of the prototype system the following two products are produced: (a) distilled water of high quality and (b) dry salt. Both products have increased market potential;
- Energy autonomous operation. Solar thermal collectors are used for delivering hot water (delivered at 80°C approximately) and a photovoltaic generator for electricity. All energy requirements are covered exclusively through the use of solar energy; and
- Use of state-of the art technology: the evaporation of water is realized through custom designed vacuum evaporation technology (evaporator and crystallizer) and solar dryer.

The SOL-BRINE concept is summarized in the following Figure.

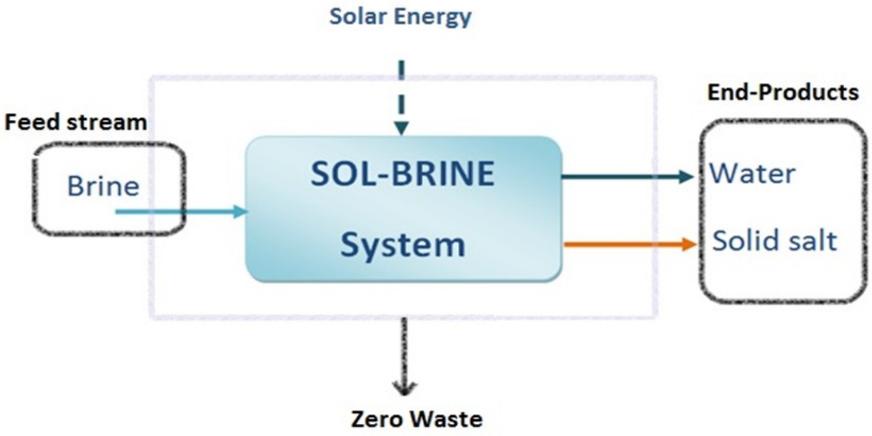

Figure 33. The SOL-BRINE concept

The SOL-BRINE system

In the course of the project, an innovative, energy-autonomous (through solar energy) pilot system was developed for the treatment of brine from an existing desalination plant. The system was installed in Tinos Island with a capacity of 2m^3/day (feed volume rate of brine effluent). It was able to treat a small portion (<1%) of the total quantity of brine effluent produced from the desalination plant.

The system comprises three treatment stages: (a) an evaporator unit, (b) a crystallizer unit and (c) a dryer unit (see also Figure 34).

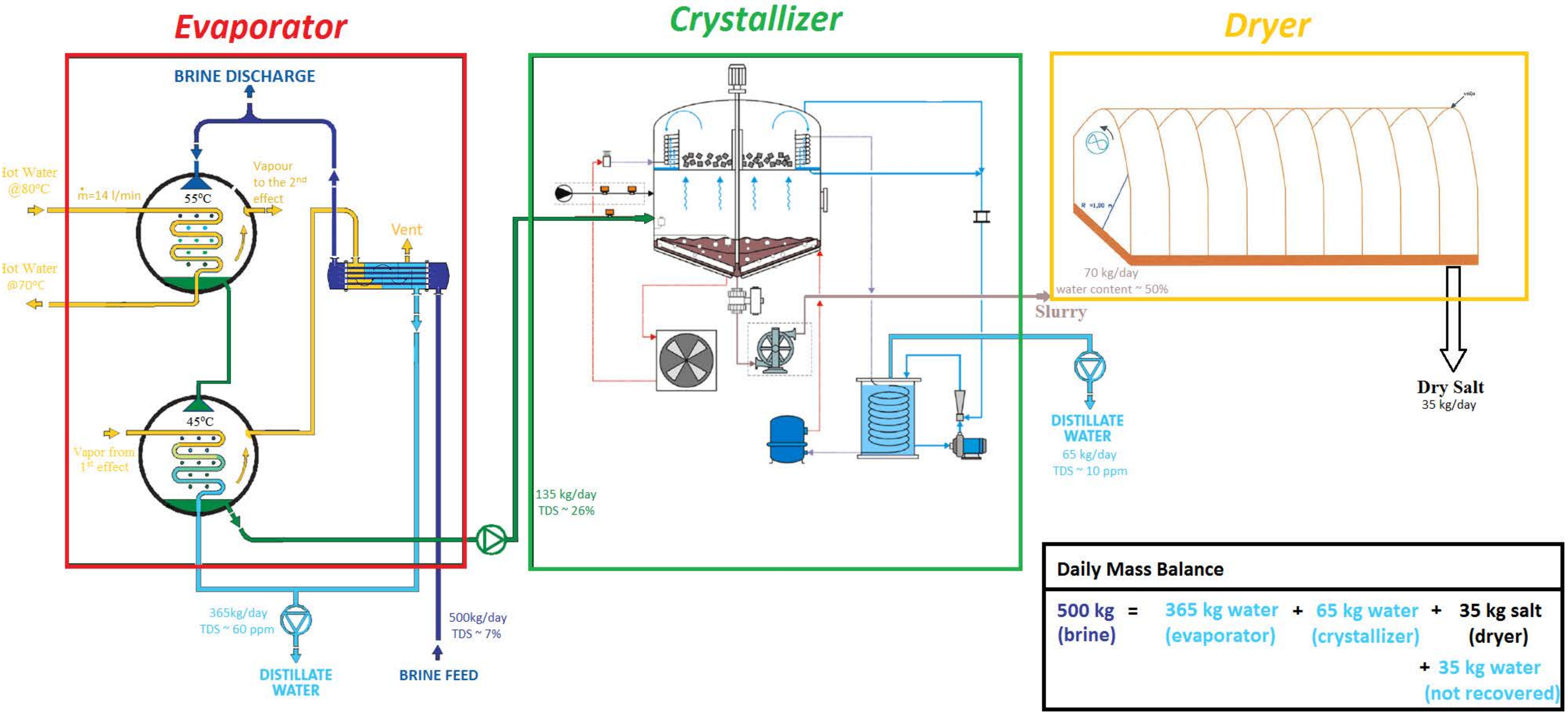

Figure 34. Process flow diagram of the SOL-BRINE system. The figures represent the daily mass balance of the system

The prototype system has been tested thoroughly and the technology has been demonstrated in pilot scale. The system results are very promising and can be further exploited with its market uptake. The results of the project are available in the project website (http://uest.ntua.gr/solbrine).

FULL-SCALE SUGGESTIONS

From the experience obtained by the operation of the prototype brine treatment system, a number of critical aspects have been identified, so as to improve its efficiency and its economic viability. These include, but are not limited to the following:

- Control of the concentration of the exit stream from the evaporator, through fine monitoring and recirculation of the brine stream;

- Suggestion of suitable materials that combine high corrosion resistance and cost effectiveness;

- High energy performance through energy recovery and use of low-grade or/and waste heat;

- Promotion of integrated approaches through the development of triple purpose plants: (a) Concentrated Solar Power plants, for electricity production, (b) desalination plants (RO) for water production and (c) ZLD plants for water and salt recovery. These plants can be ideally suited to regions with high solar energy yields, more significantly in the Middle-East and North-African (MENA) region and the Mediterranean.

This technology can be used as an end-of pipe wastewater treatment equipment to every existing desalination unit (thermal or membrane desalination plants) and eliminate the brine effluent. Except for eliminating the need for brine disposal, this innovative brine treatment process results to the production of valuable end-products that can recover part of the capital cost and therefore increase the economic viability of the whole system.

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(85) Modelling aerobic methane oxidation in a municipal WWTP

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Abstract

Methane is an potent greenhouse gas and its emission from municipal wastewater treatment plants should be prevented. One way to do this, would be to promote the biological conversion of methane over stripping in the aeration tanks. In this study we extended Activated Sludge Model n° 1withbiological methane oxidation to verify the effect of aeration rate, solids retention time and influent methane concentration on the balance between conversion and stripping. This knowledge helps to stimulatethe methane oxidizing capacity of activated sludge to abate methane emissions to the atmosphere.

Keywords

Activated sludge, ASM, climate footprint, greenhouse gases, methane

INTRODUCTION

Municipal wastewater treatment of gives rise to the emission of the greenhouse gases carbon dioxide, nitrous oxide and methane. Methane is a potent greenhouse gas with a global warming potential of 25 CO_2-equivalents (IPCC, 2007). In an long-term study on a municipal wastewater treatment plant (WWTP) methane was found to make up 13.5 % of the plants greenhouse gas footprint, exceeding the amount of emitted carbon dioxide related to the plant's electricity and natural gas consumption(Daelman et al., 2013).Globally, sewage treatment accounts for 4 % of the total methane emission (Conrad, 2009).

Basically, the methane that is emitted from a WWTP can be traced back to two sources. Either it is stripped from the incoming wastewater after it has been produced in the sewer (Guisasola et al., 2008), or it is produced during the storage and manipulation of sludge (Daelman et al., 2012). Dissolved methane can be biologically converted, besides being stripped.It was recently discovered that about 80 % of the dissolved methane entering an aerated activated sludge tank was converted with the remainder being stripped(Daelman et al., 2012).Aerobic conversion of methane is performed by methanotrophic bacteria(Ho et al., 2013). Stimulating this methane oxidizing capacity of activated sludge could be a way to avoid the emission of methane. In the end, this could lead to more sustainable wastewater treatment.

The objective of this study was to investigate the effect of a number of operational process conditions on the fate of dissolved methane in an activated sludge plant. To this end, the Activated Sludge Model n° 1 (ASM1) was extended with aerobic methanotrophic growth.The resulting model, called ASM1m, was implemented in Benchmark Simulation Model n° 1 (BSM1)(Copp, 2001) and termed BSM1mTaking into account biological oxidation and stripping of methane, BSM1m is the first model describing dynamic emissions of methane during wastewater treatment. As such, it complements existing models for the emission of nitrous oxide in estimating greenhouse gas emissions from WWTPs.

MATERIALS AND METHODS

ASM1m adds two processes to ASM1: aerobic growth and decay of methanotrophs. The two additional state variables are methane as substrate (S_{CH4}) and methane oxidizing bacteria (X_{MOB}).

To describe the behaviour of the overall WWTP,ASM1m was implemented in BSM1m, which consists of two anoxic tanks followed by three aerated tanks and a settler and a secondary settling tank (Copp, 2001).BSM1m was used to investigate the effect of the following three operatingvariableson methane conversion rate and methane stripping: aeration rate (in reactor 3 and 4), influent methane concentration and solids retention time.Table 1 gives an overview of the relevant parameters as well as their default values and the range over which they were varied.Besides the percentage of incoming methane that is stripped, also the conventional BSM1 criteria Effluent Quality (EQ) and Operational Cost Index (OCI) were calculated.

Table 18. Overview of the operating conditions applied in the scenario analysis.

Operating condition	Parameter	Default value	Range
Aeration rate in reactor 3 and 4	$k_L a_{O_2}$	240 d^{-1}	0 - 400 d^{-1}
Influent methane concentration	$S_{CH_4,infl}$	10 g COD.m^{-3} (*)	0 - 50 g COD.m^{-3}
Solids retention time	SRT	9.18 d(**)	2 – 12 d

(*)Daelman et al. (2012)

(**) Calculated from solids balance

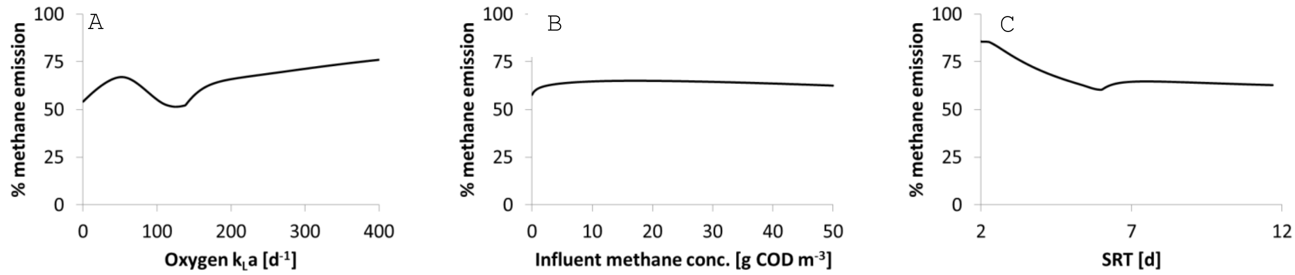
RESULTS AND DISCUSSION

Figure 35shows the influence of the operating conditions on thepercentage of incoming methane that is emitted and on the plant’s performance in terms of effluent quality and operational costs.

At very low aeration rates ($k_L a$ <52 d^{-1}), methanotrophs are outcompeted by ordinary heterotrophs (data not shown), while methane stripping increases with increasing $k_L a$, resulting in higher methane emissions.At higher, but still low aeration rates($k_L a$ = 52-126 d^{-1})the increasing methanotrophic growth is reflected in decreasing methane emissions. Beyond the optimum of 126 d^{-1}, stripping takes over from methanotrophic growth and the methane emission increases again. The optimal aeration rate to curb the emission does not coincide with the best effluent quality (lowest EQ) or the lowest operating costs (lowest OCI).

At low influent methane concentrations, most of the methane is converted in the anoxic tank using the oxygen entering with the recycle sludge. As the influent concentration increases, more methane passes through the anoxic tanks to the aeration tanks where it is stripped. Upon a further increase in the influent methane concentration, the conversion in the aeration tanks takes over from the stripping. The impact on the plant’s effluent quality and operational cost is negligible.

The percentage of incoming methane that is emitted decreases with increasing SRT, at least for SRT-values lower than 6 d. When the SRT increases beyond 6 d, the emission first increases and then decreases gradually. Thisis explained by the growth of methanotrophic biomass (data not shown). For SRT-values increasing up to 6 days, the amount of methanotrophic biomassincreases, which is reflected in a decrease of the methane emissions. From an SRT of 6 d onwards, the biomass increase slows down.The optimal SRT to minimize the emission does not coincide with the best effluent quality (lowest EQ) or the lowest operating costs (lowest OCI).



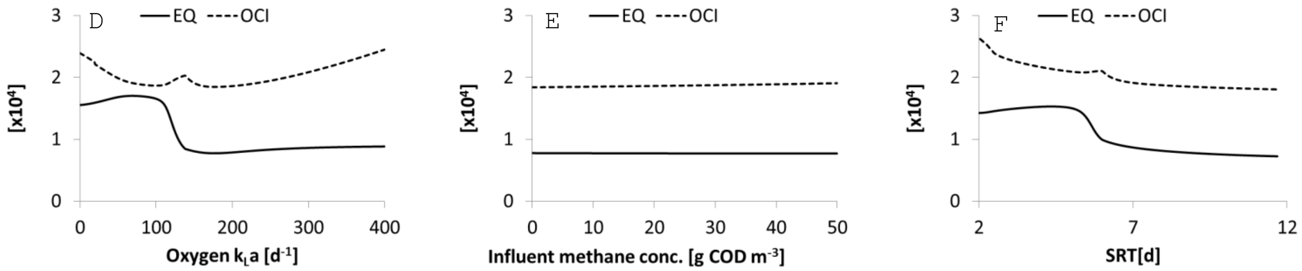


Figure 35. Top: emission of methane as percentage of incoming methane vs. aeration rate (A), influent methane concentration (B) and SRT (C).Bottom:Effluent Quality and Operational Cost Index (for both: the lower the better)vs. aeration rate (D), influent methane concentration (E) and SRT (F).

CONCLUSIONS AND PERSPECTIVES

- Aerobic methane oxidation during biological wastewater treatment was modelled (ASM1m) and its interaction with methane stripping wasassessed in a simulation study for a municipal WWTP.
- Aeration rate, influent methane concentration and solids retention timeaffect methane emission and could therefore be used for mitigatingmethane emissions from WWTPs.
- The model will be used to elucidate how the methane emission relates to the plant performance in terms of effluent quality and operational cost, resulting in a multi-criteria analysis.

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(86) Disintegration of waste-activated sludge using a novel hydrodynamic cavitation system

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Abstract

New techniques are being added to wastewater treatment schemes for reducing the sludge production and for meeting the high standards of environmental regulations. The present work highlights the use of one of these techniques, the disintegration of waste-activated sludge (WAS) by means of the hydrodynamic cavitation process. The disintegrated WAS could be used both in the denitrification process in order to supply an organic carbon source and in the anaerobic digestion process in order to increase the methane yield.

A novel hydrodynamic cavitation system has been used to break up the WAS, evaluating the solubilisation of matter, the biodegradability improvement, and the effects on microbial activity.

The system is based on a particular geometry of the constriction which create multi dimensional vortices of liquid that never hint the walls of the cavitation reactor, avoiding the problem of the erosion, allowing to harness the impressive effects of hydrodynamic cavitation for chemical-physical transformations.

The performed experiments indicated that solubilisation of chemical oxygen demand (COD) increased with the specific supplied energy applied. For specific energy inputs of 1250 kJ/kg of total solids, the microbial activity of the aerobic and anaerobic bacteria investigated was preserved, while specific energy inputs of 2500 kJ/kg of total solids damaged bacterial cells, decreasing by a half the specific oxygen up-take rate (SOUR) due to the endogenous respiration. The results confirmed low specific supplied energy induces floc disintegration and extracellular polymeric substances (EPS) destructuration, while high specific supplied energy is responsible for cell lysis.

Based on the results, different applications of the novel hydrodynamic cavitation system in wastewater treatment schemes have been suggested.

(87) Implementation of an anaerobic side-stream reactor in CAS systems

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Abstract

In recent years a lot of techniques have been developed to reduce the sludge production based on sludge disintegration and solubilisation mechanisms, such as biological, thermal, thermochemical, high temperature oxidation and mechanical treatments, ultrasonication and ozonation or by using chemical compounds.

Among all the biological treatments, one is based on the waste activated sludge recirculation between aerobic, anoxic and anaerobic conditions. The process mainly consists of an aeration tank, a settling tank and an anaerobic side-stream reactor for sludge treatment and reduction, where a portion or, in some cases, all the excess sludge of the activated sludge process is recycled. Studies reported a sludge yield (Y_{obs}) of 0.20 -0.29 kgTSS/kgCOD, which were 40-50% less than conventional activated sludge processes.

Initial experimental studies in a lab scale activated sludge system equipped with an anaerobic side-stream reactor were conducted. The activated sludge system has been operated with real wastewater for 80 days. The anaerobic side-stream reactor had been inoculated with an anaerobic sludge from the civil wastewater treatment plant of Le Forche (Italy). The anaerobic reactor has a capacity of 10 l and was operated with a sludge retention times of 15 days. During the monitoring period was not performed any extraction of excess sludge mining that the process has a low sludge production.

The anaerobic side-stream reactor allowed an increase of the soluble COD and of the ammonia, mainly due to a cell lysis process. The pH, ORP and temperature in the anaerobic side-stream reactor were kept free to vary. After few days, they were 7.71, -430 mV and 31°C, respectively. Further, sludge settleability was not compromised by the presence of the anaerobic side-stream reactor.

Future research should clarify the questions concerning the main operative parameters and the possible mechanisms involved in the sludge reduction in the anaerobic side-stream reactor.

(88) Constructed wetlands with Vetiver grass: an alternative for treatment of sanitary wastewater

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Abstract

The constructed wetlands system for wastewater treatment was built in dependencies of the Stadual University of São Paulo "Julio de Mesquita Filho", the plant used was the Vetiver Grass (Chrysopogon zizaniodes). The physical-chemical parameters of the effluent and the nutritional conditions of Vetiver grass were analyzed during one year, after this period it can be concluded that the system of constructed wetlands is a simple and efficient alternative to treatment of wastewater and Vetiver grass has characteristics which make it suitable for this use.

Key words

Sanitary Wastewater, *Chrysopogon zizaniodes*, Effluent Treatment, Constructed Wetlands.

INTRODUCTION

Among the major environmental problems humanity will face in the future is the depletion of water resources. Pollution from human activity and its indiscriminate use contribute to the decreased availability of water quality.

The scientific community has dedicated to solve this problem. Despite the advances made, a challenge for the researchers is to make these technologies accessible to the community, in front that, simplified technologies has been studied. Among these technologies are the Constructed Wetland (CW). These systems are designed to use plants, in which, naturally, and under suitable conditions, different processes occur for the treatment of wastewater (MATOS et al., 2010).

The choice of plant species to be implanted is important to project success. The vetiver grass (*Chrysopogon zizanioides*), is a grass (Poaceae) perennial, known worldwide for essential oil extracted from your roots and used in the pharmaceutical industry. Its high growth rate combined with their tolerance to different environmental conditions, suggests that Vetiver grass would be an ideal plant to use large-scale wastewater treatment. (VIERITZ et al., 2010; TRUONG, et al., 2008).

The aim of this study is to evaluate the efficiency of removal of pollutants from a wastewater treatment plant that uses the technology of constructed wetlands and evaluate the performance of plant chosen, the Vetiver grass.

MATERIAL AND METHODS

The wastewater treatment plant (WWTP) is installed in the dependences of Stadual University of São Paulo "Júlio de Mesquita Filho" (UNESP) in the city of Bauru, in São Paulo – Brazil, and was schematized in Figure 1, the vegetable species chosen was the Vetiver grass (*Chrysopogon zizanioides*), and all process is composed of five stages of treatment:

- **Preliminary treatment (PT 1):** composed by grating and sieve static hydrodynamic.
- **Primary treatment (PT)**: consisting of a decanter.
- **Secondary treatment**: is the set of three tanks (9m x 4,5m) with horizontal sub-surface flow. Each tank (1H, 2H, 3H) being composed of a kind of the substrate and have 91 copies of Vetiver grass.
- **Tertiary treatment:** consisting of three tanks (3,5 m x3,5) with vertical flow. Each tank was called 1V, 2V and 3V being composed of a kind of the substrate and have 25 copies of Vetiver grass.

- **Disinfection:** made by chlorination.

The tanks 1H and 1V comprises stone and sand, 2H and 2V are composed of polyestyrene and ground, and the tanks 3H e 3V have only ground as substrate.

The removal efficiency of pollutants and their concentrations were calculated from the results obtained in the analysis of the following physicochemical parameters: conductivity, pH, alkalinity, dissolved oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Kjeldahj Nitrogen (TKN), Ammonia Nitrogen (AN), Nitrate, Nitrite, Phosphate, Total Phosphorus, according to Standard Methods (APHA, 2005).

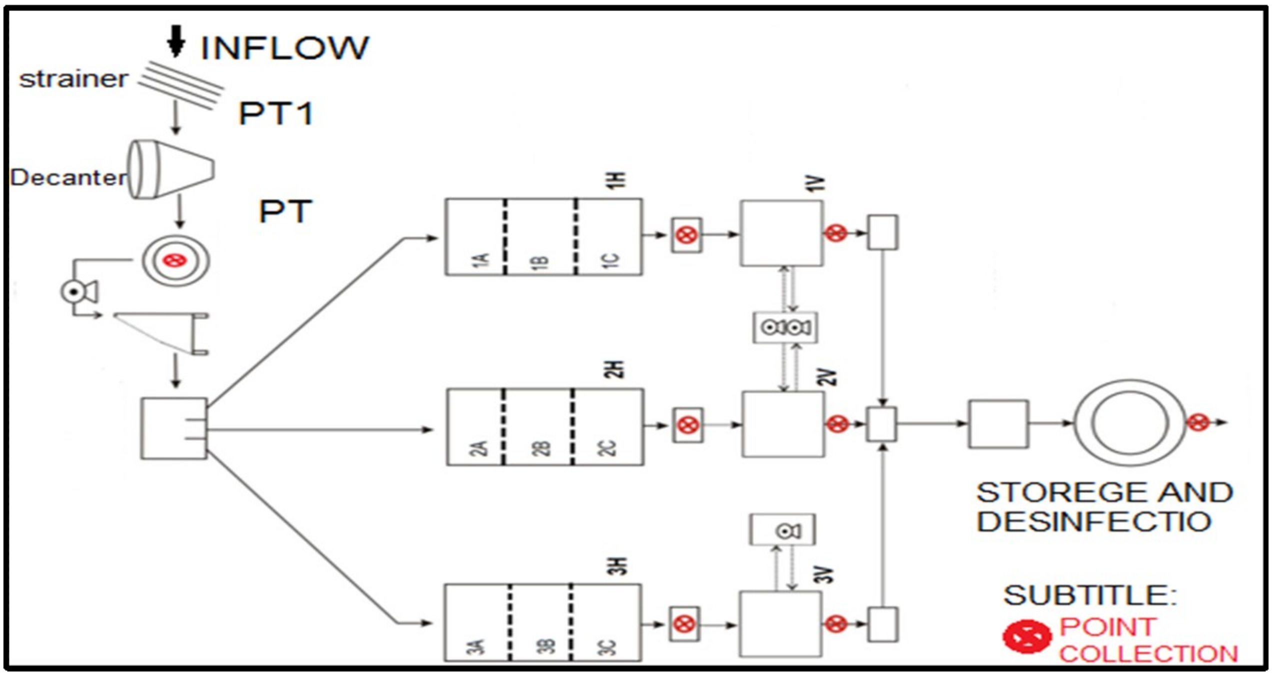

Figure 1: schematic representation of WWTP (PT1 – Preliminary Treatment; PT – Primary Treatment; 1H, 2H and 3H - Horizontal flow tank; 1V, 2V e 3V –vertical flow tank)

To evaluate the performance of Vetiver was made two collections of biomass and was be observed the following parameters: height and color of leaves, and nutritional analysis (concentrations of nitrogen, phosphorus and potassium; productivity of green mass and dry mass, and calculate of stock of nitrogen, phosphorus and potassium). The data obtained from sample collected of the tanks will be compared with the control sample, which not receives effluent. To calculate the stock of nitrogen, phosphorus and potassium in the biomass use the equation (1) (HERNARES, 2008):

$$S = D\ x \frac{C}{100} \tag{1}$$

S – stock (g/m^2) *D – Dry Matter (g/m^2)* *C – Concentration (g/kg)*

RESULTS AND DISCUSSION

The monitoring of WWTP occurred between the months of November/2011 until October/2012, and this long period was divide in other 5 shorter periods (Class 1, Vacation 1, Class 2, Vacation 2, Class 3) in accordance with campus activities and the volume of effluent input (3500 L/day during vacations and 5000 L/day in class period).

It was observed that the results of removal efficiency of pollutants were higher during the class periods, as shown by the results of BOD (Vacation 1: 50%; Class 2: 84%, Class 3: 79%), COD (Class 1: 84%; Vacation 1: 73%; Class 2: 88%; Vacation 2: 90%, Class 3: 87%), Ammoniacal Nitrogen (Class 1: 99%; Vacation 1: 83%; Class 2: 86%; Vacation 2: 62%, Class 3: 69%) and Total Nitrogen (Class 1: 83%; Vacation 1: 59%; Class 2: 83%; Vacation 2: 93%, Class 3: 60%).

One of the factors that explain these results are different activities on campus in both periods, because there is a direct relationship with the characteristic of the effluent input. During class time there are more people circling at the University and most of the pollutants are organic and biodegradable, during the vacation period the employees are dedicated to detailed cleaning of the premises of the university, therefore there is a higher concentration of chemicals derived from cleaning and greater concentration of components of inorganic origin.

When the efficiency of each tank are compared, it can be inferred that the tanks filled with sand, and the tanks filled with polystyrene performed better efficiency as can be seen in some of the parameters, and the values of COD, TKN and AN shown in Tables 1, 2 and 3.

Table 1: Values of COD removal efficiency (NOTE: the periods marked by the symbol * don´t have values of removal efficiency)

	1H	2H	3H	1V	2V	3V
Class 1	80%	87%	83%	20%	*	*
Vacation 1	61%	17%	64%	52%	*	*
Class 2	85%	79%	87%	31%	24%	8%
Vacation2	88%	*	91%	12%	15%	23%
Class 3	89%	90%	85%	16%	12%	30%

Table 2: Values of TKN removal efficiency
(NOTE: the periods marked by the symbol * don´t have values of removal efficiency)

	1H	2H	3H	1V	2V	3V
Class 1	88%	89%	88%	24%	58%	*
Vacation 1	47%	35%	48%	67%	19%	74%
Class 2	73%	71%	65%	48%	37%	54%
Vacation2	94%	87%	*	*	*	*
Class 3	30%	22%	57%	23%	47%	23%

Table 3: Values of NA removal efficiency
(NOTE: the periods marked by the symbol * don´t have values of removal efficiency)

	1H	2H	3H	1V	2V	3V
Class 1	84%	97%	95%	99%	57%	*
Vacation 1	*	31%	25%	58%	62%	80%
Class 2	72%	64%	75%	53%	50%	55%
Vacation 2	41%	34%	47%	33%	30%	50%
Class 3	37%	36%	56%	57%	81%	37%

In these tanks the Vetiver grass also showed the best results for productivity of green and dry matter and nutrient stocks (Nitrogen, Phosphorus and Potassium), highlighting the results obtained in the tanks filled with polystyrene, which were higher. The values obtained were in 2H tank: Productivity of Green

Mass: 7010 g/m^2; Productivity of Dry Mass: 2522 g/m^2; Stock Nitrogen: 235 g/m^2; Stock Potassium: 247 g/m^2; Stock Phosphorus: 26 g/m^2. The 2V tank showed the following values: Productivity of Dry Mass: 2522 g/m^2; stock Nitrogen: 103 g/m^2; stock Potassium: 167 g/m^2; Stock Phosphorus: 8.5 g/m^2; suggesting that the plant has adapted better conditions offered by that substrate.

CONCLUSIONS

After the analysis of the physic-chemical parameter is concluded that the results of removal efficiency of pollutants were satisfactory in all tanks, but those who performed better were the 2H and 3H tanks filled with sand and polystyrene, respectively.

The best results of Productivity of Dry Mass, Productivity of Green Mass and Stock of Nutrient (nitrogen, phosphorus and potassium) have been found in tanks 2H and.

Relating to the performance of the plant species with the results of removal efficiency, suggest that Vetiver grass is an appropriate species for use in Constructed Wetlands, which is consistent with the information obtained in the literature, which mentions that the Vetiver grass is a durable plant and resistant to adverse environment, the constant variation in the concentration of pollutants, and obtained satisfactory results when used for remediation of soils and aquatic environments. (TRUONG et al 2008 VIERITZ et al 2008; MAKRIS et al 2007.).

ACKNOWLEDGEMENTS

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(89) Reuse of urban wastewater: preliminary investigation on the discharges of public owned treatment plants in Veneto region (North Italy)

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Abstract

Wastewater reuse depends on the specific use and on the final quality of the considered discharges. A preliminary investigation of Wastewater Treatment Plants (WWTPs) equal or higher than 10.000 equivalent inhabitants has been performed in Veneto region (North Italy), recovering data on institutional controls from the Regional Environmental Informative System (SIRAV) managed by ARPAV. Critical parameters have been highlighted and assessed according to specific additional treatment stages necessary to meet the requirements of Italian regulation for wastewater reuse. Critical aspects have been considered and discussed.

Keywords

wastewater reuse, dangerous substances, priority pollutants, emerging pollutants, limit of quantification (LOQ), disinfection by-products, Escherichia coli.

1. INTRODUCTION

The protection of water resources is crucial for human health, for the safeguarding of the environment and in regards to an increase in industrial activities, within the context of a harmonious and well–balanced economic development. Water appears to be a very precious and scarce resource due to population growth, increasing human needs (Leverenz et al., 2011) and climatic changes. Water scarcity is one of the biggest challenges humanity is facing. Approximately 2.5 billion people –1/3 of the world's population – live in areas that the World Bank characterizes as "water stressed"; in 15 years, this will be 2/3 of the world's population (Organica, 2014). In Europe the last two decades have witnessed growing water stress, both in terms of water scarcity and quality deterioration, which has prompted many municipalities to look for a more efficient use of water resources, including a more widespread acceptance of water reuse practices (Bixio et al., 2006). This is much more evident in the Mediterranean area and in Italy; wastewater reuse appear to be one of the possible measure of intervention (Manios and Tsanis, 2006); they must be assessed according to the required technological improvement in relation with the discharge limit values and the specific use of the recovered waters (industrial use, irrigation, etc.).

The Directive 2000/60/EC (Water Framework Directive – WFD, EC, 2000) fixes environmental objectives and establishes that measures must be implemented by member States to achieve these objectives. The WFD indicates that the member States should define the *ecological* and *chemical status* of their water bodies by means of monitoring programmes. The sustainable use of water resources must be guaranteed through qualitative and quantitative aspects. Water monitoring and the control of discharges are performed with the aim of achieving the quality objectives established in the directive: a "Good" status shall be reached within 15 years from its enforcement; a Good surface water status is considered to be that achieved by a water body when both its *ecological* and *chemical status* are at least "Good" (art. 2 WFD). An approach to achieve sustainability imposes a development that meets the needs of the current situation without compromising the ability of future generations to satisfy their own needs (UNEP, 2002). Wastewater (WW) reuse contributes to sustainability.

In Italy a specific regulation on WW reuse has been established with the Italian Decree n. 185/2003 for the characteristics of wastewaters intended for reuse. This technical regulation defines the conditions for the reuse of domestic, urban and industrial wastewaters defining specific quality requirements. A case study for irrigation use in Veneto Region (North Italy) has been developed for the Fratta-Gorzone basin, interested with industrial discharges and spread pollution from agriculture (Ostoich and Carcereri, 2013). The wastewater reuse is an intervention measure established with the Water Protection Plan of Veneto Region (Veneto Region, 2009) to reduce the supply of good fresh water resource and the pressure on water bodies from discharges.

To reduce the microbiological presence, wastewater disinfection appears necessary, particularly where water use can affect human health (Cabelli, 1983) as for irrigation and near the sea coast interested with bathing and touristic activities. In general, wastewater disinfection, due to the presence of organic and inorganic materials, can produce by-products, where dangerous and priority substances can also be found. The standards for microbiological water quality represent the bacterial concentrations that should not be exceeded if human health is to be safeguarded from pathogens (Fiksdal et al., 1997). In Italy, the maximum limit values for urban wastewater discharge is set at 5000 cfu/100 mL for parameter *Escherichia coli* (decree n. 152/2006); the same parameter is included among the parameters used for the classification of the *ecological status* of water bodies. For wastewater reuse the limit value is 10 cfu/100 mL (in 80% of samples and 100 cfu/100 mL as max value), a particularly restrictive value.

2. MATERIAL AND METHODS

Italian official sampling and analytical methods were applied during this study: APAT (2003), Analytical methods (in use since 2004). Where analytical methodology was lacking in the Italian national legal framework, international official methods were also applied (i.e. APHA et al., 1998). The sampling techniques were mean–composite sampling over 24 hours for WWTP effluents (in accordance to Directive 91/271/EEC on urban wastewater treatment). Metals were detected as total form in discharges. The limit of quantification (LOQ) varies in accordance with the parameter, the objective of the determination and the methodology applied.

3. RESULTS AND DISCUSSION

This study, according to a methodological assessment approach proposed by Ostoich and Lionello (2007), presents a preliminary investigation on the most important WWTPs in Veneto region with a potentiality equal or higher than 10.000 E.I. (equivalent inhabitants). Data from the institutional control activity performed by the Veneto Regional Environmental Protection Agency (ARPAV) in the period 2005-2012 have been recovered from the Regional Environmental Informative System (SIRAV) managed by ARPAV. According to the limit values of decree n. 185/2003 for WW reuse, the critical parameters have been highlighted. Wastewater reuse can be performed if potential users are present and if the necessary treatment(s) to achieve the quality objectives of the Italian regulation (Decree n. 185/2003) are economically sustainable.

CONCLUSIONS

The most critical parameters according to the wastewater reuse requirements of the Italian regulation (Decree n. 185/2003) appear to be: *Escherichia coli*, total suspended solids, nutrients, inorganic and organic micro-pollutants. Emerging pollutants, according to the applied test list and the achieved limits of quantification (LOQs), have been investigated according to the parameters encompassed in the Directives 105/2008/EC and 39/2013/EC for the environmental quality standards (EQSs) of surface waters and the results have been discussed. In a specific part of the territory (the Venice lagoon catchment) the WWTPs' upgrading has already been done according to the very restrictive discharge limit values of the specific regulation already applied to this part of the regional territory. For the conformity of the very restrictive value for *Escherichia coli* for discharge reuse most of the plants should be implemented with an adequate disinfection system (plant up-grading). Appropriate disinfection systems are a very urgent issue according to the potential production of disinfection by-products (DBPs). For this purpose a more sensitive monitoring (for the parameters and the LOQ applied) and a verification of the applied treatment technologies (technologies and operative data) should be performed. In Veneto region since December 2012 disinfection systems with Chlorine and Chlorine products have been forbidden due to the potential production of trihalomethanes (THMs) and other substances (Veneto region 2009): this aspect must be considered in the design of new disinfection systems.

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(90) Study of Inhibiting Effect of NaCl on the Produced Biogas from Algerian Dairy Wastes in Mesophilic Conditions

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Abstract

A series of experiments in batch reactors with 0.0, 16, 20, 30 and 40 gNaCl/l were performed to evaluate the effect of various sodium chloride concentrations on biodegradability of Algerian dairy waste in mesophilic phase. The characterization of substrate show that the dairy waste COD was 222045.937 mg/l, with the percentage in volatile mater of 91.879 % in TVS. After an incubation period (over 54 days), the liquid phase of the residue obtained was characterized. The obtained results show that the elimination rate of TVS is between 30 and 60 % in some cases. Also, the results show that increasing the concentration of NaCl added has a regular effect on the volume of produced biogas and decreases with increasing NaCl concentration added. Or decreases from 2252.55 to 462.15 in the case of increasing the NaCl concentration from 0.0 to 40 g / l. the inhibition percentage in this case was about 20%. So the total cumulative volume of produced biogas is due to the presence of the substrate (dairy waste) where it represents a 80 % of total volume of produced biogas. Generally the added of 30 to 40 g/l of NaCl have a remarkable inhibiting effect on the anaerobic digestion of considered dairy waste.

Keywords

Sludge waste; Co-digestion; mesophilic; biogas; Bio-energy; dairy waste

(91) Photocatalytic Degradation Of Three Direct Dyes

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Abstract

Three direct dyes widely used in textile's industry: red solophenyl 3BL (DR), orange TGL (DO) and Brillant Blue BL (DB) are submitted, in the laboratory, for photocatalytic systems: TiO_2 (P25) / UV and ZnO /UV. A comparison of the behavior of each dye about each system was made. The effects of several parameters on the discoloration were studied: adsorption of dyes on TiO_2 (P25) and ZnO, initial concentration of the dye, H_2O_2 concentration and initial pH. The experimental results show that the importance of adsorption in the photocatalytic process differs from one dye to another and according to the photocatalyst used, the adsorption process is essential in the presence of TiO_2 (P25) and negligible for ZnO. The photocatalytic activity also varies according to the dye/photocatalyst pair. For dyes DR and DB, the semiconductor P25 has a higher photocatalytic activity than ZnO one, however, the decolorization of DO dye in the presence of ZnO is better. A kinetic study of the photodegradation of three dyes with TiO_2 (P25) was also proposed.

Keywords

Decolorization; photocatalysis; POA process; solophenyl dyes; titanium dioxide; zinc oxide

(92) Alkali Elutriated Acid Fermentation using Raw Sewage for Primary Sludge Treatment

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Abstract

The performance of elutriated acid fermentation (EAF) for primary sludge using sewage as elutriating water was investigated. EAF is one of anaerobic digestion processes which used water to elutriate volatile fatty acids (VFAs) generated in the fermenter. The aim of these treatments on primary sludge is to improve solubilization, and then to make them more easily biodegradable and produce VFAs as carbon source in further study such as in UASB processes. In addition, it was carry out 3 different elutriating rate (feed sludge:elutriant) conducted at mesophilic (35 ℃) under pH 9 with a short HRT (5day). In three different elutriating rate (1:3.3; 1:10; 1:15) the solubilization are 0.94, 0.99 and 0.98 $gSCOD_{prod.}/gICOD_{rem}$, VFAs production are 0.52, 0.37 and 0.49 $gVFA_s/gSCOD_{eff}$, respectively. And another feature of this study was using sewage as elutriating water to treat the primary sludge as well as sewage.

Keywords

Elutriated acid fermentation; primary sludge; raw sewage; solubilization

INTRODUCTION

The primary sludge treatment by the elutriated acid fermentation, which using water to wash the fermentation sludge for the recovery of acids and to thicken the sludge for reducing volume is a viable process as a sludge treatment process. The recovered acid may be used as a carbon source in the biological nutrient removal treatment plant with influent of low ratio of carbon to nitrogen concentration for improving the denitrified.

MATERIALS AND METHODS

In this study, the EAF process used a combination of the elutriated flow (raw sewage) and the influent flow (primary sludge). The lab scale experimental setup is shown in Fig. 1. The EAF reactor was constructed of a plexi-glass column with a diameter of 10cm and height of 140cm. To exclude outside air, the top of the reactor was sealed. The internal temperature of the reactor was measured by a temperature sensor. The temperature of the elutriant and influent sludge in refrigerated storage was raised by using a preheater, after which they were injected into the reactor through the pump. The experimental apparatus was installed in a thermostatic chamber to maintain mesophilic temperature (35℃±1) (Ahn et al., 2004).The wasted sludge was the effluent from the bottom of the reactor, and a pump was used to circulate the elutriated flow.

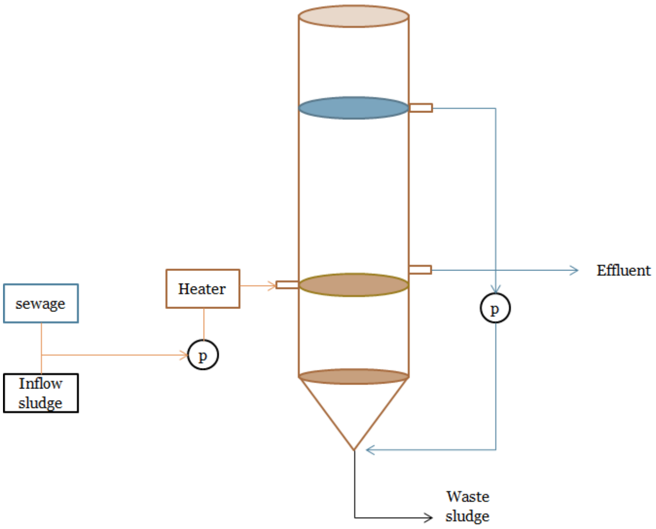

Figure 1. Schematic diagram of the elutriation acid fermenter

During the initial 5 days, sewage sludge was used as the influent seeding sludge, and hydrolysis occurred while the pH of the influent sewage was maintained at 11 using 1 mol/L NaOH solution. The continuous elutriation of fermentation products was conducted to remove the potential for SCFA loss and to increase solid destruction. When the primary sludge was used as the inflow sludge, the elutriation ratio (influent sludge: influent sewage) is 1:3.3, 1:10 and 1:15.

All samples were analyzed through the standard method (APHA, 2005), with the theoretical background according to Wastewater Engineering Treatment and Reuse (Metcalf and Eddy, 2004). The analysis items were pH, $TCOD_{cr}$, $SCOD_{cr}$, TS, VS, TKN, NH_4^+-N, TP, SP, VFAs and alkalinity.

RESULTS AND DISCUSSIONS

Volume reduction and Volatile solids (VS) removal efficiency

For the alkalinity treatment of raw sewage, NaOH is added until the pH reaches 9, which breaks up the microbial cell wall and reduces the VS effectively. With three different elutriation ratios (1:3.3; 1:10; 1:15) the sludge volume reduction was 85%, 84% and 86% and the VS removal efficiency was 86%, 76% and 81%, respectively. From these results, the elutriation ratio had no significant effect on the VS removal efficiency and volume reduction. Therefore, it could be concluded that the EAF process can not only reduce the organic wastes but also treat a great deal of sewage.

SCOD production and solubilisation ratio

EAF is a process in which organic wastes can be transferred into SCOD suitable for anaerobic microorganisms (Ahn et al., 2006). The SCOD produced after the fermentation reaction of organic wastes and the transfer of organic substances from non-soluble material into soluble material. The elutriate flow which was adjusted to pH 9 by using NaOH was used to wash the organic wastes comprised of cellulose to increase the bulk and hence increase the solubilization. With the different inflow, the SCOD concentration was different at the initial period of approximately 10 days, after which steady state condition was attained. While the elutriation ratio is 1:3.3, 1:10 and 1:15, the solubilization ratio is 0.94, 0.99 and 0.98, respectively; the SCOD production is 5.42g/d, 2.69g/d, 0.36g/d, respectively, more than 90% of the ICOD was removed and converted to SCOD. ICOD in the sewage and primary sludge is transferred into SCOD in the effluent in the EAF process. When the elutriation ratio is 1:3.3, the inflow COD (COD_{sewage}+COD_{sludge}) is 15.17g/d, after the EAF process, the effluent COD reach 9.68 g/d, of which 6.26 g/d is SCOD. The use of raw sewage as the elutriate flow in the EAF process not only improved the biodegradability of the primary sludge for later processing such as up-flow anaerobic sludge blanket (UASB), but also demonstrated the high economic feasibility of the sewage treatment.

Volatile fatty acid (VFA) production

The VFA concentration at different elutriation ratios using primary sludge for the EAF process is shown in Fig. 2. VFAs (acetate, formate, lactate, propionate) are found in the effluent of the EAF process. The primary sludge with three different elutriation ratios of 1:3.3, 1:10, and 1:15, the VFA production is 1,211 mg/L, 497 mg/L, and 309 mg/L, respectively. The effluent containing the VFA can be used in later processing such as UASB and BNR processes.

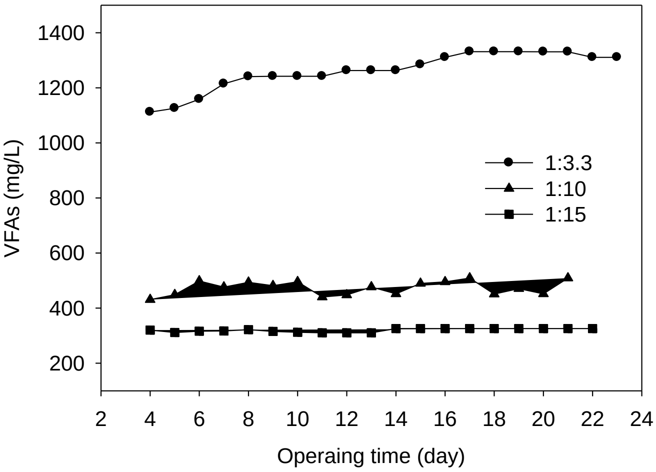

Figure 2. VFA production with different elutriation ratios

Nitrogen and phosphorus release

Nutrients like nitrogen and phosphorus are present in sludge and can be used as an effective fertilizer. Both nitrogen and phosphorus have been reported to be released during organic waste fermentation (Engeler et al., 1998). In this context, the magnitude of nutrient (nitrogen and phosphorus) solubilization by hydrolysis was investigated and the results obtained are shown in Fig. 3. With three elutriation ratios (1:3.3, 1:10, 1:15), the nitrogen elution percentage was 44%, 46% and 46%, and the elution percentage of dissolved phosphorus was 22%, 20% and 17%, respectively. Further investigation should focus on the released nutrients that could be recycled such as magnesium ammonium phosphate (MAP) and hydroxyapatite (HAP).

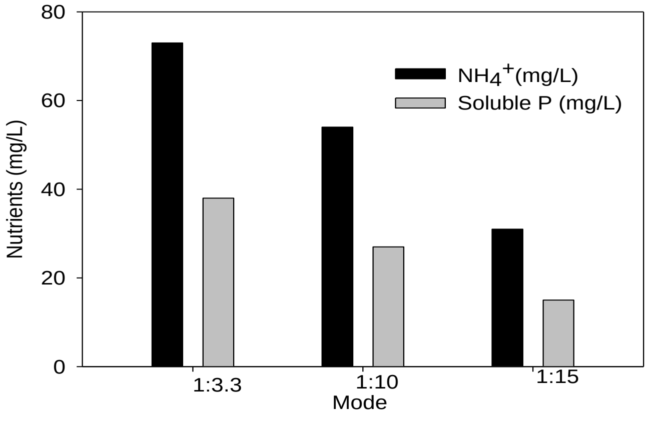

Figure 3. Nutrient release in elutriated acid fermentation systems

CONCLUSIONS

Based on the present experimental results outlined above, the following conclusions were drawn. The elutriation ratio had no significant effect on the VS removal efficiency and volume reduction. The mass balance was based on flow, COD, N and P during the process of attaining a steady state. Table 1 presents the characteristic of the fermentation effluent and the primary sludge during the steady state periods. With increasing elutriation ratio, the SCOD and VFA production decreased, but the primary sludge afforded a similar high solubilization ratio of more than 90%. This improved their biodegradability and enabled the production of VFAs that could be used as a carbon source for further processing such as UASB. Meanwhile, soluble ammonia and phosphorus were observed to be released.

Table 1. Characteristic of EAF effluent and waste sludge

Organic wastes	Elutriation ratio	item	pH	TS (mg/L)	VS (mg/L)	TCOD (mg/L)	SCOD (mg/L)	NH_4^+-N (mg/L)	SP (mg/L)
Primary sludge	1:3.3	Effluent	7.73	98	74	3,892	2,519	74	42
		Wasted sludge		41,538	34,740	31,170	301	653	550
	1:10	Effluent	7.58	89	65	2,044	1,374	54	27
		Wasted sludge		34,742	22,320	17,808	198	210	63
	1:15	Effluent	7.75	77	61	1,082	643	31	16
		Wasted sludge		11,910	6,023	10,620	72	107	119

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(93) Evaluation of tablet chlorinator in pathogen inactivation

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Abstract

The disinfection of sewage aims to inactivate pathogenic organisms which were not removed during treatment in order to combat the spread of waterborne diseases, thereby safeguarding the population of possible diseases. Thus, the control of waterborne diseases spread is closely linked to the protection of water sources and disinfection of water supplies and wastewater. The importance of disinfection in sewer treatment can be understood as the last protective barrier against pathogens. There are currently several ways to accomplish the disinfection in sewage treatment plants, such as chlorination, ozonation, ultraviolet radiation, but they are usually expensive and with technologies of difficult manipulation.

The use of chlorinators tablet is an inexpensive simple alternative, which can be used for disinfection in small treatment plants, directed to small communities. This research aimed to present the removal efficiency of total coliform and fecal coliform in a constructed wetland system through chlorination tablets, as well as evaluating the durability of the tablet and the residual chlorine related to the system´s flow. The effluent prior to disinfection showed pH 3.56 to 6.86, the total coliform $1.010^5$to 9.310^6 NMP/100mL and fecal coliform 5.010^4 3.510^5 the NMP/100mL. The disinfection promoted a removal of approximately 2.5 log for fecal coliforms and total coliforms to 3 log, thus promoting concentrations of < 2 to 1.3 10^3 NMP/100mL and < 2 to 1.5 10^4 NMP/100mL respectively.

Keywords
Alternative Disinfection, Tablet Chlorinator, waterborne diseases.

INTRODUCTION

Sewage dumped raw or insufficiently treated contains high load of pathogens that survives in the environment, outside the host´s body, which provides its increase in quantity and spatial distribution in regions with high population density and intense human activities (TUNDISI, 2003). Due to the importance of sanitary sewer in spreading pathogens is evident the great need of quality control of waters used for recreation, irrigation and supply (Gonçalves, 2003).

The disinfection of sewage aims to inactivate pathogenic organisms which were not removed during treatment in order to combat the spread of waterborne diseases, thereby safeguarding the population of possible diseases (Medeiros, 2010). Thus, the control of the waterborne diseases spread is closely linked to the protection of water sources and disinfection of both water supplies as residuary. The importance of disinfection in the treatment of these waters can be understood as the last protective barrier against pathogens (WEF, 1996).

There are currently several ways to accomplish the disinfection in sewage treatment plants, such as chlorination, ozonation, ultraviolet radiation, but they are usually expensive and have technologies with difficult manipulation.

The use of chlorine tablets is an inexpensive simple alternative, which can be used for disinfection in small treatment plants, aimed at small communities.

OBJECTIVE

The research aimed to present the removal efficiency of total coliform and fecal coliform in a constructed wetland system through chlorination tablets, as well as evaluating the durability of the tablet and the residual chlorine in relation to the flow of the system.

METHODS

The wastewater used in the study was collected in the sewage treatment station, located in the Department of Physical Education, São Paulo State University/UNESP, Bauru, which operates through a constructed wetland system and treats sewage from approximately 280 students, 43 teachers and 3 officials, which generates an average flow of 10 000 L.day^{-1} sewer. The effluent showed pH 3.56 to 6.86, the total coliform 1.010^{5}to 9.310^{6} NMP/100mL and fecal coliform 5.0 10^{4} to 3.5 10^{5} the NMP/100mL.

The constructed wetland system comprises preliminary treatment consisting of gratings, formed by two primary tanks, with 15.000 L each, and working as decanters, formed by three secondary horizontal subsurface flow beds and tertiary treatment consisting of three beds vertical subsurface flow. The beds are filled by vertiver grass. After tertiary treatment the effluent is routed to the outbox, where it is intended for a 15 000 L tank where chlorination is done. The treated effluent is discarded in the soil after the disinfection tank.

Disinfection is performed by chlorine tablets of approximately 200 grams, added to the tank through floating chlorinator plastic pellets using ready to release residual chlorine through the phenomenon of progressive abrasion. The chlorinator is hanging by a string to facilitate the exchange of the tablet. In Figure 1, it can be seen that the opening to the contact of the effluent along the gum is very small, being done by various gaps of about 2 mm each. In Figure 2 (a), (b), (c) and (d) the inserted floating chlorinator and disinfection tank is displayed.

Figure 1. Opening the chlorinator.

For the analysis of fecal and total coliforms, samples of the disinfection tank subjected to the action of chlorine were collected. The samples were analyzed at the Laboratory Wastewater belonging to the campus of UNESP, Bauru. The concentration of residual chlorine was determined by the DPD colorimetric method (Rice et al., 2012). For bacteriological analyzes, it was used the technique of substrate Colitag defined, determining E. coli and total coliforms.

Figure 2.(A) A tablet of chlorine, (B and D) floating Chlorinator (C) disinfecting tank.

RESULTS AND DISCUSSION

According to the manufacturer's data, the tablet offers a concentration of 90% chlorine active in 200 g of the product, in other words, 180g of active chlorine. The consumption of the tablet was on average of 6.9 g per day, with a mass of 200 g, allowing its use for about 29 days. The price of the tablet is around R$ 4.00 in Brazil, what is considered a low price, since the system uses one tablet per month.

The disinfection promoted a removal of approximately 2.5 log for fecal coliforms and total coliforms to 3 log, thus promoting concentrations of <2 to 1.310^3 NMP/100mL and <2 1.510^4 NMP/100mL respectively.

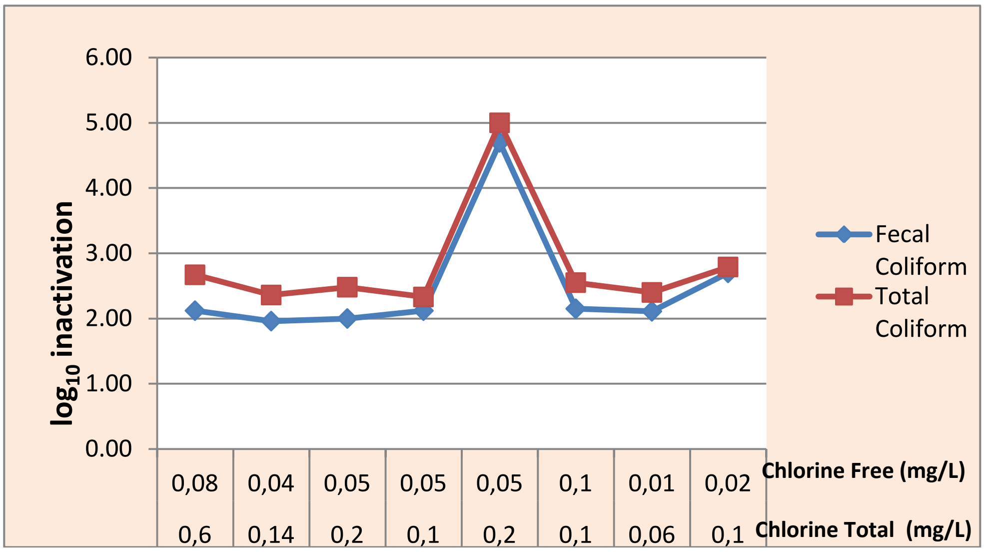

Figure 3. Relationship of inactivation of total coliforms and fecal coliforms to the concentration of chlorine free and total.

CONCLUSION

According to the research, the sewage disinfection using a tablet chlorinator was efficient, getting high range of coliforms removal. Besides the removal efficiency, this method is also positive because of the tablet´s chlorinator price, considered low. Nevertheless, special care is needed for disposal or reuse of effluent disinfected due to residual chlorine present in the same.

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(94) Carbon and Energy Footprint of a WWTP in Southern Italy

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Abstract

The estimation of the operational carbon footprint of a wastewater treatment plant for municipal and industrial wastewater, activated sludge system with nutrient removal and filtration; was carried out on the basis of data relating to one year . In different parts of the world legislators and public opinion are increasing their focus on greenhouse gas emissions from the water sector. Different guidelines for determining the carbon footprint for the water sector and the sewage treatment plant are available, specific to operating conditions ofa given geography and the specific regulatory needs of a country or a region. In Italy there are still few studies of carbon footprint in the water sector and the first objective of this study was to identify a methodology to adapt and apply to the specific technical characteristics of the treatment plant and its geographical location. The WWT plant “Medio Sarno - SubComprensorio 4(SC4)” is located in Nocera Superiore (SA) in southern Italy, and is managed by Consorzio Nocera Ambiente on behalf of “Regione Campania – Settore Ciclo Integrato delle Acque”.

Keywords

Carbon Footprint; WWTP; Energy Footprint; Greenhouse gas; Protocols; Activated sludge

INTRODUCTION

The impacts of greenhouse gases emissions produced by human activities on climate change have been the subject of considerable study, debate, legislation and international treaties in the last twenty years. The IPCC Fifth Assessment Report, presented in September 2013, shows new evidence of the effects of man on the climate system and added a new scenario with measures to reduce GHG emissions, proving how global action for reduction of greenhouse gases is possible and necessary. Estimates put emissions from water sector from 3-10% of the global total (IPCC , 2007). For wastewater handling category (6B) ISPRA, in National Inventory Report 2013, estimates N_2O emissions values of 6.25 Gg/ year and CH_4 emissions values of 7.04 Gg/year. Considering that the estimation of total national emissions including LULUCF , is 458,202 Gg CO2 eq , direct emissions of the wastewater handling category is 0.7% of national emissions , not including the indirect emissions from energy consumption and disposal of sludge. Energy consumption in wastewater treatment plants is steadily increasing due to increasingly stringent treatment requirements. GHG are a direct result of energy consumption and energy use is the principal source of GHG emission at any water or wastewater treatment plant (WRF , 2013).

The growing demand for energy conflicts with the need to reduce GHG emissions. Research has been conducted to understand the processes of formation of GHG in wastewater treatment plants (GWRC , 2011) and to define control strategies to minimize energy consumption and the GHG emissions (Flores et al. 2011). Different methodologies, protocols and tools for GHG accounting and energy assessment in water sector are available(WRF , 2013). Few studies of WWTP carbon footprint are available (Solini, 2010) and there aren’t national specific protocol. Aim of this study is to collect operational data of a medium dimension sewage treatment plant and carry out a study of the carbon footprint based on international protocols and available literature data e adapted to the specific characteristics of the plant and its geographical location.

METHODOLOGY

The methodology used in this work is based on " Methodology Guide for Evaluating Greenhouse gas emissions by water and sanitation services" (2013) prepared by ASTEE and based on IPCC Guidelines for National Greenhouse Gas Inventories (2006) and the GHG Protocol prepared by WBSCD and WRI. In the absence of Italian specific protocols, a French methodology was chosen, considering geography and adapting it to the specific characteristics of the case study.

The boundaries of this study include operation of Medio Sarno SC4 WWTP. Main greenhouse gas, CO_2, CH_4 and N_2O can be produced in all phases of operation of a sewage treatment plant. GHG emissions, as required by the GHG Protocol, were quantified in the following order: Scope 1 direct emissions from the sewage process and discharge into surface water; Scope 2 indirect emissions associated with the consumption of electricity, steam or gas; Scope 3, other indirect emissions related to production and transport of chemicals, transport and treatment of sludge and by-products. Table 1 shows the emission factors and assumptions used .

Table 1. Assumptions for greenhouse gas emission calculations

Scope	Activity	Assumed value	Units	Reference /Source
1	Sewage process - N_2O	0.073	ton N_2O/t TKN eliminated	IPCC (2006)
1	Sewage process -CH_4	0.0002	ton CH_4/ton COD eliminated	GWRC (2010)
1	Discharge into surface water - N_2O	0.79	%kg of N_2O emitted per TKN discharged	IPCC(2006)
1	Discharge into surface water - CH_4	0.025	kg of CH_4 per kg of COD discharged	IPCC (2006)
2	Italian energy Mix	0.65	kg CO_2eq/kWh	Ecoinvent v2.2
3	Peracetic Acid production	1340	g CO_2eq/l of pure product	ARKEMA
3	Polymer production	813	g CO_2eq/kg of pure product	SNF
3	Biosolids landfilling	0.56699	ton CO_2/t MS	ADEME (2010)
3	Screenings landfilling	0.182	ton CO_2/t MS	ADEME (2010)
3	Grit landfilling	0	ton CO_2/t MS	ADEME (2010)
3	Road Transport, lorry > 28 & 3.6 to 5 ton	0.00013	ton CO_2eq/t*km	ADEME (2010)

Case study description

Medio Sarno SC4 WWTP is located in the municipality of Nocera Superiore, in the province of Salerno , southern Italy (40 ° 45 ' 2.355 " N 14 ° 40 ' 18,578 " E) . The plant treats urban and industrial (manly tomato industry)) and has a design capacity of 300,000 PE (Population Equivalent). Water line, discharging into Casarzano channel which is a tributary of Sarno River, includes: a primary treatment section (coarse screening, fine screening, grit and oil removal), a rainwater section (primary settling, aerated storage), a secondary treatment section (nitrification-denitrification, final settling), a tertiary treatment section (gravity filtration on sand , disinfection with peracetic acid). Sludge line includes dynamic thickening and belt press dewatering . Sludge line also includes anaerobic digestion with biogas recovery and heat drying, which are not in operation for technical and administrative reasons. A full description of the WWTP under study is provided in De Feo et al. (2009).

Data Collected

The inventory analysis was performed by collecting primary data relating to the period from November 2011/October 2012. Total annual flow treated was 11,450,610 m^3, equal to 31,372 m^3/day, and the characteristics of influent are summarized in Table 2. Table 3 summarizes the operational data required for the calculation of GHG emissions. A full description of the Life Cycle Inventory Analysis is provided in

Pucci et al. (2013).

Table 2. Wastewater average characteristics

	COD (mg/l)	**TKN (mg/l)**	**SST (mg/l)**
Influent	289	4.86	117
Effluent	33	0.88	12

Table 3. Operational data for greenhouse gas emissions calculations

Scope	**Operational data**	**Units**	**Value**
1	TKN eliminated	ton/yr	47.03
1	COD eliminated	ton/yr	2,982.38
1	TKN discharged	kg/yr	10,090
1	ton of COD discharged	ton/yr	367
2	electricity consumption	MWh/yr	5,115
3	Peracetic Acid consumption	l/yr	36,316
3	Poly consumption	kg/yr	17,850
3	sludge landfilled	ton TSS/yr	1,878
3	screenings landfilled	ton TSS/yr	66
3	grit landfilled	ton TSS/yr	209
3	annual transport for peracetic acid	t*km/year	116,154
3	annual transport for poly	t*km/year	30,769
3	annual transport for biosolids	t*km/year	1,470,769
3	annual transport for grit	t*km/year	42,308
3	annual transport for screen	t*km/year	13,846

RESULTS & DISCUSSION

Operational carbon footprint estimation of Medio Sarno SC4 WWTP is summarized in Table 4. Figure 1 shows percentage contributions of five emissions categories.

Table 4. GHG estimates (ton CO_2-eq/yr), with breakdown according to scope (IPCC, 2007)

Scope	**Description of emission**	**CH_4 (t/yr)**	**N_2O (t/yr)**	**Total (tCO_2eq/yr)**
1	Emissions linked to the sewage process	0,60	3,43	1038,0
1	Discharges into surface water	9,17	0,08	253,1
Direct emissions (SCOPE 1) Subtotal				**1291,1**
2	Indirect emissions linked to energy consumption			3324,6
Indirect emissions associated with energy (SCOPE 2) Subtotal				**3324,6**
3	Indirect emissions (reagents and consumables)			40,9
3	Indirect emissions (biosolids, screenings&grit)			1275,0
Other indirect emissions (SCOPE 3) Subtotal				**1315.9**
OPERATIONAL CARBON FOOTPRINT				**5931,7**

Operational carbon footprint per m^3 of treated wastewater is equal to 0.52 kg CO_2eq/m^3. A comparison with studies performed in the United States, Australia and India is summarized in Table 5. Hammer et al. (2011) identify opportunities to reduce the Operational CFP in water facilities; for sewage treatment plants a neutralization of GHG emissions up to 82% is assumed. Considering specific characteristics of the case study, the opportunity to reduce the Operational Carbon Footprint apply to the following aspects: energy saving actions (process optimization, energy efficiency of pumps and compressors), use of renewable energy (solar, biogas) upgrading of sludge line (activation of anaerobic digestion and sludge drying line and resulting decreased transport of sludge); sludge reuse in agriculture and wastewater reuse (agricultural or industrial).

Table 5. Plant Operational Carbon Footprint benchmark values

Facility	**Protocol**	**Operational CFP (kg CO$_2$e/m^3)**	**Reference**
Medio Sarno Sc4 (Nocera Sup.,Italy)	ASTEE2013	0.52	
Hanover Park (Chicago, US)	LGO2008	0.39	Pagilla et al. (2009)
35 WWTPs (SE Queensland, Australia)	NGA2008	1.0-2.5	De Haas et al (2009)
Uttar Pradesh (Noida, India)	IPCC 2006	0.25	Gupta et al. (2012)

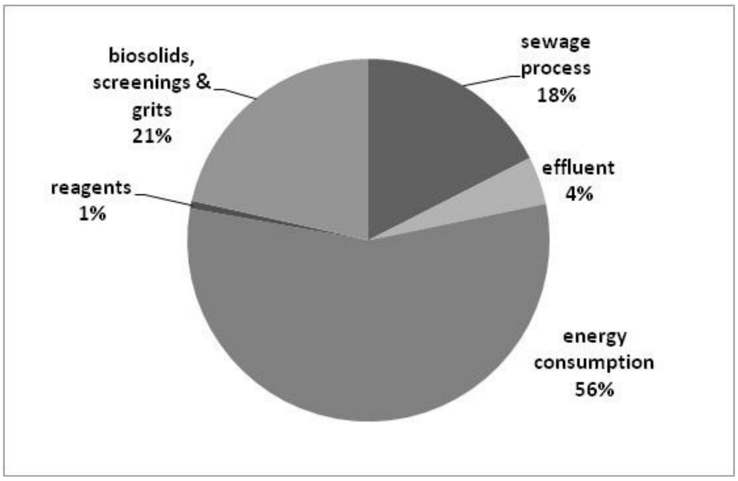

Figure 1. Carbon Footprint % breakdown at Medio Sarno sc4 WWTP

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(95) Integrated Wastewater and Watershed Management – A Case Study

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Abstract

Wastewater treatment is a vital function of watershed management. It is embedded into a large framework of hydrological, environmental and socio-economic activities within a region. The case of awater association is presented, which was established as a corporation under public law in 1959. The Federal State of North Rhine-Westphalia, Germanymandated formation of an independent entity charged with counteracting the significant impact of brown coal mining on the water resources of the Erft region. As such, Erftverband has emerged as a service–provider to stake holders in the region, which pursues all water related functions from a holistic viewpoint of watershed management. Several examples illustrate how wastewater treatment is carried out under that perspective.

Keywords
advanced wastewater treatment,resource protection,holistic watershed management

INTRODUCTION

The 104 km-long Erft river drains a 1,920 square km area from the Eifel hills to the Rhine river near the City of Düsseldorf in the western part of Germany. Receiving 700 mm annual precipitation, the landscape contains forests, wetlands, meadows and fertile farmland along with numerous large and small settlement areas which are home to nearly one million people. Numerous cherished historic edifices such as medieval moated castles along the Erft speak to the longevity of habitation.

Here also is the enormous Rhenish brown coal open cast mining operation, run by a single large company. An average of 90 million tons of lignite is extracted annually. The electric power produced from this coal amounts to more than12% of the electricity consumption of Germany. Currently, 500 million cubic meters per year of groundwater are pumped out to keep the pits dry, so coal can be extracted. The activity creates a far-reaching lowering of groundwater level which greatly influences the hydrological profile, this in a region where inhabitants and commercial enterprises stake out their own strong claims on the land and its water.

In this region, the Erftverband (which literally translates into Erft river water association) was established more than 50 years ago as a service provider for municipalities, counties, public water supply companies, mining and electricity industry, commercial and industrial enterprises, agriculture and fishery.

WASTEWATER AND WATER MANAGEMENT AT THE ERFTVERBAND

The Erftverband owns and operates numerous wastewater treatment plants (WWTP) and other facilities of sewage treatment and transportation.Table 1shows some key figures of the association’s sewage operations.

Further functions of the Erftverband comprise research and surveillance of water management conditions within the Rhenish brown coal district and management of groundwater securing water supply of 2.7 million people in the greater Erft region, protection of wetlands, maintenance and renaturation of surface waters and flood protection.

Erftverband views the watershed under its care as a complex ecosystem, subject to human intervention on a large scale, in which the many components function interconnectedly. Since every management choice is capable of influencing the water of the entire region, no decision is independent of other decisions. Pride is taken in implementing measures which promise multiple benefits in the context of fulfilling a balanced set of long term objectives(Lindner, 2012).

Table 1. Wastewater technology at the Erftverband

Number of WWTPs	39
Total WWTP capacity	1.07 million population equivalents
Annual quantity of wastewater	68.8 million m^3
Rate of nitrogen removal	> 79 %
Rate of phosphorus removal	> 94 %
Number of stormwater basins	368
Total volume of stormwater basins	568,000 m^3
Number of pumping stations	120
Total length of sewers	660 km
Association area	1.920 km²

EXAMPLES OF A HOLISTIC APPROACH

Threeoutstandingexamples may serve to illustrate the integrated approach that is followed in fulfilling Erftverband's key functions.

Flood protection and wastewater treatment

The Erftverband maintains a network of 70 rainfall gauges and 41 water gauges supplemented by radar-based rainfall forecast. Natural flood protection is carried out along the Erft river and its tributaries, 40 controllable weirs and 19 flood reservoirs are maintained. This provides an integrated system of early warning and flood protection (Kern et al., n.d.)but also a detailed planning data base. Computational simulations of hazardous flood incidents have shown that all wastewater treatment plants are sufficiently protected against flooding by the retention reservoirs. Even in case of extreme flooding, wastewater treatment can thus be secured.

Safeguarding a drinking water supply

The WWTP of Bergheim – Glessendischarges into a small stream in a groundwater protection area. A few kilometres downstream the water reaches a wetland and drains away in a pervious geological gravel formation. This wetland feeds directly into the groundwater body which provides drinking water for the city of Cologne. There was growing concern, that pathogens originating from the wastewater operations could contaminate this important fresh water source. Although a sufficient reductiontonon-critical levels within the entire technological and natural system could be found(Lindner et al., 2004) additional precautionary measures were commanded by regulating authorities.

From 2006 to 2008 the exisitingWWTP was retrofitted. A newly built membrane bioreactor, equipped with submerged hollow fibre ultrafiltration membranes, capable of eliminating microbial pathogens from the plant effluent was installed. At the same time, the treatment capacity of the plant was increased from 5.000 to 9.000 population equivalents.The existing stormwater overflows from the sewer system were channelled to newly built retention soil filters, whichsignificantly reduces hydraulic stress and pollution loads to the river.Where the existing land-use allowed for it, the river bed was renaturalized to further enhance the streams ecological potential.

Recent studies have shown a potential of additionally reducing micro-pollutants from storm water overflows by soil filters (Bester and Schäfer, 2009; Mertens et al., 2012). Currently plans are considered to supplement the membrane bioreactor with an additional activated carbon adsorption to reduce the level of micro-pollutants which can be found effluent and in the river water.

Long-term planning

The various areas of water management operation are treated as interrelated functions, integrated within a future oriented concept for the catchment which takes into account the following key factors: (a) Measures to attain compliance with the European Water Framework Directive, which calls for renaturation of water courses and assurance of good water quality, will continue to be undertaken in view of multiple benefits, including preservation of aquatic biotopes and enhanced flood protection; (b) Coal mining will gradually wind downand will cease entirely around 2035. Cessation of groundwater pumping willraise groundwater levels, affecting diverseaspects of regional developmentplanning. (c) Ongoing monitoring of source water forquality helps assure a safe, reliable drinking water supply; (d) Considerable opportunities exist inwastewater treatment to improve treatment outcomes through application ofadvanced techniques while achievingcost savings through greater economiesof scale.

Guidelines for actions based on these factors are set down in a series of 15 to 50-yearMaster Plans covering the following topics: redesigning watercourses; groundwater management in relation to coal mining; drinking water supply requirements;and future concepts ofwastewater treatment operations.

The future of wastewater operations in the Erft region was envisioned by a so-called Masterplan Wastewater 2025(Brepols et al., 2013). The plan was developed based on economical, technological and hydrological considerations to pro-actively deal with challenges in wastewater treatment of the next decade and beyond:compliance withcurrent and new environmental policies, containment of cost, aging ofregional wastewater infrastructure, improvement ofenergy and resource efficiency of wastewater operations and removal of micro-pollutants.

As a consequence many small, over-aged or inefficient wastewater treatment plants will be decommissioned. New connection sewers have to be built and the wastewater will thus be treated at larger, central facilities. Benefits are expected through economies of scale but also higher treatment performance of large facilities. Overall energy consumption is expected to decrease further, as well as road haulage of sludge between WWTPs.

ORGANISATION AND GOVERNANCE

Making sound management decisions and implementing them requires an expert staff with many academically qualified, interdisciplinary specialists. Just as the watershed itself is considered in terms of connectedness of components, relationships among various areas of water management, from hydrological engineering to wastewater treatment, are kept in view. Erftverband specialists consult with one another on a multidisciplinary basis as they formulate and cross-check planned actions. At the same time, they participate in numerous national and international research projects to gain and exchange state-of-the art knowledge and techniques.

The core of water management in the sensitive Erft watershed has been entrusted to a non-profit, multidisciplinary association under its own independent administrationin 1959. To ensure participation of a broad spectrum of society with interests in water, the founding legislation specified key public institutions and private groups as obligatory members who would share costs through a fee-paying structure: counties acting as local water authorities; municipalities with their citizens as generators of wastewater; agricultural, commercial and industrial groundwater users; water utilities drawing water for supply; electric power producers requiring cooling water for their plants; and the coal mining company pumping out groundwater.

CONCLUSIONS

The authors of the Erftverband founding legislation showed foresight in empowering the newly constituted entity to function as an independent water authority for the entire catchment. Wide-ranging technical expertise collected under one roof, free from political interference, has shown to carry the potential for water resource management formulated and executed with a broad view.It is considered that preparedness for future challenges can best be attained under a holistic perspective.

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(96) The recent SWAT modelling experiences at the Joint Research Centre

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Abstract

In order to monitoring efficiently the impact of policy implementations on water quality, such as the Nitrates directive and Waste Water Treatment Directive, the JRC (Joint Research Centre of the European Commission) works on creating robust eco-hydrological modelling using the SWAT model. In this article recent applications of SWAT model in some pilot areas are shown. These areas were selected for different purposes in order to achieve a complete and robust calibration procedure for water, sediment and nutrients predictions.

Keywords
SWAT model; water quantity and quality; European databases

INTRODUCTION

The impact of nutrient excess and emergent pollutants on surface water quality in Europe is an important issue for the European Commission. The Nitrates Directive (EEC, 1991a), the Urban Waste Water Treatment Directive (EEC, 1991b), the Water Framework Directive (EEC, 2000) and the Common Agricultural Policy are the main legislations for controlling and reducing contaminant loads into receiving surface and groundwater. After more than 20 years of implementation of Directives some improvements were seen concerning the quality of the European surface waters. However, the correct evaluation of measures to combat the nutrient pollutions is difficult due to the temporal and spatial lags between the management action and the environmental response (Bouraoui et al., 2011; Jackson et al., 2008; Schröder et al., 2004; Behrendt et al., 2000). As a consequence, models have been used to predict the effects of the mitigations measures on water quality (European Commission, 2012; Hartnett et al., 2007). The Soil Water Assessment Tool (SWAT) (Arnold et al., 1998) is currently used to predict water quantity and quality at European Scale applying an innovative modelling protocol that involves sensitivity analysis, multi-variables calibration and regionalization of the calibrated parameters (Pagliero et al., 2014; Malagò et al., 2014). In this context, the main objective of this paper is to present some of the major achievements of the Joint Research Centre with the eco-hydrological modeling in some pilot areas.

MATERIALS AND METHODS

SWAT model and European Database.

The SWAT model is a physically based watershed-scale model developed to predict the impact of land management practices on water, sediment, and agricultural chemical yields with varying soils, land use and management conditions on river basins of different sizes (Lam et al., 2010; Ullrich, and Volk, 2010). This model is demanding in terms of input data (DEM, Landuse and Soil Map, Climate data), assessment of processes and parameters of calibration.

Pollutant Sources

The Wastewater treatment plants and industrial direct discharges were quantified using UWWTD database (European Topic Centre on Inland, Coastal and Marine waters). In addition, the scattered dwelling emissions was quantified at catchment level using loads not collected, considering the typology of population living in each catchment and the connection rates. The total amount of point sources and scattered dwelling emissions was grouped at catchment level and introduced in SWAT as point sources.

Diffuse sources

The non-point sources were performed in SWAT considering the management of different crops from agricultural lands. Fertilization was based on outputs from the CAPRI model (Common Agricultural Policy Regional Impact Analysis). Major management operations were based on the heat unit approach (Wriedt et al., 2009). The auto-irrigation option was selected using the irrigated areas and volume from FAO Global Irrigation Map (Siebert et al., 2007), national statistics (EUROSTAT) and the Global data set of monthly growing areas (Portmann et al., 2008).

Water quantity and quality monitoring stations

In Europe we collected more than 3000 water quantity data stations, about 723 of nutrient concentration data (N total, N-NO3, N-NO2, N-NH4, P total and P-PO4) and more than 500 points for sediment data (concentrations and more rarely loads).

Pilot Areas

Different pilot areas were considered in order to develop methodologies for water quantity and quality calibration. The Danube Basin was selected as strategic area to provide support to regional stakeholders. The Danube Basin (803,000 km^2) was divided into 4663 catchments with an average size of 179 km^2 and it was considered suitable in order to perform an innovative water calibration approach (step-wise calibration) at large scale (Pagliero et al, 2014). The Upper Danube ($132 \cdot 10^3$ km^2 across Austria, Germany, Czech Republic and Slovenia) was selected for its topological characteristic and high level of human activities in order to study the impact of topography on sediment loads and anthropogenic activities on nutrient pollution. Scandinavia and Iberian Peninsulas were studied in order to assess the spatial variation of hydrological calibrated parameter sets (Malagò et al., 2014). The Scandinavian Peninsula (10^6 km^2) covers Norway, Sweden and Finland, and it was divided into 5447 sub-basins; the Iberian Peninsula ($556 \cdot 10^3$ km^2) covers Spain and Portugal and it was divided in 3019 sub-basins. Finally, Crete was selected as pilot areas to assess the karst areas and their influence on the hydrological processes and nutrient balance. A total of 353 sub-basins were delineated with an average area of 19 km^2.

Calibration of crop yields

The first step before the calibration of stream flow is the calibration of crop yields. The correct amount of crop yield improves the reliability of model water balance (Akhavanet al., 2010; Faramarzi et al., 2010). In this study, we have compared the simulated mean annual crop yield with that reported by EUROSTAT.

Calibration of water discharge

A step-wise calibration approach was developed in order to calibrate the stream flow. This methodology involves sensitivity analysis, multi-variables calibration and regionalization of the calibrated parameters. As described by Malago` et al. 2014, the methodology required the selection of the headwaters and their calibration using SUFI-2 (Abbaspour, 2008) algorithm. In particular, the discharge was subdivided in different components (surface runoff, lateral flow, baseflow) that were calibrated in steps using different objective functions. The final calibrated parameter set (NOP, Near Optimal Parameter Set) reproduces better the behaviour and the characteristics of the specific flow component. In the end, this set of parameters was transposed to ungauged sub-basins using the hydrological 'similarity approach'. The performance of the modelling was evaluated comparing the calibrated monthly discharge and observed data using the coefficient bR^2, Nash-Sutcliffe coefficient NSE (Nash and Sutcliffe, 1970) and the percent bias (PBIAS) (Moriasi et al., 2007).

Calibration of water quality

The water quality calibration procedure requires sequentially the sediment loads calibration and then the nutrient loads according to Arnold et al. (2012). Monthly and annual calibration will be performed using the SWAT automatic calibration tool, SWAT_CUP (Abbaspour, 2011). The Preliminary results will be discussed during the Danube Conference 2014.

RESULTS

The main results concerned the water discharge predictions. In the Danube Basin, Pagliero et al. (2014) has obtained for all four watersheds calibrated NSE values ranging from 0.65 to 0.75 and R^2 from 0.73 to 0.82. The step wise calibration was applied also in Scandinavia and Iberian Peninsula (Malago' et al., 2014) where in each region the bR^2 and NSE increased with the transposition of calibrated parameter sets in 'similar sub-basins'. It has emerged that in each studied region, the calibration is mostly controlled by baseflow process and only in Scandinavia by the snowmelt process. In addition, the analysis of spatial variability of NOP showed that ranges of calibrated parameters are very different between the two studied regions. About the calibration of water discharge in the Upper Danube, more efforts were done in collecting new data for the calibration of sediment and nutrients loads. The preliminary results of CreteSWAT model have demonstrated that the model appears to be able to capture the monthly variability of flow. However, site specific knowledge of complex hydrogeological setting has been necessary to improve model results.

CONCLUSION

The results illustrates that the step-wise calibration is a good methodology that allows calibrating the stream flow with good statistical performance and gaining a good knowledge of each hydrological process. The current work focuses on the development of sediment and nutrient calibration in the Upper Danube. The continuous collaboration with in-loco experts and stakeholders remains the important issue in order to be able to create a robust modelling that helps to achieve the target of Water Framework Directive and associated Directives.

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(97) Photoelectrochemical AOPs based on Nanotubular Titanium Dioxide

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Abstract

This work describes a novel Advanced Oxidation Process (AOP) for water treatment consisting in electrochemical photocatalytic oxidation occurring on polarizable nanostructured TiO_2 catalysts. The catalyst was grown by anodic oxidation directly on Ti wire meshes and its morphology and crystalline structure were characterized by means of SEM and XRD, respectively. The photoactivity of the catalyst was evaluated by photoelectrochemical tests. The TiO_2 catalyst was integrated in a columnar reactor working in semi-batch mode under anodic polarization (+1.5 V and +3.5 V vs. SCE) and UV irradiation (254 nm), and the feasibility of the process was tested by decolourization of the azo dye Drimaren Red 243 X-6BN (RR243). Preliminary decolourization tests demonstrated that neither UV irradiation of the TiO_2 catalysts nor the electrical bias individually considered significantly reduced the dye concentration within the first 60 minutes of the treatment. On the contrary, the irradiation of the catalysts with UV light while applying an electrical bias to the same lead to a complete decolourization of the dye within 60 minutes. This approach shows some advantages over current photocatalytic treatments, which are often based on dispersed catalyst particles, since no filtration of the catalyst is required. Moreover, in the present process the anodic polarization of the TiO_2 is possible, leading to a synergistic effect with UV irradiation. Despite the studies on this photoelectrochemical AOP are still at an early stage, compared to other well-established advanced processes for water treatment, the results obtained in the latest years demonstrated that this approach is a promising response to the problem of the treatment of persistent organic pollutants or even of the emerging organic micropollutants.

Keywords

Advanced oxidation processes; photocatalysis; bias; titanium dioxide; persistent organic pollutants.

INTRODUCTION

Advanced Oxidation Processes (AOPs) are among the most investigated methods for the removal of refractory organic compounds, such as dyes, solvents or pesticides from waste waters [1]. The heterogeneous photochemical catalysis based on the use of titanium dioxide [2,3] is known to be an alternative approach to conventional chemical oxidation treatments involving transient radical species. Indeed, Titanium dioxide is a semiconductor which, in the presence of water or air, produces highly reactive radicals when irradiated with UV light (λ<380 nm). Good photoactivity of titanium dioxide is based on the presence of the anatase crystal phase in the catalyst. Titanium dioxide can be used in the form of dispersed nanopowders [4], with the main disadvantage of a separation treatment required after use. This problem is overcome by depositing TiO_2 nanopowders onto metallic wire meshes [5] or by growing self-assembled nanotubular titanium dioxide coatings by anodic oxidation onto titanium wire meshes [6]. These works also opened new perspectives in the field, since supported nanostructured titanium dioxide offer the additional option of being polarizable and working as an electrode. Preliminary studies demonstrated the potentialities of this new class of AOPs [7], but still leaving the applicability of the electrophotocatalytic processes based on TiO_2 catalysts to a variety of aqueous pollutants an open issue.

In the present study, an electrophotocatalytic AOP for water treatment is described. The decolourization of an organic recalcitrant azo-dye of use in the textile industry is carried out in a laboratory reactor working in semi-batch mode. The UV-C activation of the catalysts was coupled to the electrochemical activation of the same, leading to more than 90% decolourization of the azo-dye RR243 in 60 minutes of processing time.

EXPERIMENTALS

Preparation of self-organized nanotubular TiO_2 catalyst

The nanotubular titanium dioxide films were obtained by conventional anodization (CA) of Titanium wire meshes (540 cm^2) of Grade 1 commercial purity Titanium in 1M H_2SO_4 + 78.5 mM HF at 20 V and 25°C for 24 hours. A two electrodes cell has been used, where the counter-electrode was a graphite bar. Annealing pre- and post-treatments were carried out at 400°C for 2 hours in air. The nanotubular titanium dioxide coating had an approximate thickness of 500 nm, pore size of 150 nm and pore spacing of 150 nm (Nanomaterials.it Srl).

Morphological and structural characterization of the TiO_2 catalysts

The surface morphology was investigated by means of Scanning Electron Microscopy (SEM – Zeiss® EVO 50) equipped with LaB_6 source, operated at 20 kV accelerating voltage. The crystallographic structure of the titanium dioxide coatings was assessed by X-ray diffraction (XRD) using a Philips PW1830 instrument, with Cu Kα1 radiation and Bragg-Brentano geometry. An approximate measure of the grain size can be evaluated by calculating the crystal coherence extensions according to Scherrer. The weight fraction of anatase f_A was calculated according to Spurr [8].

Photoelectrochemical characterization of the TiO_2 catalysts

The photoelectrochemical properties of the titanium dioxide coatings were assessed by linear sweep voltammetry in a three electrodes cell. The working electrode was a nanoporous titanium dioxide disc obtained by anodic oxidation. An Ag/AgCl electrode (3 M KCl, + 0.210 V *vs.* NHE) was taken as reference and the counterelectrode was a DSC. The electrolyte consisted in a 4.2 mM KCl solution prepared using distilled water. For measurements, a potentiostat/galvanostat (AMEL 2549) was used. For irradiation, a monochromatic UV commercial lamp (Helios Italquartz) emitting at 254 nm and having a nominal power of 30 W was used. The irradiance on the titanium dioxide catalyst was about 20 W m^{-2} as measured by quantum-photo-radiometer (HD 9021, Deltaohm) working with a detector having a spectral response in the wavelength range 100 ÷ 280 nm.

Preparation of the dye solution

For the decolourization experiments, the azo-dye Drimaren Red 243 X-6BN (RR243) was selected as target molecule, whose molecular structure is shown in Figure 1. Aqueous solutions containing 25 mg/l RR243 + 4.2 mM KCl were used. The volume treated in each decolourization experiment was 2 L.

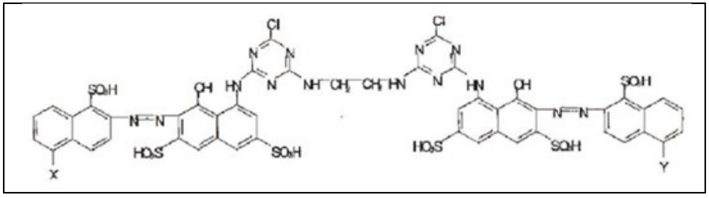


Figure 36. Molecular structure of RR243.

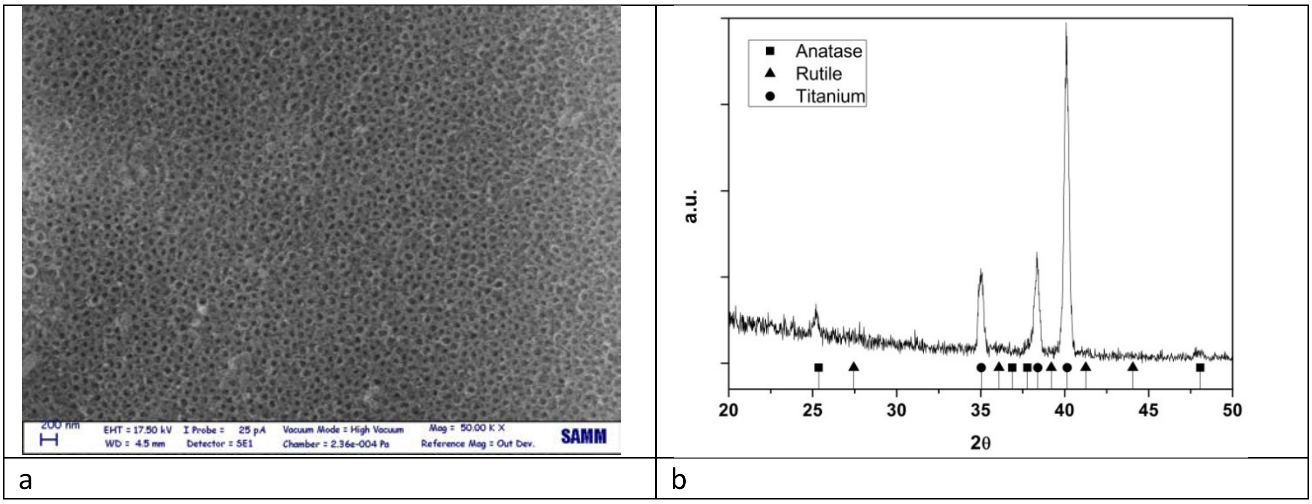
Electrophotocatalytic decolourization experiments

The decolourization experiments were carried out by using a laboratory scale reactor operating in semi-batch mode. The reactor consisted of PMMA tube having a bottom water inlet and an upper outlet, containing a UV source surrounded by the titanium dioxide mesh and a steel mesh working as counter electrode. The photoactive anodes consisted of a titanium tubular wire mesh coated with a nanotubular titanium dioxide coating. The irradiation was done by means of a UV commercial lamp (Helios Italquartz) emitting at 254 nm. The measured irradiance on the titanium dioxide catalyst in the presence of the dye was about 8 W m^{-2}. During the decolourization experiments, a constant cell voltage in the range 1.5÷3.5 V was applied by means of a potentiostat/galvanostat (AMEL 2549). The flow rate was kept constant at the value of 700 l/h. The annular cross-section was 9 cm^2. During the decolourization experiments, 5 ml sampling was carried out every five minutes, and the concentration of RR243 was determined by UV–Vis spectrophotometric measurements (HP 8453).

RESULTS AND DISCUSSION

Morphology and crystal structure of the TiO_2 catalyst

A surface micrograph of nanotubular TiO_2 catalysts obtained by anodic oxidation is showed in Figure 37-a. The TiO_2 coatings obtained by CA show a typical self-organized nanotubular morphology, the average diameter of the tubes being around 80 nm and the thickness being around 500 μm. The TiO_2 coatings showed good adhesion to the substrate



a

b

Figure 37. a) SEM micrograph of nanotubular TiO2 catalyst; b) XRD pattern of the TiO_2 catalyst.

In Figure 37-b, the XRD pattern of the same TiO_2 coating is showed. The coating consists in a mixture of anatase and rutile phases. Based on the XRD patterns, the average phase composition of the coating was calculated. Nanotubular titanium dioxide coatings obtained by CA followed by annealing contained about 84% of anatase, the remaining fraction being rutile. Furthermore, the average crystallite sizes of the TiO_2 coatings was in the range 23-26 nm for both anatase and rutile phases.

Photoelectrochemical properties of the TiO_2 catalyst

The photoelectrochemical properties of the titanium dioxide coatings were evaluated in terms of photocurrent, i.e. difference between the current response with and without irradiation, as a function of the polarization potential. In Figure 38-a the current response of the catalyst under linear sweep polarization is showed both with and without UV irradiation. The irradiation of the sample induced an increased current response, which is represented in Figure 38-b as the difference between the two irradiation conditions (UV on and UV off). The density of photocurrent measured was in the range 0.25÷0.27 mA/cm^2 in the potential range between 1 V and 3.5 V, leading to the conclusion that the catalyst might show a good photocatalytic activity under UV irradiation and polarization in the same voltage range.

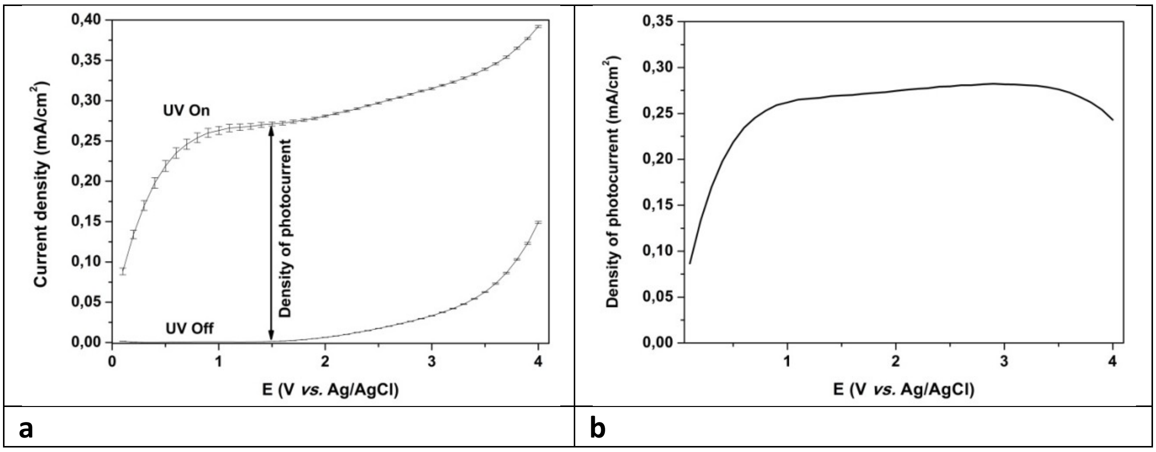


Figure 38. a) Linear sweep voltammetry of the nanotubular TiO2 catalyst with and without UV irradiation; b) Density of photocurrent vs. applied voltage.

Dye decolourization

Decolourization of the azo-dye RR243 solutions was carried out using a nanotubular titanium dioxide wire mesh obtained anodic oxidation as the photoactive electrode. Two external bias values were applied during the decolourization: 1.5 V and 3,.5 V. The decolourization process was followed by measuring the concentration of the azo-dye as a function of time, and it is represented as the ratio between the actual concentration (C) and the initial concentration (C_0) of the dye as a function of processing time in Figure 39. Each decolourization experiment was repeated three times. As already demonstrated [7], when it is not irradiated, the TiO_2 catalysts, whether polarized or not, did not significantly reduce the concentration of the dye, which varied of about 30% after 60 minutes. Similarly, UV irradiation without the use of catalysts led to a limited degradation, about 6% of the initial dye concentration within the same processing time. On the other hand, the simultaneous irradiation of the nanotubular TiO_2 catalysts and the application of an electrical bias lead to a significant reduction of the dye concentration. At 1.5 V the concentration of the dye decreased from 25 mg/l to 2.63 mg/l after 60 minutes (degradation of about 89.5%). At 3.5 V, the degradation was even more effective, the concentration reaching 1.97 mg/l in the same time range (decolourization of about 92%).

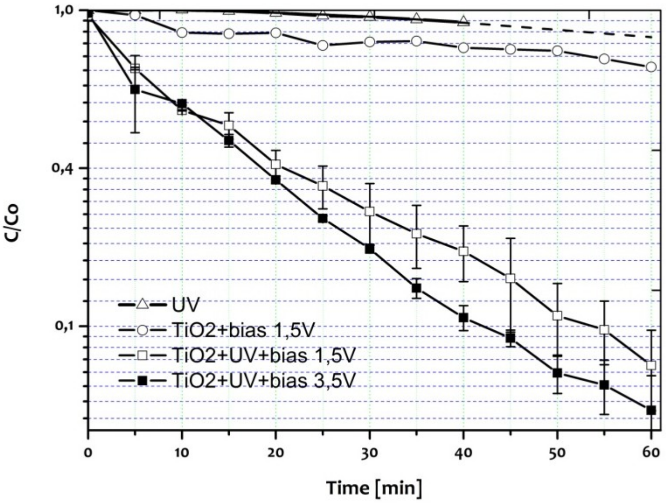


Figure 39. Residual concentration of RR243 *vs.* time at different working conditions.

CONCLUSIONS

A new class of AOPs, based on heterogeneous photocatalysis coupled to electrochemical process on nanostructured TiO_2 catalysts, is proposed. The TiO_2 catalyst, having a nanotubular morphology and grown by anodic oxidation onto Ti wire meshes, was used a photoanodein a reactor working in a semi-batch mode under anodic polarization (+1.5 V vs. SCE) and UV monochromatic irradiation (254 nm), and the process was tested by decolourization of the azo dye Drimaren Red 243 X-6BN (RR243).The irradiation of the catalysts with UV-C light while applying an electrical bias to the TiO_2 catalyst lead to a complete decolourization of the dye within 60 minutes. According to the authors, some advantages of this new process over the current AOPs should be stressed: no filtration of the catalyst is required; an evident synergy between electrochemical and photocatalytic phenomena was observed Despite this photoelectrochemical AOPs are still at an early stage, compared to other well-established advanced techniques for water treatment, the results obtained in the present work and in the previous ones demonstrated that this approach can be a promising response to the problem of wastewater treatment.

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(98) Environmental Assessment of Organic Waste and Domestic Wastewater Management in Decentralised Communities

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Development areas and, small and isolated villages can be served by decentralized wastewater treatment systems that are more simple and cost effective compared with conventional centralized treatment. In this way, the large capital investment of sewerage systems and pumping costs associated with centralized systems can be reduced. This study aims to evaluate the potential environmental impacts of four different alternatives for the decentralized co-treatment of domestic wastewater and domestic organic waste (DOW) generated in a small community of 2000 population equivalent. The core treatment technologies for the water line include upflow sludge blanket (UASB) to recover energy from wastewater and DOW and sequencing batch reactor (SBR) to biologically remove nutrients via short-cut nitrification denitrification, or membranes coupled with the UASB to enhance the efficiency of the anaerobic process. The use of food waste disposers FWDs was considered for the last two scenarios simulating situations were regular separate food waste collection from households cannot be practiced. Composting was selected and evaluated as the final treatment process in the sludge line. Life Cycle Assessment (LCA) methodology was applied for the environmental analysis. Four different scenarios were proposed and have been inventoried in detail. The functional unit selected for this purpose was one inhabitant equivalent. The environmental performance was assessed in terms of climate change (CC), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME) and fossil depletion (FD), using characterization factors reported by the ReCipe Midpoint. The best option from an environmental point of view for the combined treatment of wastewater and DOW was identified. In addition, the most important '*hotspots'* were recognized and potential environmental improvements were proposed.

Keywords

Decentralized wastewater treatment, Composting, Environmental profile, Environmental credits, Sludge disposal, Waste management, Food waste disposers

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