



# Performance of ozone and peroxone on the removal of endocrine disrupting chemicals (EDCs) coupled with cost analysis

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## ABSTRACT

Micropollutants such as endocrine disruptors are one of the most important groups of chemicals polluting water resources. Conventional treatment systems may not be effective for the removal of endocrine disrupting chemicals (EDCs), and the fate of these chemicals should be carefully monitored in the effluent of wastewater treatment plants (WWTPs). Additional treatment methods such as advanced oxidation processes can be used for the removal of endocrine disruptors. This study presents the existence of endocrine disruptors in 4 different effluents: (i) municipal WWTP effluent, (ii) textile industry WWTP effluent, (iii) organized industrial zone (OIZ) WWTP effluent and (iv) pharmaceutical industry discharge and also presents their removal efficiencies by ozonation and peroxone oxidation. A broad spectrum of removal efficiencies was observed for the EDCs present in the samples since the oxidation efficiency of wastewaters containing EDCs mainly depends on the wastewater matrix and on the type of the EDCs. Ozonation was found to be a lower-cost option than peroxone oxidation at the investigated conditions.

**Key words** | cost analysis, endocrine disrupting chemicals, ozonation, peroxone process

## HIGHLIGHTS

- Performances of ozonation and peroxone processes were investigated for endocrine disrupting chemicals.
- A broad spectrum of removal efficiencies was observed.
- Treatment efficiency was powerfully dictated by the wastewater matrix.
- Ozonation was found to be a lower-cost option than peroxone oxidation.

## INTRODUCTION

Over the past 20 years, there has been an increased awareness of the incidence of toxic and/or recalcitrant chemicals, collectively known as micropollutants, in the aquatic and terrestrial environment. Water pollution due to the presence of micropollutants such as pharmaceuticals, personal care products,


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endocrine disrupting chemicals (EDCs), pesticides, and so on lead to a variety of adverse effects in both humans and wildlife (Snyder *et al.* 2003). Of these, EDCs are chemicals that affect/interfere with the action of hormones in the endocrine system by acting as hormone mimics, receptor agonist/antagonists, altering the synthesis and metabolism of natural hormones or modifying hormone receptor levels (US EPA 1997; WHO 2012). EDCs can potentially cause adverse health effects at concentrations in the milligram/nanogram per liter range (Benotti *et al.* 2009). They may originate

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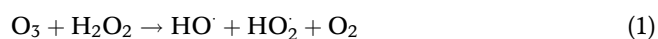
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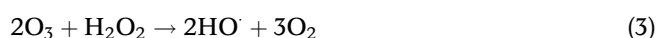
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from natural or anthropogenic sources such as industrial, agricultural and domestic uses. In conventional wastewater treatment plants (WWTPs), many of these hydrophilic organic compounds are poorly removed, and are detected in secondary effluents (Choubert *et al.* 2011; Deblonde *et al.* 2011; Margot *et al.* 2013). Therefore, additional tertiary treatment units should be considered for WWTPs, since this would be the best strategy to reduce the release of EDCs into the receiving water bodies. The current quest to achieve a reliable and efficient removal of EDCs involves adsorption onto activated carbon and chemical oxidation with ozone, which have been identified as the main technologies with a potential for large-scale application in terms of efficiency, cost and energy requirements (Margot *et al.* 2013; Kårelid *et al.* 2017). The implementation of these specific advanced treatment systems is seriously considered by wastewater managers and decision makers.

Ozone (O<sub>3</sub>) and the hydroxyl radicals (HO<sup>•</sup>) produced spontaneously during decomposition are powerful oxidizing agents. Ozonation is a prominent technique in elimination of colour, taste, and odour as well as in disinfection and degradation of micropollutants (Margot *et al.* 2013). In ozonation, O<sub>3</sub> can react directly with an organic molecule, or indirectly through several reactions involving HO<sup>•</sup>. These pathways are regulated by different parameters and lead to unknown reactive degradation products due to partial oxidation of the compounds and to reaction with matrix components (von Gunten 2003). These degradation products might even be more toxic than the original pollutant, and might also be more biodegradable and able to be removed during biological post-filtration (Stalter *et al.* 2010a, 2010b). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be added to the reaction medium in a process described as the peroxone process to increase the rate of O<sub>3</sub> decomposition and HO<sup>•</sup> formation (Gago-Ferrero *et al.* 2013; Bottrel *et al.* 2014; Liu *et al.* 2015; Xiong *et al.* 2018). In the peroxone process, H<sub>2</sub>O<sub>2</sub> will promote the degradation of O<sub>3</sub> by electron transfer or alternatively O<sub>3</sub> will activate H<sub>2</sub>O<sub>2</sub>, which generates HO<sup>•</sup> and hydroperoxyl radical (HO<sub>2</sub><sup>•</sup>). O<sub>3</sub> can react with the HO<sup>•</sup> to generate less reactive radicals like HO<sub>2</sub><sup>•</sup>, which can be converted to HO<sup>•</sup> and O<sub>2</sub> by O<sub>3</sub> (Boczka & Fernandes 2017; Xiong *et al.* 2018):



Overall reaction



Peroxone process provides a more effective reaction with pollutants compared to the process in which only O<sub>3</sub> is used, due to the formation of HO<sup>•</sup> (Acero & von Gunten 2001; Liu *et al.* 2015). H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> molar ratio corresponding to a stoichiometric O<sub>3</sub> decomposition is 0.5 (Acero & von Gunten 2001). This ratio has been extensively used in water/wastewater treatment applications (Pocostales *et al.* 2010; Meshref *et al.* 2017).

Practical usage of ozonation is limited due to the low solubility of ozone in water, high energy consumption, sensitivity to various factors such as pH, temperature and micropollutant concentrations as well as side reactions consuming HO<sup>•</sup> (Oturán & Aaron 2014). Nonetheless, ease of operation is one of the main advantages of ozonation and the peroxone process. The removal efficiency of specific pollutants such as EDCs by ozonation and peroxone process depends on the presence of many inorganic and organic compounds in water and/or wastewater.

The aim of this study is to evaluate the removal of EDCs with ozone and peroxone processes from different wastewater samples, which are (i) municipal WWTP effluent (WWTP-A; advanced biological wastewater treatment), (ii) textile industry WWTP effluent (WWTP-B; biological treatment), (iii) organized industrial zone (OIZ) WWTP effluent (WWTP-C; chemical and biological treatment) and (iv) pharmaceutical industry discharge. The goals were to evaluate and compare the efficiency of ozonation and peroxone processes for (i) the degradation of a broad range of EDCs in WWTP effluents and (ii) to determine the feasibility of these advanced treatments in terms of operating costs.

## MATERIALS AND METHODS

### WWTPs surveyed and sampling procedure

The effluents of three different WWTPs (WWTP-A, WWTP-B, WWTP-C) were monitored for their EDC concentrations over one year, and a discharge channel (DC) of a pharmaceutical manufacturing facility was chosen as the fourth sampling point. Wastewater samples taken during a spring sampling campaign were subjected to experimental studies to elucidate the level of EDC removal achieved by ozonation and peroxone oxidation. WWTP-A, with a capacity of 25,000 m<sup>3</sup>/day, was designed to treat municipal wastewater and operated for biological nitrogen and phosphorus removal. WWTP-B, receiving a flow of 220 m<sup>3</sup>/day industrial wastewater from a textile

finishing mill, was comprised of a conventional activated sludge process as a secondary treatment. WWTP-C was built for an equivalent population of 100,000 in an OIZ with over 200 establishments primarily involved in the metal and chemical industry sectors. Wastewaters originating from pharmaceutical manufacturing processes were initially directed to the DC, and subsequently treated in an OIZ WWTP, having a conventional activated sludge system. Spring sampling, which was used for tertiary treatment studies, was launched in April 2018 under dry weather conditions. All wastewater samples were collected in pre-rinsed amber glass bottles and kept refrigerated during transportation to the laboratory, where they were stored at 4 °C until undergoing experimental analysis.

### Experiments of O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment

Experiments were conducted in a 1-L capacity borosilicate glass column (internal diameter of 5 cm, height of 1 m) in a semi-batch mode. Ozone was produced using a laboratory-scale ozone generator (Sabor Electronic Ozone Systems, SE-5 Model) equipped with an oxygen concentrator. The outlet gas (i.e. the ozone-oxygen mixture) was introduced at the bottom of the reactor through a sintered-glass-plate diffuser. Excess gaseous ozone passing through the column was collected in two gas washing bottles connected in series and filled with 2% potassium iodide solution. Both the concentration of ozone gas provided by the ozone generator and the residual ozone in the exit gas from the reaction vessel were determined by iodometric titration (*Standard Methods 2017*). The utilized (consumed) ozone dose after each experimental run was calculated by subtracting the exhausted ozone from the amount of total applied ozone.

The removal of EDCs detected in the investigated wastewater samples was evaluated by testing two different inlet dosages of ozone (12 and 92 mg O<sub>3</sub>/L). Hydrogen peroxide dosages for peroxone tests were maintained at H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> molar ratio of 0.5 throughout the studies according to the related scientific literature (*Acero & von Gunten 2001*; *Pocostales et al. 2010*; *Meshref et al. 2017*). To investigate the effect of contact time on the abatement rate of each EDC, the feeding period was fixed at 5 and 10 min for ozonation, where shorter exposure times (namely, 3 and 5 min) were preferred for peroxone application. The bench-scale experiments were carried out at room temperature (20 ± 2 °C) and two replicates were performed for each operating condition.

### Sample pretreatment and analysis

EDC analysis was performed with liquid chromatography (LC)-mass spectroscopy (MS)/MS, gas chromatography (GC)-MS/MS, GC/MS and inductively coupled plasma (ICP)-MS techniques according to *Standard Methods (2017)* and developed in-house methods. The details of analysis can be found as Supporting Information.

## RESULTS AND DISCUSSION

### Composition of EDCs in wastewater samples

Concentrations of the target compounds fluctuated greatly from the limit of detection (LOD) to thousands of ng/L since they belong to various groups of EDCs displaying different physicochemical properties such as cyclodien pesticides, dichlorodiphenyltrichloroethanes (DDTs), phthalates, polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Phthalates (4 of the 17 detected EDCs) were the major contaminants yielding 48% of the total concentration of detected target analytes according to monitoring of EDCs present in the secondary effluent taken from WWTP-A (municipal). At this sampling site, four kinds of phthalates were measured, of which the contamination level of di-sec-octylphthalate (DEHP – DOP) was the highest, closely followed by mono-2-ethylhexylphthalate (MEHP) and di-cyclohexylphthalate (DCHP). PAHs were the second major contaminant group exerting 30% contribution of the total EDC content (8 compounds) which was calculated as the sum of the determined concentrations of individual target compounds. Octamethylcyclotetrasiloxane (D4) was identified as the main compound among 16 EDCs in the effluent obtained from WWTP-B (textile), constituting 44% of the total EDC level. EDCs were also dominated by 4 different PAHs (especially naphthalene) and 8 members of phthalate group, accounting for 24 and 18% of the total EDC concentration, respectively. EDC analysis performed on WWTP-C (OIZ) effluent revealed that PAHs (9 of the 28 EDCs, particularly naphthalene) were clearly the dominant compounds, corresponding to 81% of the effluent EDC content. For the DC of the pharmaceutical facility (WWTP-D), phthalates were found as the main contributors to the total EDC concentration (61%) with 8 compounds out of 19 detected EDCs while octamethylcyclotetrasiloxane (D4) (18%) and PAHs (with 5 compounds, mainly, benzo[b]fluoranthene) (14%) similarly appeared as the other significant substances.

## Removal of EDCs by ozonation process

The samples collected from each site were subjected to ozonation at varying doses (namely, Dose 1: 12 mg O<sub>3</sub>/L and Dose 2: 92 mg O<sub>3</sub>/L) and periods (i.e. 5 and 10 min) to elucidate the effect of inlet dosage of ozone and contact time on the elimination efficiency of each target compound detected. For WWTP-C effluent, more than 95% of the ozone generated was consumed at each operating condition. Likewise, almost all ozone was used when the dose was set as 12 mg O<sub>3</sub>/L for the remaining samples; but ozonation application with an inlet dosage of 92 mg O<sub>3</sub>/L resulted in a decrease of ozone consumption ratio to 25–35% range. The experimental data depicted in Figure 1 indicated that the degradation rates of EDCs achieved by ozonation varied considerably depending on the types of the investigated compounds. However, it should be noted that the removal efficiencies were limited to the ratio of the monitored concentration of the relevant EDCs over their LOD levels. Thus, the treatment efficiency evaluations have been made according to the achievable maximum removal rate of each particular EDC. Within this context, target substances were grouped based on the comparison of their removal efficiency to their achievable maximum removal rate (AMRR), as (i) efficiently removed (>80% of AMRR), (ii) moderately removed (from 40 to 80% of AMRR), and (iii) slightly removed (<40% of AMRR). AMRR values of each individual EDC are available as Supporting Information.

As visualized in Figure 1(a), ozonation of WWTP-A effluent provided elimination levels exceeding 80% of AMRR for 10 of the tested 17 compounds (anthracene, acenaphthylene, fluoranthene, fluorene, pyrene, mono-2-ethylhexylphthalate (MEHP), di-cyclohexylphthalate (DCHP), di-sec-octylphthalate (DEHP – DOP), 4-nitrotoluene and resorcinol) even at a lower dose of 12 mg O<sub>3</sub>/L. Nearly complete removal of gestodene could be achieved at the higher ozone dose. Independent of the operating conditions adopted, only acenaphthene out of 17 single substances was slightly removed.

Experimental findings shown in Figure 1(b) confirmed that benzo(g,h,i)perylene, mono-n-butylphthalate, di-n-octyl phthalate (DnOP), benzylbutylphthalate (BBP), 4-nitrotoluene, mirex and saccharin exhibited high abatement rates among 16 individual pollutants. More than 80% degradation was also obtained for mono-2-ethylhexylphthalate (MEHP), di-cyclohexylphthalate (DCHP), diethylphthalate (DEP), di-sec-octylphthalate (DEHP – DOP) and octamethylcyclotetrasiloxane (D4) under experimental conditions of 5 min Dose-1. For the ozonated WWTP-B effluent, slightly

removed compounds included naphthalene and di-n-butylphthalate (DBP).

Results presented in Figure 1(c) disclosed that ozonation proved to be moderately effective in removing the target analytes of the WWTP-C effluent since 9 of the 28 examined EDCs reached more than 80% of AMRR degradation (PCB52, nonylphenol, octylphenol, diethylphthalate (DEP), dimethyl phthalate, hexachlorobenzene (HCB), vinclozolin, drospirenone and dutasteride). Implementation of the ozonation process at the elevated dosage of 92 mg O<sub>3</sub>/L still reflected minor removal characteristics for 2 substances; namely, phenanthrene and di-n-butylphthalate (DBP). For octamethylcyclotetrasiloxane (D4), no removal was observed under all operating conditions tested.

Evaluating the outcomes illustrated in Figure 1(d), it can be stated that ozonation was extremely efficient at removing benzo[b]fluoranthene, chrysene, fluoranthene, mono-2-ethylhexylphthalate (MEHP), mono-n-butylphthalate, di-cyclohexylphthalate (DCHP), benzylbutylphthalate (BBP), endosulfan (alpha), endosulfan (beta), o-phenylphenol and drospirenone when the DC of the pharmaceutical facility served as the sampling site. Raising the inlet dosage of ozone, and thus increasing the amount of utilized ozone achieved an elimination degree of more than 80% of AMRR for di-n-octyl phthalate (DnOP) and letrozole. Three out of 19 compounds were classified as slightly removed due to their abatement rates being below 40% (naphthalene, phenanthrene, diethylphthalate (DEP)). Similar to the ozonation of WWTP-C effluent, no removal was determined for octamethylcyclotetrasiloxane (D4) because of its ozone-refractory character.

## Removal of EDCs by peroxone process

Figure 2 summarizes the data extracted from peroxone experiments conducted at two different ozone doses (Dose 1: 12 mg O<sub>3</sub>/L and Dose 2: 92 mg O<sub>3</sub>/L) and reaction periods (i.e. 3 and 5 min). As aforementioned, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> molar ratio of 0.5 was used for all peroxone experiments. Similar to ozonation experiments, all the applied ozone was consumed for WWTP-C effluent at each investigated operating condition. For Dose-1, applied ozone was utilized, whereas 35–50% ozone consumption was realized for Dose-2 for the rest of the samples. As illustrated in Figure 2, a broad spectrum of removal efficiencies was observed for the EDCs present in the samples. This was an expected result since the treatment efficiency is highly dependent on the investigated wastewater matrix, and also on the types of the EDCs.

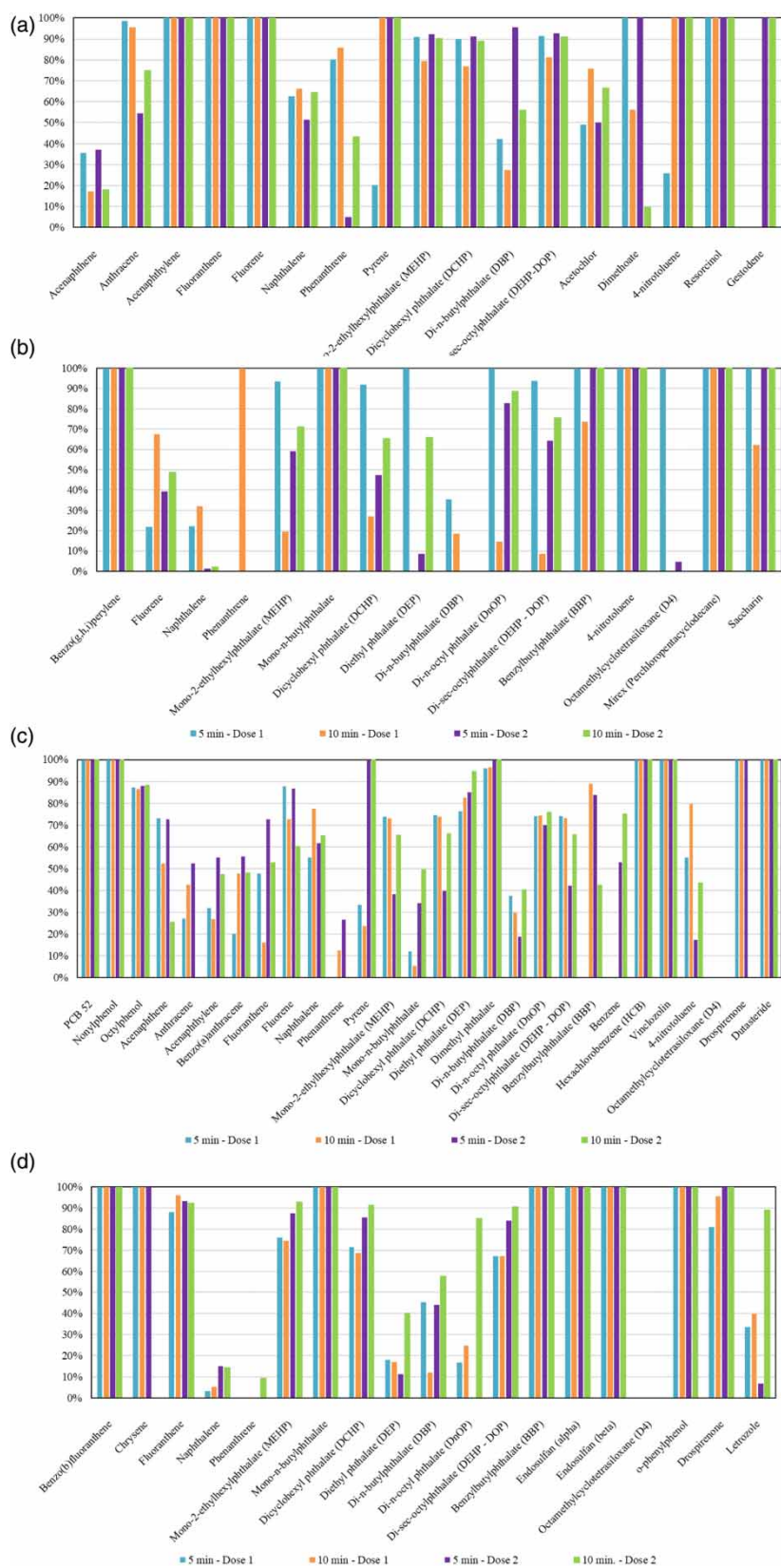


Figure 1 | Treatment efficiencies of EDCs after ozonation for (a) WWTP-A, (b) WWTP-B, (c) WWTP-C, (d) pharmaceutical DC based on achievable maximum removal rate.

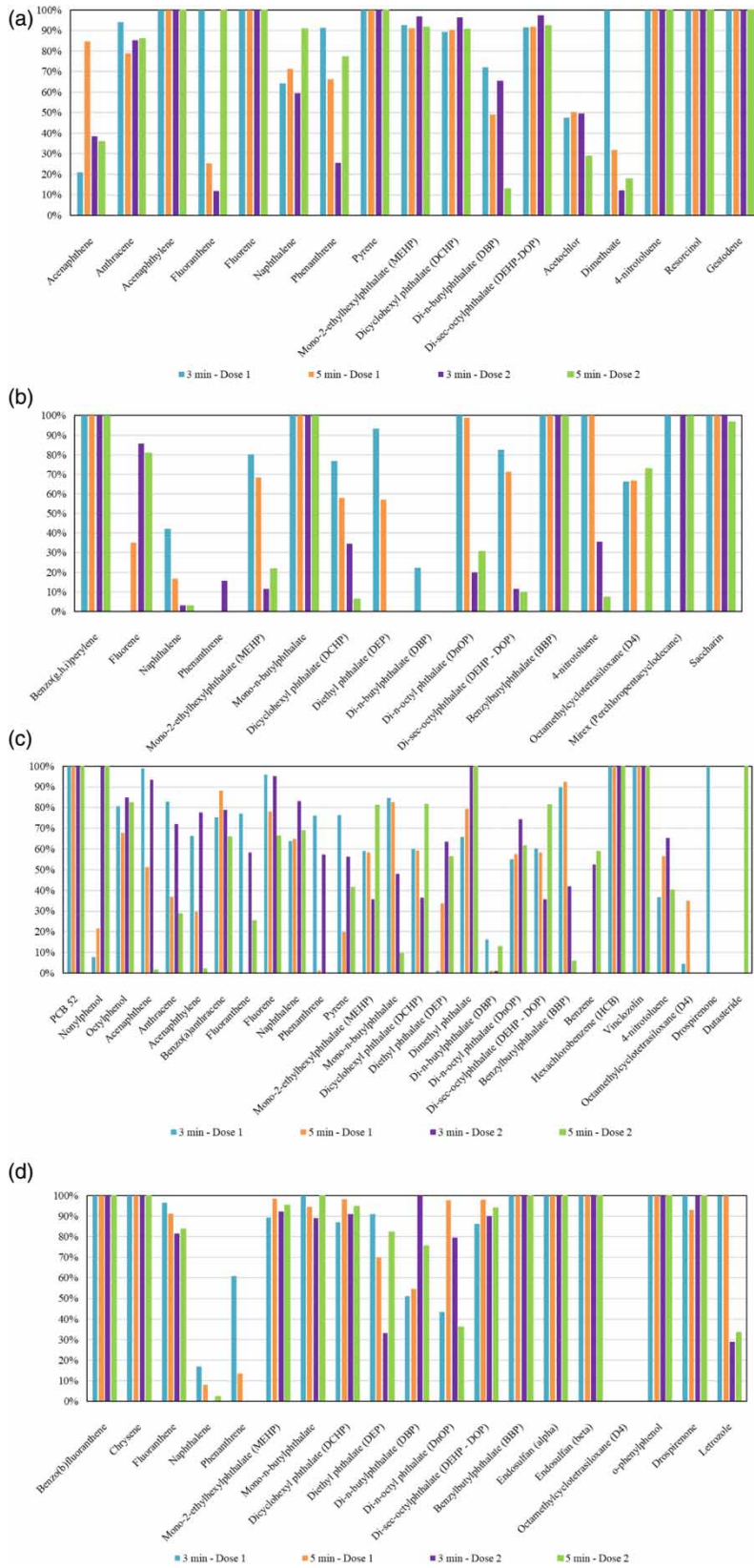


Figure 2 | Treatment efficiencies of EDCs after peroxone process for (a) WWTP-A, (b) WWTP-B, (c) WWTP-C, (d) pharmaceutical DC based on achievable maximum removal rate.

Results of the peroxone experiments conducted on WWTP-A (Figure 2(a)) showed that anthracene, acenaphthylene, fluorene, pyrene, mono-2-ethylhexylphthalate (MEHP), di-cyclohexylphthalate (DCHP), di-sec-octylphthalate (DEHP – DOP), 4-nitrotoluene, resorcinol and gestodene were removed  $\geq 80\%$ . On the other hand, the removal efficiencies varied for some EDCs and no correlation was evident between the treatment condition and the removal rate. For example, acenaphthene was removed higher than 80% at 3 min peroxone application for Dose-1 while all other conditions were kept the same; the abatement rates were found to be lower than 40%. Similar results were observed for dimethoate (only  $\geq 80\%$  removal with 3 min peroxone application for Dose-1). High removal efficiencies were also observed for fluoranthene during the peroxone experiments at 3 minute Dose-1 and 5 minute Dose-2.

As can be seen from Figure 2(b), the only EDCs that were removed with efficiency higher than 80% of AMRR were benzo(g,h,i)perylene, mono-n-butylphthalate, benzylbutylphthalate (BBP), mirex (at all doses except 5 min Dose-1) and saccharin. Three EDCs remained degraded  $\leq 40\%$  of AMRR at all conditions. These were naphthalene, phenanthrene and di-n-butylphthalate (DBP). Fluorene was removed  $\geq 80\%$  for Dose-2 whereas  $\leq 40\%$  efficiencies were achieved for Dose-1. On the contrary,  $\geq 80\%$  and  $\leq 40\%$  di-n-octyl phthalate (DnOP) removals were observed for Dose-1 and Dose-2, respectively. A similar removal pattern was also evident for 4-nitrotoluene. It is interesting to note that increasing the ozone dosage and treatment time decreased the di-cyclohexylphthalate (DCHP) removal efficiency from  $\approx 80\%$  to  $\approx 10\%$  for the peroxone process.

In the case of WWTP-C, the lower degradation ( $< 40\%$ ) with the peroxone process was seen for di-n-butylphthalate (DBP) and octamethylcyclotetrasiloxane (D4) (Figure 2(c)). Around and/or higher than 80% removal rates were observed for PCB52, octylphenol, benzo(a)anthracene, fluorene, dimethyl phthalate, hexachlorobenzene (HCB) and vinclozolin. The EDCs that were removed  $\geq 80\%$  at least for two treatment conditions were nonylphenol (Dose-2, 3 and 5 min), fluorene (Dose-1, 3 min and Dose-2, 3 min), acenaphthene (Dose-1, 3 min and Dose-2, 3 min), mono-n-butylphthalate (Dose-1, 3 and 5 min) and benzylbutylphthalate (BBP) (Dose-1, 3 and 5 min). Similarly, it is important to point out that no correlation was recognised between the removal efficiencies of EDCs and the operating conditions of the peroxone process.

The peroxone process could degrade benzo[b]fluoranthene, chrysene, fluoranthene, mono-2-ethylhexylphthalate

(MEHP), mono-n-butylphthalate, di-cyclohexylphthalate (DCHP), di-sec-octylphthalate (DEHP – DOP), benzylbutylphthalate (BBP), endosulfan (alpha), endosulfan (beta), o-phenylphenol and drospirenone in pharmaceutical manufacturing facility effluent at all conditions investigated. More than 80% of AMRR degradation was also achieved for letrozole under experimental conditions of 3 min Dose-1 and 5 min Dose-1. The phthalates, including diethylphthalate (DEP), di-n-butylphthalate (DBP) and di-n-octyl phthalate (DnOP), were also removed  $\geq 80\%$ ; however, no relationship was evident between the removal efficiencies and applied treatment conditions. One of the 19 EDCs detected in this wastewater was degraded by less than 40% of AMRR, which was naphthalene. Besides, phenanthrene was removed by 60% for 3 min Dose-1 application while limited/no removal was achieved for the other conditions investigated.

### Comparative evaluation of EDCs removal by ozonation and peroxone processes

Experimental results obtained in this study show that the removal efficiencies of EDCs are highly dependent on the wastewater matrix as well as on the type of EDCs. Some persistent organic pollutants group members such as phthalates and PAHs, in addition to compounds like octamethylcyclotetrasiloxane (D4), have been determined to be recalcitrant in terms of ozonation and peroxone processes in several wastewater matrices. The impact of the wastewater matrix is clearly evident when EDC compounds are individually investigated. Naphthalene, for instance, has shown different removal ratios in different effluents although the same process conditions were applied; that is, while moderate removal rates could be achieved in domestic wastewater (WWTP-A effluent) and OIZ effluent (WWTP-C), it was slightly degradable in textile finishing mill (WWTP-B) and pharmaceutical DC effluents.

Ozonation and peroxone processes have also exerted different performances for some cases. Treatment of domestic effluents in WWTP-A present an example for this condition. While acenaphthene has been efficiently removed by peroxone at 5 min Dose-1, it could only be slightly removed by ozonation at the same dose and contact time. EDCs such as acenaphthylene, fluorene, pyrene, 4 nitrotoluene etc. in WWTP-A were completely removed when subjected to peroxone treatment at the lower  $O_3$  dosage (12 mg  $O_3/L$ ) and lower contact time (3 min). By considering the required removal efficiency of a specific EDC and if there is no need for complete removal, it might be possible to shorten the contact time and/or to

lower the applied  $O_3$  dosage, since a shorter contact time and/or lower applied  $O_3$  dosage will reduce the operational costs. In general, the performance of the peroxone process has been proven to be more effective than ozonation, since higher removal rates could be obtained for more EDCs. Nevertheless, the decision of  $H_2O_2$  addition to the ozonation process as an advanced oxidation process application for EDC removal will be made by the operators based on the type and required removal efficiency in addition to the operating costs.

### Operating cost analysis of ozonation and peroxone processes

Since ozone is an unstable gas, it has to be produced on-site where it is going to be used. Generally, electrically powered ozone generators and electrolytic ozone generators are used in ozone production. The most commonly preferred category is the electrically operated ozone generators. In such generators, ozone production in relatively high concentrations and amounts is achieved by passing an oxygen-enriched gas (oxygen or air) through a strong electric field. Due to the intense energy, oxygen molecules present in the gas are broken, and these newly-arisen oxygen atoms combine with oxygen molecules to create ozone ( $O_3$ ) molecules. When air is fed into the electric field, the efficiency of ozone production would be 1–3% in terms of mass, while the same value increases up to 6% in the case of pure oxygen. If oxygen is used as a gas supply in ozone production with electrically powered generators, specific energy consumption of large-scale generators is approximately 10 kW/h for 1 kg ozone. In the case of using air, this value becomes twice as high (Gottschalk *et al.* 2010).

Operating an efficient and cost-effective treatment process is the goal of every successful WWTP. Therefore, pre-process development and scale-up economic analysis must be considered. The two main components of ozone operating costs are energy and oxygen consumption. Use of electricity and/or (liquid) oxygen greatly affects the cost per  $m^3$  of treated effluent. Additionally, ozone consumption is also an important parameter in ozone processes, since it can be correlated to the operating costs. Ozone consumption is defined as the amount of ozone consumed for a given mass of organic carbon content (i.e. chemical oxygen demand) removed. It is expected that the ozone processes will be operated at low ozone consumption values to maximise the ozone utilisation, and thus reduce the operating costs (Tizaoui *et al.* 2007; Xiong *et al.* 2016, 2017). In this work, a simplified economic evaluation of operating costs (the costs of the main reagents and the electricity used)

related with the ozonation and peroxone process is presented. As a basis for the evaluation, the experimental conditions used throughout the present study have been considered. It is assumed that ozone is produced from oxygen using electrically powered generators, these being the most preferred ozone generators in large-scale applications. Based on electricity consumption for producing the two studied ozone dosages, an approximate cost for ozone production was computed. In the calculations, the industrial electrical tariff for unit-price of unit electrical energy (current tariff for single-term low-voltage industry group subscribers, namely 0.063 €/kWh) was used (Energy Map 2018). The electricity cost used in the study was similar to 0.072 €/kWh (0.08 \$/kWh), which was provided by the United States Environmental Protection Agency Water Office (USEPA 2005) for pumps and ozone generation. While making the cost analysis for the peroxone process, the costs of  $H_2O_2$  were also considered along with the ozonation process. In the market, the unit price (included 18% VAT) for technical-quality 50% pure  $H_2O_2$  is 1.86 €/L (Balumcu Kimya 2018). While the same ozone dosages were used in peroxone as in ozonation, contact times of the investigated processes exhibited differences. A constant ratio of  $H_2O_2:O_3$  of 0.5 was taken into account to evaluate the cost analysis of the peroxone process. The calculated costs for ozonation and peroxone applications are included in Table 1.

As presented in the table, the total operating cost for ozonation and peroxone processes ranged from 0.04 to 0.58 €/m<sup>3</sup> and 0.06 to 0.83 €/m<sup>3</sup>, respectively, depending predominantly on the composition of the wastewater matrix to be treated and also to some extent on the capacity of the WWTP.

These data were essentially in agreement with the results of a previous study performed by Baresel *et al.* (2017) who reported an ozonation operating cost varying between 0.03 and 0.17 €/m<sup>3</sup> for a population equivalent up to 100,000 inhabitants. Likewise, data derived from cost analysis fall within the range of values provided by USEPA (2005). In the latter study, the operating costs were found to be 0.07 €/m<sup>3</sup> for an average flow of 20,000 m<sup>3</sup>/day, whereas a flow-rate of only 200 m<sup>3</sup>/day resulted in a 10 fold increase of the operating expenditure. The operating costs for the peroxone process also showed a remarkable similarity to those obtained by Yoon *et al.* (2014), who calculated a figure of 0.33 €/m<sup>3</sup> considering a treatment capacity of 20 m<sup>3</sup>/day and a total operating time of 20 h/day as the design factors. Research studies covering cost analysis of advanced oxidation processes recommend performing pilot-scale tests in order to determine the plant-specific



**Table 1** | Operating costs of ozonation and peroxone processes

Application	Ozone dose (mg O <sub>3</sub> /min)	Contact time (min)	Applied ozone dose (g O <sub>3</sub> /m <sup>3</sup> )	Applied H <sub>2</sub> O <sub>2</sub> dose (g/m <sup>3</sup> )	Consumption of energy (kWh/kg)	Consumption of specific electricity for applied ozone dose (kWh/m <sup>3</sup> )	Price of electricity (€/kWh)	Cost of electricity for applied ozone dose (€/m <sup>3</sup> )	Price of H <sub>2</sub> O <sub>2</sub> (€/m <sup>3</sup> )	Cost of applied H <sub>2</sub> O <sub>2</sub> (€/m <sup>3</sup> )	Total cost (€/m <sup>3</sup> )
	a	b	a × b = c	d	e	c × e = f	g	f × g = h	i	d × i / 0.565 <sup>a</sup> = j	h + j
Ozonation	12	5	60	–	10	0.60	0.065	0.04	–	–	0.04
	12	10	120	–		1.20		0.08			0.08
	92	5	460	–		4.60		0.29			0.29
	92	10	920	–		9.20		0.58			0.58
Peroxone	12	3	36	12.75		0.36		0.02	1.86	0.04	0.06
	12	5	60	21.25		0.60		0.04		0.07	0.11
	92	3	276	97.75		2.76		0.17		0.32	0.49
	92	5	460	163		4.60		0.29		0.54	0.85

<sup>a</sup>The density of H<sub>2</sub>O<sub>2</sub> is 1.13 g/mL. 0.565 g/mL because of 50% purity.

costs (Krishnan *et al.* 2017). The treatment performance and the flow-rate are considered as the major factors affecting the cost (Kommineni *et al.* 2000; Munter 2001; Canizares *et al.* 2009; Mahamuni & Adewuyi 2010). In case of high treatment requirements, the initial investment costs would rise significantly along with operational costs. Additionally, other factors such as the required time for treatment, location of treatment facility, environmental concerns and social pressure over environmental pollution should be taken into consideration while performing the cost analysis (Krishnan *et al.* 2017).

## CONCLUSIONS

The study has been conducted to investigate the removal efficiencies of EDCs with ozone and peroxone processes appearing in different wastewater samples. A wide range of EDC removal efficiencies were obtained for the investigated effluents. It has been observed that while ozone and peroxone processes proved to be highly efficient for one EDC in a wastewater sample, poor removal performances could be achieved in both processes for another effluent sample. These findings definitely verify that the treatment efficiency is powerfully dictated by the wastewater matrix because of the presence of many inorganic and organic compounds. Therefore, the effectiveness of advanced oxidation processes such as ozone and peroxone should be investigated with adequate experimental studies, as exemplified in this study, prior to the design of these processes as tertiary treatment options.

Removal performances of ozone and peroxone were comparable for most of the EDCs present in the wastewater samples, where either of the processes could have more

competence for the same EDC. Consequently, the choice of the process to be implemented should be based on (i) the required removal performance of a specific EDC, (ii) the significance of contact times in the application of the process and (iii) operational cost of the oxidation process.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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