Ozone tertiary treatment for pharmaceuticals and personal care products removal from municipal wastewater

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Summary

An ozone pilot plant was installed at a conventional WWTP to evaluate the removal rate of emerging contaminants, drugs, and fragrances, as tertiary treatment. The filtered secondary effluent flow rate ranged between 1.3÷1.9 m^3/h with a retention time of 10÷30 minutes and the plant operated with an ozone dose of 2-4 mgO_3/l. The results evidenced a high removal rate of 80-100% for most of the organic targeted compounds: Amisulpride, Azithromycin, Carbamazepine, Diclofenac, Clarithromycin and Ofloxacin. Lower removal rates from 20% to 80%, were observed for some substances e.g. Gabapentin Lactam, Galaxolidone, Irbesartan, Lamotrigine, and Tonalide. Advanced Oxidation Process (AOP) treatment with O_3/H_2O_2, (0.5–1.0–2 $molH_2O_2/molO_3$) allowed improved results for almost all these latter. In addition, ozone determined up to 42% removal of the absorbance at 254 nm and 20% of COD, wastewater disinfection, a decrease of the GC-MS chromatographic area, and no acute toxicity effect nor estrogenic and mutagen effects have been detected.

Keywords: Emerging contaminants; Ozone; Advanced Oxidation Process.

Introduction

Pharmaceutical and personal care products are ubiquitous pollutants in environmental matrices of anthropized regions (Ebele et al., 2017). Many of these compounds come mainly from wastewater treatment plants (WWTPs) (Daughton and Ternes, 1999) where they are often not completely and consistently removed during conventional processes (Dickenson et al., 2011). These chemicals are present in low concentrations (ng or μg per litre) and are constantly released into the environment where they can persist and therefore bioaccumulate with potential adverse impacts on different organisms. Pharmaceuticals are frequently detected in waterbodies and as these compounds are biologically active, they may pose a risk for human health and the environment. Synthetic musks are chemicals widely used as low-cost additives in many commercial products for house cleanings and personal care (soaps, detergents, air-fresheners, perfumes, body lotions and cosmetics). Polycyclic musks currently dominate the fragrances global market, although their use in cosmetics is under discussion (Homem et al., 2015) since they have been recognized as persistent, bioaccumulative and potentially toxic to organisms (Fromme et al., 2001; Parolini et al., 2015; Schreurs et al., 2004). Among polycyclic musks fragrances (PMFs), Galaxolide (HHCB) and Tonalide (AHTN) are employed in larger volumes, while other PMFs, such as Celestolide (ADBI) and Phantolide (AHDI), are used to a lesser extent (O.S.P.A.R. Commission, 2004). A daily and worldwide use leads to a constant release of these chemicals into the environment mainly through WWTP effluents. In addition, some of these human-made chemicals transform to other compounds (transformation products), frequently associated with detoxification of pollutants, but persistent and/or toxic products may also be formed (Schlüter-Vorberg et al., 2015). As regards metals the oxidation of chromium to the most toxic hexavalent form should be assessed (Li et al., 2014).
The main objectives of the present study were to determine the ozone removal efficiencies of different classes of emerging contaminants on a real WWTP effluent, identifying optimal operative condition and evaluate the tertiary treatment effect on the physical, chemical and microbiological characteristics of the treated effluent.
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Materials and methods

A pilot plant for the ozone treatment was installed at a conventional activated sludge WWTP in the North of Italy, with a nominal capacity of 30,000 PE (Population Equivalent). The pilot plant was composed by an ozone generator (Wedeco GSO40-06 fed by pure oxygen) and a contact reactor: two 6 m height stainless steel columns connected in series. Ozone pilot-scale tests were conducted on filtered secondary effluent with flow rates ranging between 1.3 to 1.9 m^3/h. Porous diffusers positioned at the bottom of each column were used to insufflate ozone in wastewater: counter-current water flow in the first column and equicurrent in the second one. Each gas line (inlet and off-gas) was equipped with a flow meter and ozone concentration analyser (BMT 964C and BMT 964 off-gas) while the wastewater sampling point was positioned at the inlet section ("IN"), and the outlet of each column ("OUT1" and "OUT2" respectively).

The experimental plan consisted of 10 analytical sessions, carried out every two/three months: from April 2019 to April 2021. It was defined to evaluate the ozone treatment performance in terms of micropollutants removal at different ozone dosages, operative conditions (flow rates/contact time) and qualitative characteristics of the treated wastewater. In addition, some advanced oxidation process (AOP) tests have been conducted by adding hydrogen peroxide (H_2O_2) in the second reaction column. Hydrodynamic study of the contact reactor has been carried out with a tracer test at the different flow rate levels.

The duration of each test was about 4 hours. Composite samples were collected for each sampling point mixing instantaneous samples collected every 20-30 minutes, with the addition of sodium thiosulfate as ozone quencher. Each composite sample was analysed according to micropollutant content, but also concerning the qualitative analysis of the organic compounds in GC-MS and to conventional physical-chemical quality parameters (COD, TOC, Alkalinity), while dissolved ozone concentration, temperature, conductivity, UV254 absorbance, pH and microbiological parameters were analysed in instantaneous samples. A panel of micropollutants was selected according to a preliminary screening analysis which allowed the identification of certain classes of micropollutants: 12 pharmaceuticals [Amisulpride (antidepressant), Clarithromycin, Azithromycin, Ofloxacin, Sulfamethoxazole (antibiotic), Carbamazepine, Lamotrigine (antiepileptic), Diclofenac, Ketoprofen, Propyphenazone (anti-inflammatory), Irbesartan, Metoprolol (antihypertensive)], 1 pharmaceutical transformation product [Gabapentin-Lactam (transformation product of Gabapentin)] and 1 industrial compound in wastewater [Methyl-Benzotriazole (corrosion inhibitor)]; 5 fragrances [Celestolide, Galaxolide, Galaxolidone, Phantolide, Tonalide] and trace element (CrIV).

Toxicity tests were carried on instantaneous samples to evaluate the effects the ozone treatment on *D,magna, V. fischeri, P.subcapitata* and the assessment of the estrogenic and mutagen potential of the wastewater subjected to the ozone treatment, on composite samples, has been carried out through e-screening and micronucleus tests, respectively.

Results and discussion

Analytical results of organic micropollutants showed drug concentrations ranging from 10 to 1,000 ng/l with a higher occurrence of hypertensive (Irbertarsan), anti-inflammatory (Diclofenac), and antibiotics (Azithromycin, Clarithromycin, and Ofloxacin). Higher concentrations have been detected for fragrances and Methyl Benzotriazole, with the former ranging from 10^1 to 10^3 ng/l while the latter revealed a concentration of 103 ng/l. Moreover, Galaxolide and Galaxolidone are the most present fragrances: their concentrations ranged from 1,000 to 10,000 ng/L, respectively 1 and 2 orders of magnitude higher than Tonalide and Celestolide. Phantolide was never detected.

The consumed ozone value has been calculated as the applied ozone dosage minus the unreacted ozone in the water and gas phases. The process was characterized by an average ozone transfer efficiency respectively of 83%±4% and 60%±10% for the first column and the second column, while the overall transfer efficiency was about 75%±7%

Based on these results, the oxidative treatment showed high removal efficiency for the majority of the analysed compounds. For most substances, removal yields higher than 95% could be obtained independently of ozone dosage (Pearson's correlation, P-value> 0.05) or, in any case, with net ozone consumption within 4 mgO_3/l. Lower removal efficiency has been obtained for Gapentin-lactam and Irbersartan among the drugs and for Galaxolidone among the fragrances. For these substances, lower removal yields (10-80%) indicated a lower reactive capacity of ozone with their chemical-molecular characteristics, in agreement with the literature. In the case of

Galaxolidone, also negative removal yields have been obtained, probably due to the production mechanisms of this substance from its oxidative precursor, namely Galaxolide. For these refractory substances, higher removal rates have been obtained in AOP tests. In particular, the removal percentage of Galaxolidone progressively increased to 67% at the highest H_2O_2 dosage tested ($2molH_2O_2$:$1molO_3$). This removal rate is almost four times higher than the one obtained without adding H_2O_2, at the same operative conditions (16%). The dosage of H_2O_2 enhances the O_3 consumption favouring the formation of $OH^{\bullet}$ radicals, which are chemical species characterized by a higher oxidative potential than dissolved O_3.

It should be emphasized that the oxidative process did not lead to the transformation of chromium into hexavalent chromium.

Regarding the organic content, a COD reduction of 20% has been achieved thanks to not selective ozone oxidation property. Reduction up to 42% of the absorbance at 254 nm has been also obtained; this parameter has been found highly correlated with the total organic micro-pollutant content, especially with fragrances ($r = 0.78$, P-value<0,05), suggesting it can be used as a proxy parameter of the process.

The GC-MS approach analysis suggested different ozone effects on the organic composition in the first and the second column. The former displays a redistribution of organic content, as shown by the reduction of relative percentages of hydrocarbon content compared to an increase in ketones and phenols, while the latter shows a general reduction in the organic content as chromatographic area, with particular reference to the fraction of hydrocarbons and ketones.

Ozone treatment also proved high disinfection performance of the treated wastewater. In particular, an average of 4-log and 5-log inactivation pathogenic indicator microorganisms (*E.coli*, Enterococci, Total Coliform) has been recorded, respectively in the first and second column.

Ozone treatment reduced the presence of substances with estrogen-like activity and none of the water samples collected and analysed showed any mutagenic activity, suggesting a good water quality. Acute toxicity tests on *D. magna*, *V. fischeri* and *P. subcapitata* showed no significant effects.

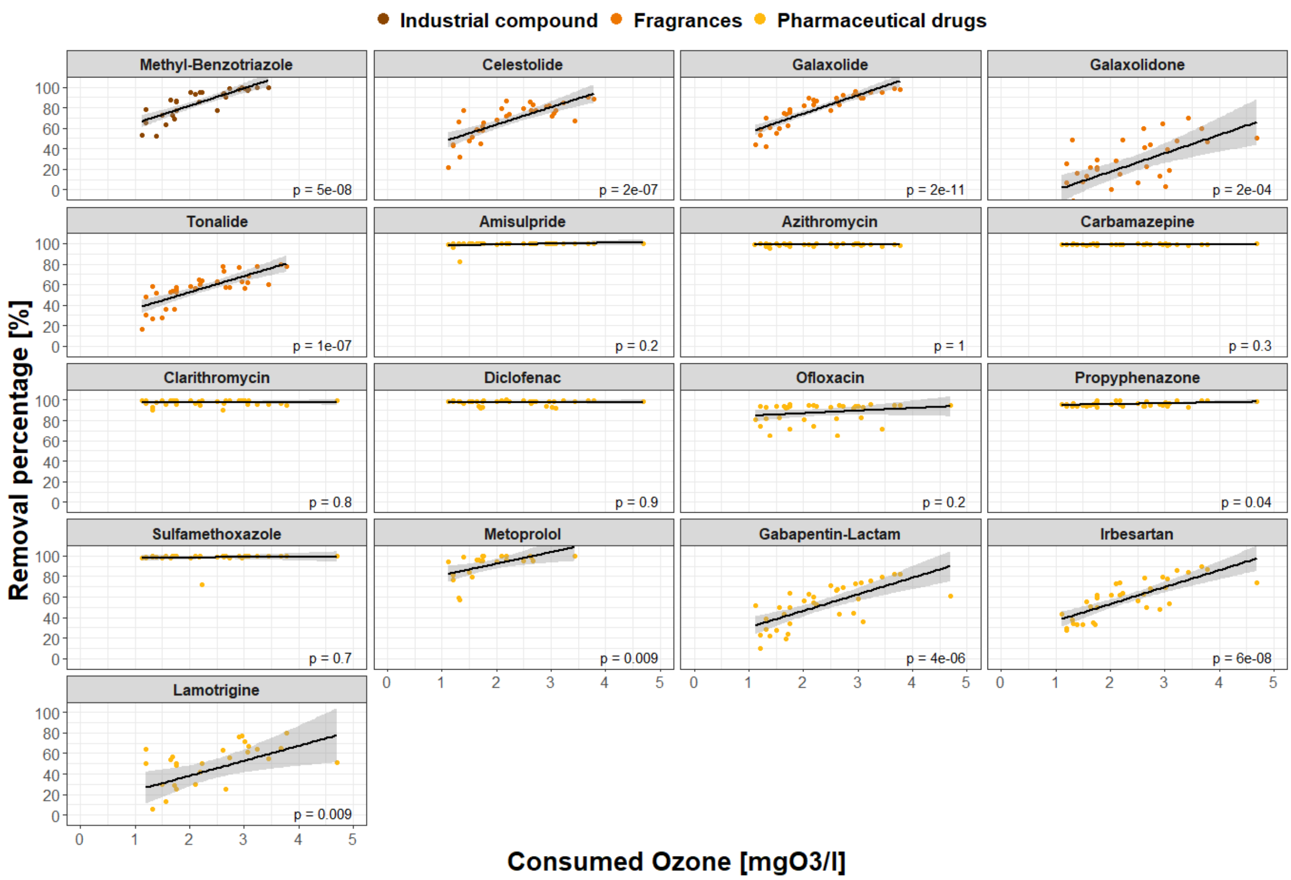

Figure 1. Removal percentages of pharmaceuticals (yellow points) and fragrances (orange points) compounds versus consumed ozone.

Conclusions

Ozone oxidation of micropollutants in WWTP effluent has been evaluated. Ozone has allowed the removal of more than 95% of the majority of the active ingredients of drugs and fragrances with dosages between 1 and 4 mgO_3/l. In case of refractory compounds, the combination with hydrogen peroxide was effective in enhancing the oxidation mechanisms, reaching removal yields up to 4 times higher than using only ozone. Moreover, a nonselective action of ozone determines a reduction of 20% of residual COD in the secondary effluent. As a secondary effect, 5-log inactivation of pathogens microorganisms was reached at the ozone dosage tested.

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