A full-scale plug-flow reactor for biological sludge ozonation

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INTRODUCTION

Sludge ozonation is a technology that reduces the production of excess sludge in biological wastewater treatment plants (WWTPs). It is based on the reaction between ozone and organic and biological suspended solids, which promotes the lysis of particulate matter, the damage of cell walls and the selection of biomass with a low cell yield (Gardoni *et al*. 2011; Torregrossa *et al*. 2012). It also allows for the elimination of filamentous organisms, including hydrophobic biological foams due to Nocardio-forms and *Microthrix parvicella* (Vergine *et al*. 7200), enhancing the settleability and the dewaterability of biologi-cal sludge (Guo *et al*. 3201). By lowering the sludge volume index, mixed-liquor suspended solids (MLSS) concentration can be increased, permitting longer sludge retention times without overloading the secondary settler. This technology is cost effective (Salsabil *et al*. 2010; Chiavola *et al*. 3201), especially in WWTPs where ozone is already used for colour and surfactant removal, disinfection, etc.

Many studies have focused on the macroscopic and microscopic consequences of the contact between ozone and sludge and on their technological implications. The approach generally used is basically empirical and aims at establishing direct correlations between ozone dose and excess sludge reduction. The results available in the literature, for example, Manterola *et al*. (8002), and Chiellini *et al*. (2014), generally refer to experimental conditions in which ozone is dosed continuously through bubble diffusion systems.

The use of continuous ozonation reactors may be effective, but it requires high reaction volumes because of the need for relatively long contact times at very low ozone concentrations in the bulk liquid, due to the high reactivity of the gas. A viable alternative is represented using a Venturi ejector followed by a plug-flow reactor, as discussed in Gardoni *et al*. (2011) and Chiavola *et al*. (2013). Contrary to a completely stirred reactor, in a plug-flow reactor the initial concentration of ozone is much higher and its transfer to the liquid phase is much faster. These two conditions allow a reduction of the volume of the reactor by orders of magnitude at the expense of a higher energy consumption. Moreover, plug-flow operation minimizes excessive ozone consumption by enhancing the selectivity of ozone for cell lysis rather than random chemical oxygen demand (COD) oxidation (Fabiyi & Colleti 2012).

From a kinetic point of view, a Venturi ejector appears to be more efficient when compared to a fine bubble contactor. This assumption can be demonstrated by considering the theory of reactive gases in water. The detailed and rigorous approach can be found in Smith & El Din (2002), Beltrán (2004) and Jiang *et al*. (2009). In non-pure water, a

kinetic description of the ozonation process can be based on the diffusion-reaction module, or Hatta number, for the first (Equation (1)) and second (Equation (2)) order

$$\mathrm{Ha}_1 = (k_1 D_a)^{1/2}/k_\mathrm{L} \quad (1)$$

$$\mathrm{Ha}_2 = (k_2 D_a C_{\mathrm{B}b})^{1/2}/k_\mathrm{L} \quad (2)$$

where D_a is the diffusivity of ozone, k_1 and k_2 are the reaction rate constants of ozone consumption reaction for the first and the second order kinetics, respectively, $C_{\mathrm{B}b}$ is the concentration of ozone in the bulk liquid and k_L is the mass transfer of ozone from the gas phase to the liquid phase.

Reactions with high Ha (>2) are considered 'fast' and occur near the gas–liquid interface, while low Ha values (<0.2) correspond to 'slow' reactions, occurring mainly in the bulk liquid. According to this approach, a fine bubble contactor appears to be in a fast kinetic regime. Under this condition, a relevant fraction of ozone decays in the liquid film, without reacting with the solid particles that are present in the bulk liquid, and the residual concentration of ozone in the bulk liquid approaches zero. The increase of turbulence (and, hence, of k_L) in the system will progressively shift the kinetic towards a moderate/slow regime, in which a more relevant fraction of the injected ozone can react with particulate matter. The results of Manterola *et al.* (2008) support this conclusion. By applying a constant flux of ozone to a mixed liquor and changing the fluid-dynamics conditions, an increase of 94% in the solubilization of COD was observed. A similar behaviour was observed by Chu *et al.* (2008) when a change in the ozonation system (from fine bubbles to micro bubbles) allowed an increase of 30% in the COD solubilization. As a consequence, the extreme turbulence of a Venturi ejector should significantly enhance the potentiality of sludge ozonation.

The purpose of the present paper is to define the influence of ozone and total suspended solids (TSS) concentrations on the process efficiency, starting from the analysis of a one-year data-set collected on a full-scale plant, in order to optimize the performances of a plug-flow contact reactor. Laboratory-scale batch tests were also performed on sludge taken from two different plants treating wastewater with different characteristics. Furthermore, the direct lethal effect of ozone on heterotrophic biomass was also evaluated.

METHODS

WWTPs and sampling

The first plant (WWTP1) is located in Bulgarograsso, near Como (Italy). It is a conventional nitrification-denitrification biological plant (80,000 population equivalent (p.e.); one p.e. means the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60 g of oxygen per day, as defined by Directive 91/271/EEC of 21 May 1991, concerning urban waste-water treatment). The influent (25,400 $m^3\,d^{-1}$) has a high contribution of textile wastewater (75% of the overall COD load, 50% of the overall flow rate). At WWTP1, a full-scale sludge ozonation plant was installed. The sludge samples were taken before and after the ozone contact reactor and stored at 4 °C before use. No intermediate sampling points were available.

The second plant (WWTP2; 550,000 p.e.) is located in Peschiera Borromeo and serves the eastern part of the city of Milan (Italy), treating typical urban wastewater. Of the two existing treatment lines, the older is a conventional activated sludge process (300,000 p.e.) designed to achieve nitrification. Sludge samples were taken from the recycle stream and stored at 4 °C before use.

Full-scale ozonation plant

The full-scale sludge ozonation apparatus installed at WWTP1 comprised a Venturi ejector (Praxair, Danbury, CT, USA) followed by a plug-flow contact reactor (a stainless steel pipe of 10 metres, 20 cm in diameter, ~0.3 m^3 in volume). Twenty percent of the recycle sludge flow (5,080 $m^3\,d^{-1}$) was ozonated and then pumped to the aeration basin in order to avoid oxygen addition in the anoxic denitrification reactor. The retention time of the contact reactor was about 5 seconds. During the experimental period, the initial ozone concentration ranged between 3 and 40 $mg_{O3}\,L^{-1}$ (0.25–3.3 $g_{O3}\,g_{TSS}^{-1}$). A 17% reduction in sludge production was achieved at an ozone dose of 20–30 $mg_{O3}\,L^{-1}$ (1.5–3.0 $g_{O3}\,g_{TSS}^{-1}$). The applied ozone dose was completely utilized and no residual concentration was detected at the end of the reactor.

Laboratory-scale ozonation setup

In the laboratory, ozone was produced with an Air Liquide TP40 generator (Air Liquide Italia S.p.A., Milan, Italy). Samples of MLSS were mixed with pre-saturated deionised

water in closed and stirred borosilicate glass vessels ($V = 0.5$ L). By operating in this way, it was possible to simulate the behaviour of a plug-flow reactor and also to define the initial concentration of O_3 in each sample. The contact time was 5 minutes, which is enough to obtain a complete reaction of ozone and its radicals. Tests were performed at 20 ± 1 °C.

Oxygen uptake rate (OUR) measurement

Respirometric tests (Ficara & Rozzi 2004) were conducted under aerobic conditions and performed by means of respirometric/titrimetric apparatus (MARTINA instrument, provided by SPES s.c.r.l., Fabriano, Italy). Endogenous OURs were measured for WWTP1 and WWTP2 sludge samples, before and after being submitted to laboratory-scale ozonation. All tests were conducted by adding 10 mg L^{-1} of allylthiourea to inhibit the respiration of autotrophic biomass. Each OUR measurement was obtained by linear interpolation of at least 10 oxygen data points with a coefficient of determination higher than 95%. Three replicates were performed for each experimental condition.

Analytical methods

Ozone concentration and TSS were measured according to Standard Methods 4500-Cl and 2540D (APHA *et al.* 2008), respectively. Soluble COD (sCOD) was measured before and after ozonation, and 240 and 60 measurements were performed on the full-scale plant and in laboratory tests, respectively. Samples had been previously filtered on 0.45 μm filter paper and the COD of the filtered liquid was measured using analytical kits (LCK314, Hach-Lange (Hach Lange Italia srl, Lainate, Italy). Range: 15–150 mg_{COD} L^{-1}) and a spectrophotometer (Xion 500, Hach-Lange).

RESULTS AND DISCUSSION

Effect of process parameters

From data collected during the full-scale ozonation tests run at WWTP1, the observed specific COD solubilisation (f_{COD}, g_{sCOD} g_{O3}^{-1}), i.e., the mass of soluble COD produced per mass of ozone applied, was computed. The same calculation was made on data collected during the laboratory-scale experimentation on WWTP1 sludge samples. These results, grouped by values of TSS concentration in the sludge (summarised in Figure 1(a)), are reported versus the initial ozone concentration because both plug-flow and batch reactors are based on a single initial ozone dosage. Results showed that the lower the initial ozone concentration, the higher the specific COD solubilisation, especially when the ozone concentration is below 10 mg L^{-1}. The relationship between these two parameters follows the same (non-linear) trend for both full-scale and laboratory-scale data.

In addition, a dependence of the specific COD solubilisation from the TSS concentration can be observed: the higher the TSS concentration, the lower the process efficiency. Unfortunately, due to the low variability of TSS concentration in the full-scale plant, this trend is observable only in the laboratory test results. Moreover, comparing data related to the same TSS concentration, a slight difference between the full-scale and the laboratory-scale results can be noticed. This difference can be reasonably associated to the mechanical stress caused by the Venturi ejector that could have enhanced the sludge solubilisation and made the process more efficient.

Since sludge from WWTP1 was acclimatized to ozone, it was interesting to verify whether this non-linearity holds for a sludge that had never been previously exposed to ozone. Therefore, laboratory tests were repeated on sludge samples collected at WWTP2. As shown in Figure 1(b), the same qualitative trend was observed for the WWTP2 sludge.

For both WWTP1 and WWTP2 sludge samples, the decrease of ozone efficiency at increasing ozone concentration can be described by an empirical negative exponential equation (Equation (3))

$$f_{COD} = a \cdot [O_3]^{-b} \tag{3}$$

where f_{COD} is the efficiency of specific COD solubilisation (g_{sCOD} g_{O3}^{-1}), $[O_3]$ is the initial concentration of ozone (mg_{O3} L^{-1}), a and b are the parameters of the curve. Fitting parameters were obtained by using the non-linear regression tool in Minitab® 16.1.0 (Minitab Inc.). From Table 1, it looks like both 'a' and 'b' depend on the origin of sludge; therefore, they do not have general validity and should be considered as plant specific.

Table 2 summarizes the f_{COD} values obtained in the present study and compares them with other data available in literature. It appears that the considered plug-flow reactor has an efficiency comparable with completely stirred reactors. However, the most relevant difference between the two reactor configurations is that the average ozone concentration is higher in a plug-flow reactor than in a completely stirred reactor (according to the theory of reactive gases discussed in the introduction). Equation (3) suggests that a higher concentration of soluble ozone entails lower specific

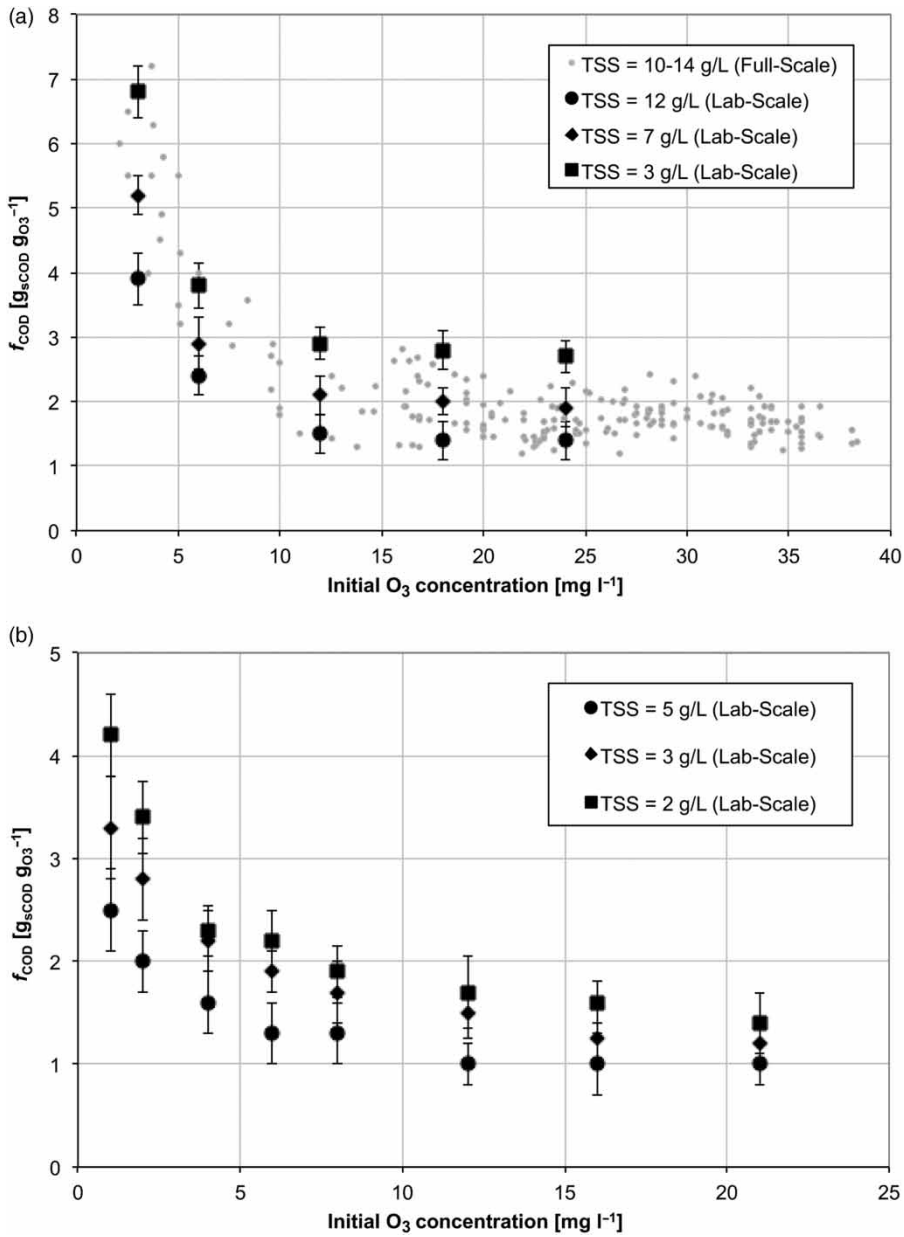

Figure 1 | Efficiency of ozonation ((a) WWTP1; (b) WWTP2), expressed as specific soluble COD production versus the initial ozone concentration.

solids solubilisation efficiency. This is confirmed in the literature and in particular, in experiments where the ozone dose is significantly lower (from 10 to 100 times lower with respect to other studies; Cheng *et al.* 2012 and Muz *et al.* 2014). As a consequence, from the results presented, a single Venturi appears to be an inefficient system, as the entire ozone dose is applied at once. If a sequence of smaller Venturi injectors is applied at intervals long enough so that ozone is depleted before the next injector point, the result is that low dosages are applied, maximising COD solubilisation. This solution preserves the advantages of plug-flow reactors (compactness and simplicity) and avoids exceedingly high initial ozone concentration.

Effect on heterotrophic biomass

In order to better characterize the role of ozone on the overall behaviour of the plant, its effect on the activity of heterotrophic biomass was quantified in terms of endogenous OUR. As reported in Figure 2, observed OUR values were not affected by sludge ozonation, as the ratio between the OUR (after ozonation) and the $OUR_{untreated}$ (untreated,

Table 1 | Conditions and parameters (mean ± standard error) for Equation (1)

	TSS concentration [g L^{-1}]	a [(g_{SCOD} g_{O3}^{-1})·(mg_{O3} L^{-1})^b]	b [-]	R^2
WWTP1: full-scale results	10–14	4.80 ± 0.19	0.040 ± 0.002	0.707
WWTP1: lab-scale results	3	6.74 ± 1.32	0.053 ± 0.021	0.951
WWTP1: lab-scale results	7	5.32 ± 1.03	0.059 ± 0.021	0.967
WWTP1: lab-scale results	12	4.20 ± 0.71	0.065 ± 0.020	0.972
WWTP2: lab-scale results	2	3.80 ± 0.37	0.067 ± 0.015	0.917
WWTP2: lab-scale results	3	3.12 ± 0.21	0.061 ± 0.010	0.896
WWTP2: lab-scale results	5	2.26 ± 0.20	0.058 ± 0.013	0.904

Table 2 | Specific production of soluble COD in this study and extrapolated from the literature, and indicative parameters of the experimental setup

Source	f_{COD} [g_{SCOD} g_{O3}^{-1}]	Ozone dose	Ozonation duration	Initial TSS [g_{TSS} L^{-1}]	Type of ozonation contact reactor	Type of ozone addition
WWTP1 (full-scale), this study	1.1–7.2	0.25–3.3 mg g_{TSS}^{-1}	Instant	12.0 ± 2.0	Plug-flow	Initial
WWTP1 (laboratory-scale), this study	1.2–6.8	0.25–8 mg g_{TSS}^{-1}	Instant	3–12	Batch	Initial
WWTP2 (laboratory-scale), this study	0.9–4.2	0.4–11 mg g_{TSS}^{-1}	Instant	2–5	Batch	Initial
Weemaes *et al.* (2000)	1.9–5.3	50–200 mg g_{COD}^{-1}	55–218 min	9.5 ± 1.2	Batch	Continuous
Paul & Debellefontaine (2007)	3.5–4.2	34 mg g_{VSS}^{-1}	up to 30 min	n.a.	Batch	Continuous
Manterola *et al.* (2008)	1.8–3.5	25–35 mg g_{TSS}^{-1}	10–60 min	4.18 ± 0.39	CSTR	Continuous
Cheng *et al.* (2012)	1.4	77 ± 7 mg g_{TSS}^{-1}	15 min	7	Batch	Continuous
Cheng *et al.* (2012)	14.3–23.2	5–11 mg g_{TSS}^{-1}	16 min	7	Batch	Pressure cycle
Chiavola *et al.* (2013)	2.5–8	1.23–1.40 mg g_{TSS}^{-1}	Instant	4–6	Plug-flow	Initial
Muz *et al.* (2014)	50–100	0.42–1.27 mg g_{TSS}^{-1}	2–6 min	2.3–4.63	Batch	Intermittent

before ozonation) was always very close to 1 on both sludges. This means that a high initial dose of ozone does not have a direct lethal effect on biomass, as already shown in Gardoni *et al.* (2011), while it favours the solubilisation of inert particulate COD. Moreover, the WWTP2 biomass was not more sensitive than the biomass from WWTP1, suggesting that the absence of lethal effects on the heterotrophic bacteria is not a result of biomass adaptation but is more likely due to the low ozone dosage applied. A further development of the research will evaluate the effects of ozonation on the autotrophic biomass.

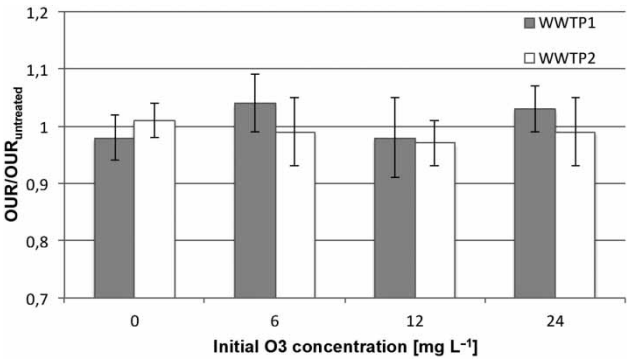

Figure 2 | Effect of initial concentration of ozone on the endogenous OUR, for both sludges. $OUR/OUR_{untreated}$ is the ratio between OUR of ozonated sludge and OUR of untreated sludge (before ozonation).

CONCLUSIONS

Interactions between ozone and biological sludge are complex as several processes and components are involved in sludge ozonation. The results obtained in this study allow the proper control of some operational parameters, which has important practical implications.

First, the concentration of ozone in the reactors: specific COD solubilisation efficiency decreases as ozone concentration increases. As a consequence, a sequence of several small Venturi ejectors should be preferred to a single bigger one.

Second, specific COD solubilisation efficiency seems to decrease when TSS concentration increases. It is preferable to avoid very high TSS concentrations in order to maintain high process efficiencies. Therefore, direct ozonation of MLSS taken from the biological reactors may be more efficient than ozonation of more concentrated sludge taken from the recycle stream.

Finally, from the biological point of view, it was observed that an initial 'shock' of ozone has negligible effects on the heterotrophic biomass. This behaviour is different from what has been observed in completely stirred tank reactor (CSTR) contactors and could be of interest, although the results obtained are intended to be site specific.

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