Removal of organophosphate esters from municipal secondary effluent by ozone and UV/H₂O₂ treatments

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ABSTRACT

Organophosphate esters (OPEs) have emerged as a new class of contaminants due to their massive use as flame retardants and plasticizers. These contaminants are toxic to aquatic organisms and some of them are not biodegradable in wastewater treatment plants. This study investigated the degradation kinetics of eight typical OPEs during ozone and UV/H₂O₂ treatments in Milli-Q water, humic acid (HA) solution, and municipal secondary effluent. The studied OPEs included three chlorinated: tris(2-chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP) and tris(dichloropropyl) phosphate (TDCP); two aromatic: triphenyl phosphate (TPhP) and tricresyl phosphate (TCrP); and three aliphatic: tri-n-butyl phosphate (TnBP), tris(2-butoxyethyl) phosphate (TBEP), and tris(2-ethylhexyl) phosphate (TEHP). Results indicate that the degradation of target OPEs conformed to the pseudo-first-order kinetics and UV/H₂O₂ was more effective than ozone for their elimination by comparing the overall removal efficiencies and energy consumptions. Two aromatic and two aliphatic OPEs (i.e., TPhP, TCrP, TnBP and TBEP) were effectively degraded by ozone and UV/H₂O₂ in the test water matrices, while all chlorinated and one aliphatic OPEs (i.e., TCEP, TCPP, TDCP and TEHP) were found to be recalcitrant to oxidation. Moreover, the presence of HA significantly enhanced the degradation of reactive OPEs in ozone treatment.

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1. Introduction

Organophosphate esters (OPEs) are an important class of commercial additives used in flame retardants, plasticizers, hydraulic fluids, lacquers, solvents, extraction agents, antifoam agents, adhesives, and electronic devices [1]. Many of the OPEs are not chemically bonded to the final products, and thus are easily released to the aquatic environment via domestic sewage, industrial wastewater, and rainfall runoff from construction sites and pavements, as well as through the disposal of OPEs-containing materials [2,3].

OPEs cannot be efficiently removed by conventional biological treatment processes in wastewater treatment plants (WWTPs), resulting in their widespread presence in secondary effluents and surface waters at concentrations ranging from ng L⁻¹ to a few hundred µg L⁻¹ [4–6]. Marklund et al. [7] identified tris(2-butoxyethyl) phosphate (TBEP), tris(chloropropyl) phosphate (TCPP) and tri-n-butyl phosphate (TnBP) as the most abundant OPEs at

concentrations ranging from 0.36 to 30 µg L⁻¹ in the effluents of seven Swedish WWTPs. Moreover, chlorinated OPEs including tris(2-chloroethyl) phosphate (TCEP), tris(dichloropropyl) phosphate (TDCP) and TCPP showed an insignificant removal after biological treatment in two German WWTPs and their maximum levels in the effluents were detected to be 0.47, 0.31 and 6.6 µg L⁻¹, respectively [8]. Previous studies revealed that TCEP, TCPP, and TDCP were the most recalcitrant and predominant OPEs in the WWTP effluents [1,9]. Although the impacts of these OPEs on aquatic ecosystems and human health are to be determined, there has been increasing interest in their treatment at sources and in WWTPs.

Advanced treatments, such as ozone and UV/H₂O₂, can achieve significant abatement of many organic micropollutants and thus improve the quality of municipal wastewater effluents [10–12]. Ozone may attack organic compounds through either direct oxidation with molecular ozone or indirect oxidation with highly reactive hydroxyl radicals (·OH) depending on the operating conditions. UV/H₂O₂ is based on the in-situ generation of ·OH, which can unselectively and efficiently oxidize a wide range of

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organic pollutants. Ozone and UV/H₂O₂ treatments are promising technologies because they are able to oxidize micropollutants, transform natural organic matter (NOM), and inactivate pathogens simultaneously [13]. Compared with other advanced treatments such as Fenton's reagent oxidation, membrane filtration and activated carbon adsorption, ozone and UV/H₂O₂ have no requirement for pH adjustment, sludge disposal, membrane backwash, or adsorbent regeneration, thus are commonly applied for water and wastewater treatment [12,14]. In addition, water matrix, especially the type and content of natural organic or inorganic matter, can affect the oxidation of organic pollutants by competing for the oxidant and/or affecting the generation of ·OH [15–17]. However, there is little research concerning the effect of water matrix on the removal of OPEs in ozone and UV/H₂O₂ treatments.

This study aimed to assess the degradation kinetics of eight widely used OPEs in ozone and UV/H₂O₂ treatments. To examine the effect of water matrix on the degradation of target OPEs, bench-scale experiments were conducted with Milli-Q water, humic acid (HA) solution and municipal secondary effluent spiked with the target OPEs at an environmentally relevant concentration (50 µg L⁻¹ each). The energy consumption of ozone and UV/H₂O₂ treatments was also comparatively evaluated based on the overall removal efficiencies of target OPEs. This study helps to better control the release of OPEs from WWTPs to the environment.

2. Materials and methods

2.1. Chemicals

TCEP, TCPP, TDCP, triphenyl phosphate (TPhP), tricresyl phosphate (TCrP), TnBP, TBEP, tris(2-ethylhexyl) phosphate (TEHP), HA sodium salt (Product No. H16752, Lot No. STBD0913V), and ammonium acetate were obtained from Sigma–Aldrich (St. Louis, MO, USA). All the OPE standards were of the highest purity available (≥95%), whose major physico-chemical properties are

summarized in Table 1. The stock solution containing all the studied OPEs was prepared in acetone at a concentration of 1000 mg L⁻¹ and stored in amber glass bottles at –20 °C. H₂O₂ (30%, by weight) was supplied by Panreac (Barcelona, Spain). Milli-Q water was produced by an Advantage A10 water purification system (Millipore, Billerica, MA, USA). High performance liquid chromatography grade acetone and methanol (>99%) were purchased from Merck (Darmstadt, Germany).

2.2. Sample collection and preparation

Ozone and UV/H₂O₂ experiments were performed in three different water matrices: Milli-Q water, HA solution and municipal secondary effluent. The HA solution was prepared and filtered through 0.22 µm filters (Millipore, Billerica, MA, USA) before use, whose characteristics were as follows: TOC = 4.7 mg L⁻¹, COD = 36.6 mg L⁻¹, and pH = 7.3. Municipal secondary effluent was collected from the Gavà-Viladecans WWTP close to Barcelona (Spain). This facility, serving a population of about 172,000 inhabitants, consisted of screen, grit chamber, primary clarifier, conventional activated sludge process, and secondary clarifier. The secondary effluent was transported to laboratory immediately after collection, filtered through 0.22 µm filters to remove suspended solids, and stored in the dark at 4 °C until use. The characteristics of the filtered municipal secondary effluent are shown in Table 2.

2.3. Reaction systems

Ozone experiments were performed in a 2.0 L jacketed glass reactor (inner diameter = 9.6 cm, height = 27.7 cm) with the reaction solution temperature controlled at 20 °C. Ozone gas stream was injected into the reactor through two stainless steel diffusers at a flow rate of 60 L h⁻¹ and with a gaseous ozone concentration of about 10 mg L⁻¹. Detailed description about the ozone treatment system can be found elsewhere [18]. Two ozone analyzers,

Table 1
Major physico-chemical properties of target OPEs.

Compound (acronym)	CAS no.	Molecular formula	Molecular weight	Henry's constant ^a	Solubility ^a (g L ⁻¹)	Log K _{ow} ^a	Structure ^b
Tris(2-chloroethyl) phosphate (TCEP)	115-96-8	C ₆ H ₁₂ Cl ₃ O ₄ P	285.48	5.98	37.06	2.67	
Tris(chloropropyl) phosphate (TCPP)	13674-84-5	C ₉ H ₁₈ Cl ₃ O ₄ P	327.56	5.61	7.65	3.9	
Tris(dichloropropyl) phosphate (TDCP)	13674-87-8	C ₉ H ₁₅ Cl ₆ O ₄ P	430.89	6.97	1.94	4.99	
Triphenyl phosphate (TPhP)	115-86-6	C ₁₈ H ₁₅ O ₄ P	326.29	6.29	0.047	5.6	
Tricresyl phosphate (TCrP)	1330-78-5	C ₂₁ H ₂₁ O ₄ P	368.37	6.16	7.0e–3	7	
Tri-n-butyl phosphate (TnBP)	126-73-8	C ₁₂ H ₂₇ O ₄ P	266.32	3.88	0.40	4.18	
Tributoxyethyl phosphate (TBEP)	78-51-3	C ₁₈ H ₃₉ O ₇ P	398.48	9.31	0.13	3.68	
Tris(2-ethylhexyl) phosphate (TEHP)	78-42-2	C ₂₄ H ₅₁ O ₄ P	434.64	2.41	1.5e–4	8.95	

^a Calculated by ACD/Lab.

^b Predicted by ChemBio Office 2012.

Table 2
Characteristics of filtered municipal secondary effluent.

Parameter	Value	Parameter	Value
TOC (mg L ⁻¹)	7.8	NH ₄ ⁺ (mg L ⁻¹)	13.9
COD (mg L ⁻¹)	28.4	Ca ²⁺ (mg L ⁻¹)	115.4
UV254 (cm ⁻¹)	12.4	Mg ²⁺ (mg L ⁻¹)	52.1
Inorganic carbon (mg L ⁻¹)	66.5	NO ₃ ⁻ (mg L ⁻¹)	24.9
pH	8.2	NO ₂ ⁻ (mg L ⁻¹)	7.35
Turbidity (NTU)	1.99	SO ₄ ²⁻ (mg L ⁻¹)	203.3
Alkalinity (mg L ⁻¹)	325.3	Cl ⁻ (mg L ⁻¹)	624.2

BMT 963 and BMT 964 (BMT Messtechnik, Germany), were installed respectively at the inlet and outlet of the reactor with UV detection at 254 nm. Ozone concentrations digitally displayed by the analyzers were already corrected to the normal temperature and pressure conditions. Each ozone experiment lasted for 120 min. The transferred ozone dose (TOD), defined as the accumulative amount of ozone absorbed by the reaction solution per unit of volume, was calculated based on ozone mass balance as follows:

$$\text{TOD} = \int_0^t \frac{Q_{\text{gas}}}{V_{\text{sol}}} \times ([\text{O}_3]_{\text{in}} - [\text{O}_3]_{\text{out}}) \times dt \quad (1)$$

where Q_{gas} , V_{sol} and t represent the gas flow rate, reaction solution volume and reaction time, respectively; and $[\text{O}_3]_{\text{in}}$ and $[\text{O}_3]_{\text{out}}$ represent the gaseous ozone concentrations at the inlet and outlet of the reactor, respectively.

UV/H₂O₂ experiments were carried out in the same glass reactor with the reaction solution temperature controlled at 25 °C. Three low-pressure mercury lamps (8 W, 26% UVC efficiency, Philips TUV G8T5) emitting 254 nm light, with each protected by a quartz sleeve, were placed equidistantly in the reactor. Detailed information about this device can be found in Souza et al. [19]. By using an actinometrical method [19], an incident photon fluence of $1.49 \times 10^{-5} \text{ E s}^{-1}$ was measured, which corresponded to an average fluence rate of 8.04 mW cm^{-2} in the reactor. The UV lamps were initially warmed up outside the reactor for at least 15 min to ensure a relatively stable output. H₂O₂ was added to the reactor to reach an initial concentration of 20 mg L^{-1} , and then the lamps were inserted into the quartz sleeves to start the irradiation. Each UV/H₂O₂ experiment lasted for 60 min.

The ozone and UV/H₂O₂ experiments were conducted in triplicate with the pH of test water unbuffered. A desired volume of the stock solution (i.e., 100 µL) containing all the target OPEs was spiked into a test water matrix to reach an initial concentration of $50 \mu\text{g L}^{-1}$ for each compound. After the reaction was initiated under magnetic stirring conditions, samples were taken at pre-selected time intervals for OPEs and/or H₂O₂ analysis. The residual ozone in the sample was quenched by NaHSO₃, and the residual H₂O₂ was quenched by catalase or NaHSO₃ depending on the analysis to be performed.

2.4. Analytical methods

Chromatographic separation of the target OPEs was performed on an Acquity ultra performance liquid chromatography system (Waters, Milford, MA, USA) equipped with an Eclipse XDB-C18 column (150 mm × 2.1 mm, 5 µm) (Agilent, Wilmington, DE, USA). The column temperature was maintained at 30 °C and the injection volume was 50 µL. Ammonium acetate in methanol (A, 5 mM) and Milli-Q water (B) were used as the mobile phases with a total flow rate of 0.3 mL min^{-1} . The gradient elution program (time in min, % mobile phase A) was set as follows: (0, 50), (1, 50), (16, 100), (20, 100), (24, 50), and (28, 50). A Triple Quadrupole Detector (Waters, Milford, MA, USA), equipped with an electrospray ionization source and operated in the positive ion mode, was employed to detect the

target OPEs. The MS system was operated under the following conditions: capillary voltage = 3.5 kV, source temperature = 120 °C, desolvation temperature = 350 °C, nitrogen gas flow rate for desolvation = 550 L h^{-1} , cone gas flow rate = 20 L h^{-1} , and argon gas flow rate for collision = 0.19 mL min^{-1} . For each compound, the cone voltage, collision energy (CE), and multiple reaction monitoring mode (MRM) transitions were optimized (Table 3). MassLynx Workstation Software (V4.1, Waters) was employed for both instrument control and data acquisition/analysis. The OPE concentrations in each sample were analyzed in duplicate. In the tested municipal secondary effluent, it was found that all the studied OPEs were below their method detection limits (i.e., 2–60 ng L⁻¹).

OPE standard samples prepared in water at 5 and $50 \mu\text{g L}^{-1}$ were injected at the beginning and the end of each injection sequence to check the instrumental variations. For most of the target OPEs, the percent variation was within the ranges of 0–20% at the $5 \mu\text{g L}^{-1}$ level and 3–15% at the $50 \mu\text{g L}^{-1}$ level, indicating an overall robustness of the method employed. H₂O₂ concentration was determined by the metavanadate spectrophotometric method at 450 nm [20].

3. Results and discussion

3.1. Ozone treatment

The degradation of target OPEs versus TOD during ozone treatment in Milli-Q water, HA solution and municipal secondary effluent is depicted in Fig. 1, and the observed pseudo-first-order rate constants (k , min⁻¹) in the three water matrices are presented in Fig. 2.

In Milli-Q water, ozone reacted with the target OPEs in a selective way. The aromatic and aliphatic compounds (except TEHP) underwent a fast reaction with ozone, while the chlorinated compounds and TEHP were slowly degraded (Fig. 1a). More than 70% of the aromatic and aliphatic compounds were removed at TOD = 9.4 mg L^{-1} , and their reaction rates followed a descending order: TBEP > TPhP > TCrP > TnBP. However, less than 30% of the chlorinated OPEs (TCPP, TDCP, and TCEP) and TEHP were removed even at TOD = 31.2 mg L^{-1} , so they can be considered as ozone recalcitrant compounds.

It is well known that ozone reacts with organic compounds through direct oxidation via molecular ozone and indirect oxidation via ·OH generated from a series of chain reactions of ozone with hydroxide ions [21]. In Milli-Q water, the ozonated solution was slightly acidic (pH varying from 5 to 6), so the indirect pathway was less important. Molecular ozone selectively attacks organic compounds with electron-rich functional groups such as double bonds, aromatic rings, and deprotonated amines [22]. The aliphatic chains bonded to the phosphate of TnBP increased the reactivity toward ozone, and the presence of heteroatoms (O) in the aliphatic chains of TBEP further promoted the direct ozonation. TPhP and TCrP, because of their aromatic rings, were also reactive

Table 3
Optimal MS/MS parameters for target OPEs under MRM positive ionization mode.

Compound	Retention time (min)	Cone voltage (V)	Quantification transition (CE, eV)	Confirmation transition (CE, eV)
TCEP	5.6	30	287 > 99 (25)	287 > 63 (25)
TCPP	9.7	25	327 > 99 (25)	329 > 99 (25)
TDCP	12.1	30	431 > 99 (17)	431 > 209 (17)
TPhP	12.2	45	327 > 152 (30)	327 > 215 (30)
TCrP	15.0	50	369 > 166 (28)	369 > 243 (28)
TnBP	13.4	25	267 > 155 (12)	267 > 99 (12)
TBEP	14.0	35	399 > 199 (15)	399 > 299 (15)
TEHP	19.9	15	435 > 99 (9)	435 > 323 (9)

Fig. 1. Removal of target OPEs during ozone treatment as a function of TOD in different matrices: (a) Milli-Q water; (b) HA solution; and (c) municipal secondary effluent. Error bars represent the standard deviations of triplicate experiments.

toward ozone. These OPEs could be classified as ozone reactive species. Concerning the ozone recalcitrant compounds, the presence of Cl atoms in TCP, TDCP and TCEP and the ramification of the aliphatic chains of TEHP decreased their reactivity toward ozone (Fig. 2).

NOM is ubiquitous in surface and ground waters. As an important component of NOM, humic substances can directly or indirectly react with ozone [23]. When the target OPEs were exposed to ozone in the presence of HA, more than 80% of TBEP, TPhP, TCrP and TnBP were degraded at TOD = 12.2 mg L⁻¹ (Fig. 1b). Compared to the case in Milli-Q water, ozonation in HA solution led to significantly faster degradation rates of the reactive OPEs and the degradation rates of TBEP, TPhP, TCrP, and TnBP were also increased by 21%, 37%, 70%, and 42%, respectively (Fig. 2). Ozonation of HA could inherently lead to considerable ·OH production as a result of the reactions between ozone and the electron-rich moieties of HA

[24]. Nevertheless, the produced radicals had little impact on the removal of the recalcitrant OPEs because they were preferentially consumed by the reactive OPEs. Therefore, the removal efficiencies of TCP, TDCP, TCEP and TEHP were only 32%, 35%, 22%, and 33%, respectively, at TOD = 123.1 mg L⁻¹.

As shown in Figs. 1c and 2, the degradation rates of target OPEs in municipal secondary effluent were relatively lower than those in Milli-Q water and in HA solution, except TEHP. TBEP, TPhP, and TCrP were totally removed at TOD = 50.3 mg L⁻¹, while a total removal of TnBP needed a higher TOD value of 72.2 mg L⁻¹. The removal of chlorinated OPEs was less than 20% at the end of the reaction. As mentioned above, ozone reaction is highly dependent on the solution pH. The original pH of the municipal secondary effluent was 8.2 and then remained above 8.0 during the ozonation treatment. Therefore, both the direct oxidation via molecular ozone and the indirect oxidation via ·OH would account for the OPEs removal. Note that there were various ions existing in the municipal secondary effluent, including Cl⁻, SO₄²⁻, HCO₃⁻, and NO₃⁻ (Table 2), which could act as radical scavengers. More importantly, the effluent organic matter (EfOM) could also react with molecular ozone and ·OH, thus considerably impacting the degradation of target OPEs. EfOM is a complex mixture of NOM, soluble microbial products and organic micropollutants, which consists of both dissolved and colloidal organic compounds [25]. EfOM was reported to be the main ·OH scavenger in municipal secondary effluents, due to its moderate reactivity toward ·OH and its relatively high concentration [26,27]. The removal of most of the target OPEs was inhibited because of the complex matrix materials present in the municipal secondary effluent (e.g., EfOM, CO₃²⁻, HCO₃⁻) that could compete for ozone and ·OH [28]; however, the removal of TEHP was enhanced notably through some unknown mechanisms.

3.2. UV/H₂O₂ treatment

The degradation of target OPEs during UV/H₂O₂ treatment in Milli-Q water, HA solution and municipal secondary effluent is shown in Fig. 3, and the observed pseudo-first-order rate constants (*k*, min⁻¹) in the three water matrices are summarized in Fig. 4. Our preliminary experiment had shown that direct UV photolysis for 15 min (UV fluence = 7200 mJ cm⁻²) could remove 100% of the aromatic TPhP and TCrP, 40% of TBEP and 18% of TnBP, but the removal of the chlorinated compounds and TEHP was negligible.

Fig. 2. Comparison of the pseudo-first-order rate constants for the degradation of target OPEs by ozone treatment in different matrices. Error bars represent the standard deviations of triplicate experiments.

Fig. 3. Removal of target OPEs during UV/H₂O₂ treatment as a function of H₂O₂ consumption in different matrices: (a) Milli-Q water; (b) HA solution; and (c) municipal secondary effluent. Error bars represent the standard deviations of triplicate experiments.

The reactivity of target OPEs exhibited a similar trend in UV/H₂O₂ to that in ozonation, that is, the recalcitrant OPEs still had relatively lower degradation rates (Fig. 3). In Milli-Q water, the reactive OPEs (TPhP, TCrP, TBEP, and TnBP) were rapidly removed in the first 2 min (H₂O₂ consumption = 0.7 mg L⁻¹) (Fig. 3a), which was primarily ascribed to the indirect oxidation of ·OH although direct UV photolysis also made a certain contribution as mentioned above. The electron-rich aromatic rings of TPhP and TCrP were readily attacked by ·OH, and the heteroatoms (O) in the aliphatic chains of TBEP also increased the reactivity toward ·OH [29]. To the contrary, the presence of Cl atoms in the aliphatic chains of chlorinated OPEs significantly reduced the reactivity toward ·OH.

Fig. 4. Comparison of the pseudo-first-order rate constants for the degradation of target OPEs by UV/H₂O₂ treatment in different matrices. Error bars represent the standard deviations of triplicate experiments.

In particular, TDCP, with the highest degree of chlorination, had the lowest degradation rate among the chlorinated OPEs. TEHP was still the least degradable, probably because of the steric effect of its long and ramified chains. After 1 h reaction, the removal efficiencies of the recalcitrant TCPP, TDCP, TCEP, and TEHP were 97%, 84%, 91% and 74%, respectively (Fig. 3a).

The degradation of target OPEs was notably inhibited in HA solution, as compared to the results obtained in Milli-Q water (Figs. 3b and 4). The reactive OPEs were removed by more than 90% in the first 10 min (H₂O₂ consumption = 2.3 mg L⁻¹); while after 1 h reaction, the recalcitrant TCPP, TDCP, TCEP and TEHP were only removed by 72%, 53%, 61% and 65%, respectively. On the one hand, UV irradiation of HA may produce ·OH and other secondary oxidants to enhance the removal of organic pollutants [30]; on the other hand, the removal of organic pollutants may be inhibited because HA competes for not only UV light against H₂O₂ but also ·OH against target pollutants [15,31]. In this study, the inhibitory effect of HA seemed to dominate in the degradation of target OPEs by UV/H₂O₂.

As shown in Figs. 3c and 4, the removal efficiencies of target OPEs in the municipal secondary effluent were generally comparable to those in HA solution. The aromatic OPEs were rapidly removed in the first 5 min (H₂O₂ consumption = 1.7 mg L⁻¹); the aliphatic TBEP and TnBP needed 6.7 and 10.1 mg L⁻¹ of H₂O₂ consumption to reach a total removal, respectively; and the chlorinated OPEs were removed by less than 55% at the end of the reaction. Similar to HA, the complex matrix materials in the municipal secondary effluent could compete for UV light and ·OH to inhibit the degradation of target OPEs. Again, it is noted that the degradation of TEHP in the municipal secondary effluent was faster than in HA solution, which is similar to that observed in ozone treatment.

3.3. Energy consumption

The energy consumption for ozone and UV/H₂O₂ treatments in the municipal secondary effluent was calculated and compared. The electrical cost in Barcelona (Spain) was 0.125 € kW h⁻¹ (February 2014). The H₂O₂ consumption cost was also considered and the cost of the laboratorial H₂O₂ was 5 € kg⁻¹ (30%, by weight). Table 4 shows the electrical energies of UV and ozone together with the H₂O₂ cost to treat each cubic meter of municipal secondary effluent with different reaction times. For example, for ozonation with a reaction time of 10 min, the total treatment cost was 0.344 € m⁻³. The removal of the reactive TBEP, TCrP, TPhP, and

Table 4Energy consumption for the degradation of target OPEs during ozone and UV/H₂O₂ treatments in municipal secondary effluent.

Treatment	Reaction time (min)	Ozone energy cost (€ m ⁻³)	UV dose (mJ cm ⁻²)	UV energy cost (€ m ⁻³)	H ₂ O ₂ cost (€ m ⁻³)	Total cost (€ m ⁻³)	OPEs removal
Ozone	5	0.171				0.171	TEHP < 10%; TDCP, TCPP, TCEP < 1%; TBEP: 48%; TCrP: 67%; TPhP: 61%; TnBP: 39%
Ozone	10	0.344				0.344	TEHP: 10%; TDCP, TCPP, TCEP < 1%; TBEP: 77%; TCrP: 86%; TPhP: 79%; TnBP: 57%
Ozone	30	1.031				1.031	TEHP: 56%; TDCP, TCPP, TCEP < 5%; TBEP: 97%; TCrP: 97%; TPhP: 96%; TnBP: 81%
UV/H ₂ O ₂	5		2412	0.125	0.0169	0.1414	TEHP, TDCP, TCPP, TCEP ≤ 12%; TBEP: 65%; TCrP: 98%; TPhP: 97%; TnBP: 49%
UV/H ₂ O ₂	10		4824	0.25	0.029	0.279	TEHP, TDCP, TCPP, TCEP ≤ 21%; TBEP: 80%; TCrP: 100%; TPhP: 99%; TnBP: 67%
UV/H ₂ O ₂	15		7236	0.375	0.0543	0.4293	TEHP: 40%; TDCP, TCPP, TCEP < 20%; TBEP: 92%; TCrP: 100%; TPhP: 100%; TnBP: 82%
UV/H ₂ O ₂	30		14472	0.75	0.1123	0.8623	TEHP: 46%; TDCP, TCPP, TCEP ≤ 30%; TBEP: 100%; TCrP: 100%; TPhP: 100%; TnBP: 97%

TnBP varied from 57% to 86%, while the removal of the recalcitrant TEHP, TDCP, TCPP and TCEP were almost negligible (<10%). For UV/H₂O₂ with a reaction time of 10 min, the total treatment cost was 0.279 € m⁻³. The reactive OPEs were removed by 67–100%, while the recalcitrant OPEs were removed by 9–21%. Therefore, UV/H₂O₂ appeared to be more efficient than ozone in regard to the removal of OPEs in the municipal secondary effluent.

In addition, it is seen that the cost for ozone generation or UV irradiation occupied a primary portion of the total cost in ozone and UV/H₂O₂ treatments, respectively. Although this economical assessment is quite simple and does not consider other operation and maintenance costs, it provides some practical considerations about the OPEs removal by ozone and UV/H₂O₂ treatments in municipal secondary effluent.

4. Conclusions

Advanced treatments (ozone and UV/H₂O₂) were evaluated for the degradation of eight widely used OPEs at an environmental relevant concentration (50 µg L⁻¹ each) in Milli-Q, HA solution, and municipal secondary effluent. The degradation of target OPEs followed the pseudo-first-order kinetics, and UV/H₂O₂ exhibited better performance than ozone in terms of removal efficiency and energy consumption. The aromatic TPhP and TCrP as well as the aliphatic TBEP and TnBP were rapidly degraded by ozone and UV/H₂O₂, while the chlorinated TCPP, TDCP and TCEP together with the ramified aliphatic TEHP were more recalcitrant to oxidation. Compared to that in Milli-Q water, the presence of HA significantly enhanced the degradation of reactive OPEs in ozone treatment, but an opposite trend was observed in UV/H₂O₂ treatment. Because a significant part of the recalcitrant OPEs still remained in the municipal secondary effluent after ozone or UV/H₂O₂ treatment, further study is required to develop more effective treatment processes, identify major degradation byproducts, and determine the solution toxicity variation.

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