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# Ozone membrane contactor for tertiary treatment of urban wastewater: Chemical, microbial and toxicological assessment

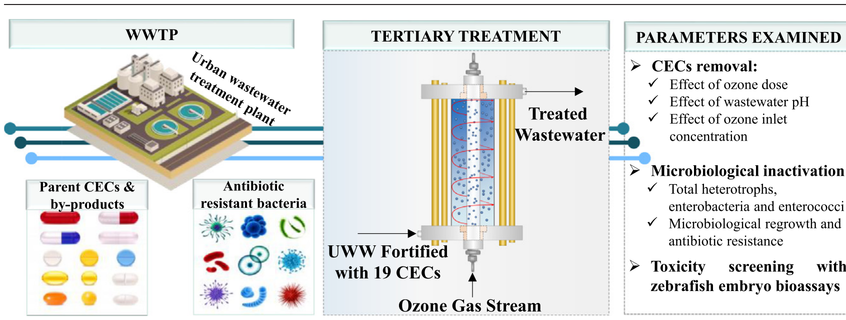
Pedro H. Presumido [a,b,c], Sara Ribeirinho-Soares [b,d], Rosa Montes [e], José Benito Quintana [e], Rosario Rodil [e], Marta Ribeiro [f], Teresa Neuparth [f], Miguel M. Santos [f,g], Manuel Feliciano [c], Olga C. Nunes [b,d], Ana I. Gomes [b,d], Vítor J.P. Vilar [a,b,*]

[a] Laboratory of Separation and Reaction Engineering, Laboratory of Catalysis and Materials (LSRE-LCM), Chemical Engineering Department, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] Associate Laboratory in Chemical Engineering (ALiCE), Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[c] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[d] Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE), Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[e] Department of Analytical Chemistry, Nutrition and Food Sciences, Institute of Research on Chemical and Biological Analysis (IAQBUS), Universidade de Santiago de Compostela, Constantino Candeira S/N, 15782 Santiago de Compostela, Spain
[f] CIMAR/CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Group of Endocrine Disruptors and Emerging Contaminants, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal
[g] FCUP – Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

## HIGHLIGHTS

- Effective technology for tertiary treatment of UWW by ozone-based processes
- $O_3$ smart-dosing through the membrane pores creating innumerable microbubbles
- 80 % removal or <LQ for 13 of the 19 target CECs but PFAS and melamine persisted
- High disinfection ability and antibiotic-resistant bacteria reduction
- No toxic effects for a dilution factor of 4 after $O_3$ and 2 after $O_3$ + GAC

## GRAPHICAL ABSTRACT

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## ABSTRACT

A membrane ozone contactor, operated under continuous mode, was applied to promote the tertiary treatment of urban wastewater (UWW), targeting the removal of contaminants of emerging concern (CECs), bacterial disinfection, and toxicity reduction. This system relies on the homogeneous radial distribution of ozone ($O_3$) in the reaction zone by "titration" through a microfiltration borosilicate tubular membrane, while the UWW swirls around the membrane and drags the $O_3$ microbubbles generated in the membrane shell-side. The membrane is coated with titanium dioxide ($TiO_2$-P25) and radiation can be externally supplied via four UV lamps. The ozonation tests were carried out with secondary-treated UWW collected in different seasons (winter and summer) and spiked with a mix of 19 CECs (10 μg $L^{-1}$ each). For an $O_3$ dose of 18 g $m^{-3}$, the best performance was obtained by increasing the $O_3$ concentration (maximum $[O_3]_{G,inlet}$ of 200 g $Nm^{-3}$) and decreasing the gas flow rate (minimum $Q_G$ of 0.15 $Ndm^3$ $min^{-1}$), providing the highest ozone transfer yield (88 %) and, thus higher specific ozone dose (g $O_3$ per g dissolved organic carbon). Under these conditions, removals >80 % or concentrations below the limit of quantification were obtained for up to 13 of the 19 CECs and reductions up to 5 log units for total heterotrophs and below the limit of detection for enterobacteria and enterococci. Tests including a UVC dose of 0.10 kJ $L^{-1}$ enhanced disinfection ability but had no

* Corresponding author at: Laboratory of Separation and Reaction Engineering, Laboratory of Catalysis and Materials (LSRE-LCM), Chemical Engineering Department, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
*E-mail address:* vilar@fe.up.pt (V.J.P. Vilar).

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impact on CECs oxidation. After ozonation, the abundance of antibiotic resistant bacteria was reduced but not eliminated, and microbial regrowth after 3-day storage was observed. No toxic effect was detected on zebrafish embryos using a dilution factor of 4 for the ozonized UWW and when granular activated carbon adsorption was subsequently applied the dilution factor decreased to 2.

## 1. Introduction

In recent years, several efforts have been made to modernize the tertiary treatment of wastewater treatment plants (WWTPs) in order to improve the quality of the final effluents discharged and, consequently, prevent the dissemination of contaminants of emerging concern (CECs) and potentially harmful bacteria (i.e., antibiotic-resistant bacteria (ARB) and antibiotic-resistance genes (ARGs)) in the environment (Rizzo et al., 2020; Rizzo et al., 2019). Moreover, the United Nations reported that around 1.2 billion people live in areas affected by severe water scarcity conditions (United Nations, 2014), while the European Parliamentary Research Service estimates that at least 11 % of the population and 17 % of the territory of the European Union have been affected by water scarcity (European Parliamentary Research Service (EPRS), 2022). Therefore, alternative water sources to conventional ones, such as the reuse of urban wastewater (UWW), arise as an option that can contribute to solving the problem of water scarcity (López-Vinent et al., 2020). For this purpose, reclaimed UWW must follow quality guidelines for its use and be adequate in terms of public health and environmental protection (Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse, 2020), particularly with regard to the removal of CECs (such as pesticides, pharmaceuticals, illicit drugs, synthetic and natural hormones, personal care products) and ARB&ARGs. In this sense, and in line with the Circular Economy Action Plan, the European Commission recently published a proposal for the new Urban Wastewater Treatment Directive (UWWTD) (European Commission, 2022) targeting new standards and limit values, including new requirements for CECs abatement in WWTPs, and focusing on promoting the widespread reuse of treated UWW.

The intrinsic poor biodegradability of many CECs places a cap on how well they can be removed using standard biological treatments (Krzeminski et al., 2019). As a result, advanced treatment technologies, such as advanced oxidation processes (AOPs), ozonation, membrane filtration, and adsorption using activated carbon (Rizzo et al., 2019), are needed. In order to maximize the removal of the broadest range of CECs, the current trend entails merging or integrating technologies. This is done by utilising the advantages of each technology while minimizing the drawbacks of each one. It has been demonstrated that the application of AOPs (e.g., $H_2O_2$/UV, $O_3$/UV, $O_3$/UV/$H_2O_2$, UV/$H_2O_2$/$TiO_2$, persulfate AOPs, photo-Fenton, electrolysis/Fenton, electro-oxidation) is effective against bacteria and other microorganisms, toxic and persistent organic compounds (Vilar et al., 2020; Castellanos et al., 2020; Díaz-Angulo et al., 2021; Alfonso-Muniozguren et al., 2021; Castellanos et al., 2022; Seibert et al., 2020; Cuerda-Correa et al., 2020). The most frequently integrated or combined technical methods for CECs removal at full/commercial scale are: (i) ozonation + adsorption with granular activated carbon; (ii) ozonation and biological active filters; (iii) membrane filtration (nanofiltration, reverse osmosis); and (iv) adsorption/ion-exchange (Rizzo et al., 2019). The application of the ozonation process in full-scale urban WWTPs is being increasingly implemented, mainly in Switzerland, Germany, the Netherlands and Canada (Margot et al., 2013; Hollender et al., 2009; Kienle et al., 2022), showing a high ability to oxidize CECs and disinfection when applied to secondary-treated UWW (van Gijn et al., 2022; Wünsch et al., 2022; Smuts et al., 2022; Lee et al., 2022; Ribeirinho-Soares et al., 2022; Moreira et al., 2021). In this process, ozone ($O_3$, $E^\circ = 2.07$ V vs. NHE) is able to selectively and rapidly react with electron-rich moieties such as aromatic and amine groups, while its self-decomposition can lead to the in situ production of a secondary oxidant, the less selective but more reactive hydroxyl radical ($OH^\bullet$, $E^\circ = 2.87$ V vs. NHE) (Gottschalk et al., 2010). However, major limitations are pointed out for the current $O_3$ injection systems, such as the high $O_3$ supply requirements (poor gas/liquid mass transfer rates), prolonged reactor contact times and, consequently, the bulky size of the equipment (Schmitt et al., 2022). To overcome these constrains, ozone membrane contactors have become a promising alternative to conventional systems (Pabby and Sastre, 2013) and have already been tested in some water/wastewater treatment applications, including decolourization (Hanh Le et al., 2021; Le et al., 2022), removal of specific organic contaminants (Li et al., 2019; Stylianou et al., 2018; Stylianou et al., 2015), and bromate minimization (Merle et al., 2017). Another important issue in ozonation is the generation of by-products that are potentially more toxic than the parent compound. In this regard, it has been proposed that multiple injection sites can be used to maintain low local $O_3$ concentrations and decrease the occurrence of by-products during treatment (Merle et al., 2017). However, most of these studies have focused on applying flat membranes, and few have described experimental investigations into the use of tubular membrane ozone contactors (Stylianou et al., 2018; Stylianou et al., 2015).

Presumido et al. (Presumido et al., 2022) proposed a tubular membrane contactor for continuous-flow "titration" of $O_3$ that generates innumerable micro-sized bubbles in the water to enhance gas/liquid mass transfer rate. The membrane side surface in contact with the liquid is coated with titanium dioxide ($TiO_2$), allowing to reduce the pore size of the membrane and the occurrence of photocatalytic ozonation processes ($O_3$/UVC/$TiO_2$). Additionally, the helical flow of a thin film of the contaminated water around the shell side of the membrane provides a high level of mixing and distribution of the $O_3$ micro-bubbles, increasing the radial dispersion of $O_3$ in the reaction zone. The setup exhibited higher volumetric mass transfer coefficient values (3.5 to 9.0 $min^{-1}$ (Gottschalk et al., 2010)) compared to other membrane contactors reported in the literature (0.438 $min^{-1}$ (Wang et al., 2019), 0.7858 $min^{-1}$ (Wang et al., 2021)). The applicability of this ozone membrane contactor in removing a mixture of CECs spiked in demineralized water was also demonstrated with removals >80 % for 13 of the 19 CECs evaluated by applying an ozone dose of 12 g $m^{-3}$ and a residence time of 3.9 s.

This work intends to deepen the application of the tubular ozone membrane contactor to promote the tertiary treatment of UWW, jointly considering the removal of CECs, disinfection, and the reduction of toxicity. The efficiency of ozonation was assessed for the simultaneous removal of 19 CECs spiked in secondary-treated UWW (10 μg $L^{-1}$ each) and microbial inactivation (heterotrophs, enterobacteria and enterococci), including the removal of ARBs (amoxicillin (AMX), cefotaxime (CTX) and sulfamethoxazole (SUL)). The target CECs were selected within the scope of the NOR-WATER project (http://nor-water.eu/en/home/), according to their occurrence and persistence in the river basins and WWTP effluents located in Northern Portugal and Galicia (Montes et al., 2022; Castro et al., 2021), therefore including some highly persistent and mobile chemicals. The influence of different experimental parameters on CECs removal and disinfection, i.e., $O_3$ dose ($D_{A\text{-}O3}$), $O_3$ concentration in the gas phase ($[O_3]_{G,inlet}$) and gas flow rate ($Q_G$), wastewater pH, and UVC radiation was examined. Furthermore, the effect of effluent quality due to seasonal fluctuations (winter and summer) on ozonation efficiency, as well as microbial regrowth due to storage of the treated UWW (for reuse purposes), were also evaluated. Finally, using bioassays with zebrafish embryos, the toxicity of the effluent was assessed before and after ozonation and also after adsorption by granular activated carbon (GAC).

## 2. Materials and methods

### 2.1. Chemicals

The reference standards for the 19 selected CECs used in this work (Table 1) were all analytical grade (>98 %) and purchased from Sigma-

Aldrich (Steinheim, Germany). A 1 g $L^{-1}$ stock solution of CECs was prepared in methanol (Merck, Darmstadt, Germany) or ultrapure water (UPW) and stored at 4 °C, protected from light. Sulfuric acid ($H_2SO_4$, Pronalab) and sodium hydroxide (NaOH, Merck) solutions were used to adjust the pH when required.

$TiO_2$ Aeroxide® P25 (Evonik, Germany) ≥ 99.5 % (*w/w*) purity was used as photocatalyst and the surfactant Triton™ X-100 (Sigma-Aldrich) was used in the preparation of the $TiO_2$-P25 suspension for membrane coating. UPW (resistivity >18.2 MΩ $cm^{-1}$ at 25 °C) was supplied by a Milli-Q water system from Millipore (Massachusetts, USA). HPLC-grade methanol, acetic acid (100 %) and ammonium fluoride were provided by Merck (Darmstadt, Germany). Granular activated carbon (GAC) in pellets was purchased from ORNI-EX, LDA. According to the product specifications, the GAC had an appearance of a pelleted black granular solid, an iodine number of 1080 mg $g^{-1}$, an apparent density of 0.4–0.5 kg $L^{-1}$, a diameter with an average size of 1.5 mm, and a BET surface area of 1100 $m^2$ $g^{-1}$.

### 2.2. Urban wastewater

The secondary treated UWW used in the ozonation treatment tests was collected from a municipal WWTP in Portugal in two different seasons: winter (UWW1) and summer (UWW2); and stored at 4 °C until use. The main quality parameters are gathered in Table 2 and the respective analytical methods employed are depicted in Table S1 of the *Supplementary Material* file. Furthermore, Table S2 presents the list of CECs detected in the secondary treated UWW prior to fortification and its respective concentrations. It is important to highlight that CECs removal percentages were calculated considering the initial and final concentrations measured for each compound when the final concentration was not below the quantification limit.

### 2.3. Experimental setup

The ozone membrane contactor has already been described in detail by Presumido et al. (Presumido et al., 2022) and its schematic is shown in Fig. 1. It is composed of an outer quartz tube ($ø_{ext}$ = 4.2 cm; $ø_{int}$ = 3.8 cm; length = 20.0 cm), a concentric inner microfiltration borosilicate membrane (ASTM VitraPOR®, from ROBU, pore size = 5 μm, porosity = 45 %, $ø_{ext}$ = 2.1 cm; $ø_{int}$ = 1.1 cm; length = 20.0 cm, useful length = 17.4 cm), and four UVC lamps (Philips TL 11 W, $\lambda_{max}$ = 254 nm; photon flow = 2.89 ± 0.08 W (Presumido et al., 2022)) located externally to the reactor window. UVC radiation was chosen because it can effectively activate both $TiO_2$ and $O_3$. $O_3$ has a peak absorption band at 254 nm within the 200–300 nm range (Petruci et al., 2022; Griggs, 2003). Additionally, UVC light is used due to its disinfection properties. The microfiltration membrane was uniformly coated with a suspension of $TiO_2$-P25 (2 % *w/v*) via dip-coating technique (Dip-coater RDC 15, Bungard Elektronic GmbH), as described in a previous study (Presumido et al., 2022). An amount of 0.6 g of $TiO_2$-P25 was coated in the membrane shell-side, decreasing the membrane pore size from 5.0 to 3.8 μm. A BMT 802 N ozone generator (BMT, Messtechnik, Germany) was used to produce $O_3$ from pure oxygen ($O_2$) with a production capacity of up to 4 g $O_3$ $h^{-1}$ (at 100 g $Nm^{-3}$, 20 °C). Inlet and outlet $O_3$ gas concentrations ($[O_3]_{G,inlet}$ and $[O_3]_{G,outlet}$, respectively) were monitored with a BMT 964 ozone analyzer (Messtechnik, Germany) after passing through a gas dehumidifier (BMT DH3b, Messtechnik, Germany). The $O_3$ concentration in the aqueous

**Table 2**
Main physicochemical characteristics of the two wastewater samples collected after secondary treatment in a WWTP (UWW1, Winter and UWW2, Summer), after ozonation and after ozonation followed by adsorption with granular activated carbon (GAC).

| Parameter | UWW1 | $O_{3\text{-}WW1}$ | UWW2 | $O_{3\text{-}WW2}$ | $O_{3\text{-}WW2}$ + GAC |
|---|---|---|---|---|---|
| pH | 7.5 | 7.2 | 7.8 | 7.5 | 7.6 |
| Temperature (°C) | 15.7 | 16.4 | 23.4 | 21.4 | 22.4 |
| Conductivity (μS $cm^{-1}$) | 202 | 195 | 1442 | 1328 | 1030 |
| Turbidity (NTU) | 0.6 | 0.25 | 15 | 3.6 | 2.6 |
| Absorbance at 254 nm (AU) | 0.208 | 0.039 | 0.320 | 0.096 | 0.017 |
| Transmittance at 254 nm (%) | 62 | 91 | 48 | 80 | 96 |
| Dissolved organic carbon (mg $L^{-1}$) | 13.5 | 10.1 | 22.9 | 15.8 | 7.0 |
| Dissolved inorganic carbon (mg $L^{-1}$) | 46.5 | 45.9 | 70.8 | 74.3 | 38.9 |
| Specific Ultraviolet Absorbance ($SUVA_{254}$, L $mg^{-1}$ $m^{-1}$) | 1.5 | 0.39 | 1.4 | 0.61 | 0.24 |
| Chemical oxygen demand (mg $O_2$ $L^{-1}$) | 38.3 | 21.9 | 79.5 | 35.3 | 14 |
| Total suspended solids (mg $L^{-1}$) | 7.0 | 3.6 | 35.7 | 12.2 | 3.4 |
| Sodium – $Na^+$ (mg $L^{-1}$) | 100 | 101 | 105 | 104 | 107 |
| Ammonium – $NH_4^+$ (mg $L^{-1}$) | 1.2 | 0.9 | 62.5 | 35.8 | 30.2 |
| Potassium – $K^+$ (mg $L^{-1}$) | 23.5 | 27.1 | 26.2 | 23.8 | 25.0 |
| Magnesium – $Mg^{2+}$ (mg $L^{-1}$) | 6.4 | 7.2 | 6.9 | 6.4 | 6.6 |
| Calcium – $Ca^{2+}$ (mg $L^{-1}$) | 30.6 | 26.2 | 33.0 | 24.9 | 14.4 |
| Fluoride – $F^-$ (mg $L^{-1}$) | 0.1 | 0.1 | 0.2 | 0.1 | <0.01 |
| Chloride – $Cl^-$ (mg $L^{-1}$) | 130 | 137 | 132 | 134 | 54 |
| Sulfate – $SO_4^{2-}$ (mg $L^{-1}$) | 54.0 | 59.1 | 65.3 | 65.8 | 14.7 |
| Nitrite – $NO_2^-$ (mg $L^{-1}$) | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| Nitrate – $NO_3^-$ (mg $L^{-1}$) | 1.9 | 2.4 | 4.5 | 16.2 | 1.4 |
| Phosphate – $PO_4^{3-}$ (mg $L^{-1}$) | 4.0 | 6.1 | 17.6 | 13.6 | 5.0 |

**Table 1**
List of the 19 CECs selected for testing and respective group, abbreviations, chemical composition, and rate constants of the reactions between ozone ($k_{O3}$) and the hydroxyl radical ($k_{HO\cdot}$).

| Contaminants group | Contaminants | Abbreviation | Chemical composition | $k_{O3}$ ($M^{-1}$ $s^{-1}$) | $k_{HO\cdot}$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| Carbamazepine and metabolites | Carbamazepine | CBZ | $C_{15}H_{12}N_2O$ | $3 \times 10^5$ (Huber et al., 2003) | $8.8 \times 10^9$ (Huber et al., 2003) |
| | 10,11 Carbamazepine-epoxide | CBZ-EPX | $C_{15}H_{12}N_2O_2$ | Low[a] (Rosal et al., 2010) | Low[a] (Rosal et al., 2010) |
| Non-steroidal anti-inflammatory drugs | Diclofenac | DCF | $C_{14}H_{11}Cl_2NO_2$ | $1 \times 10^6$ (Beltrán and Rey, 2018) | $7.5 \times 10^9$ (Beltrán and Rey, 2018) |
| Hormones | 17β-Estradiol | E2 | $C_{18}H_{24}O_2$ | $2.2 \times 10^5$ (Deborde et al., 2005) | $5.12 \times 10^9$ (Naimi and Bellakhal, 2012) |
| | 17α-Ethynylestradiol | EE2 | $C_{20}H_{24}O_2$ | $3 \times 10^6$ (Huber et al., 2003) | $9.8 \times 10^9$ (Huber et al., 2003) |
| Beta blockers | Atenolol | ATNL | $C_{14}H_{22}N_2O_3$ | $1.7 \times 10^3$ (Benner et al., 2008) | $8 \times 10^9$ (Lee et al., 2014) |
| | Bisoprolol | BSPL | $C_{18}H_{31}NO_4$ | $1.83 \times 10^4$ (Mustafa, 2020) | Unknown |
| Insect repellent | Diethyltoluamide | DEET | $C_{12}H_{17}NO$ | 0.1 (Benitez et al., 2013) | $4.95 \times 10^9$ (Song et al., 2009) |
| Angiotensin II receptor blockers | Valsartan | VSTN | $C_{24}H_{29}N_5O_3$ | 38 (Lee et al., 2014) | $1 \times 10^{10}$ (Sauter et al., 2021) |
| | Irbesartan | ISTN | $C_{25}H_{28}N_6O$ | 23 (Bourgin et al., 2018) | $1 \times 10^{10}$ (Bourgin et al., 2018) |
| | Losartan | LSTN | $C_{22}H_{23}ClN_6O$ | $2.1 \times 10^5$ (Bourgin et al., 2018) | Unknown |
| Herbicide | Diuron | DRN | $C_9H_{10}C_{l2}N_2O$ | 13.3 (Chen et al., 2008) | $6.6 \times 10^9$ (Benitez et al., 2007) |
| Flame retardant | Melamine | MLN | $C_3H_6N_6$ | Unknown | 1 × 104 (Maurino et al., 2016)[a] |
| Artificial Sweeteners | Acesulfame K | AC-K | $C_4H_4KNO_4S$ | 88 (Kaiser et al., 2013) | $4.55 \times 10^9$ (Kaiser et al., 2013) |
| | Saccharin | SCH | $C_7H_5NO_3S$ | Unknown | $1.56 \times 10^9$ (Ye et al., 2022) |
| Short-chain perfluoroalkyl substances (PFAS) | Heptafluorobutyric acid | PFBA | $C_4HF_7O_2$ | Unknown | Unknown |
| | Nonafluoro-1-butanesulfonic acid | PFBS | $C_4HF_9O_3S$ | Unknown | Unknown |
| | Pentadecafluorooctanoic acid | PFOA | $C_8HF_{15}O_2$ | Unknown | $<1 \times 10^5$ (Umar, 2021) |
| | Trifluoromethanesulfonic acid | TFMS | $CHF_3O_3S$ | Unknown | $<1 \times 10^5$ (Dreizler and Roduner, 2012) |

[a] Estimated reactivity.

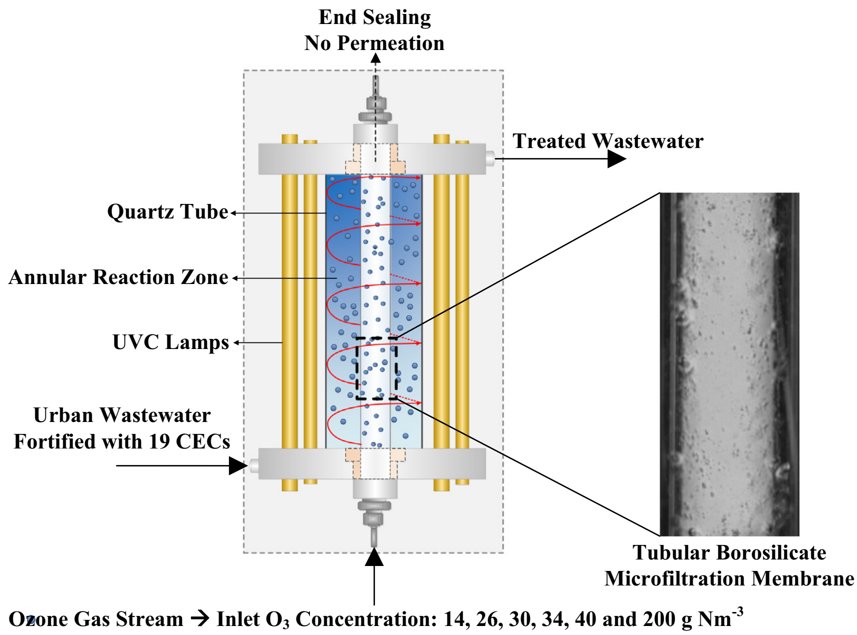


**Fig. 1.** Ozone membrane contactor schematic and membrane photograph.

phase $[O_3]_L$ was measured in-line using a measuring cell AQC-D12 with a reference electrode for $O_3$ (Grundfos Alldos, Denmark) connected to a controller Conex DIA-1 (Grundfos Alldos, Denmark). Viton O-rings ($O_3$-resistant) were used to ensure the module's air- and water-tight conditions.

## *2.4. Experimental procedure*

UWW1 or UWW2 spiked with the 19 target CECs (10 μg $L^{-1}$ each) was pumped (ISMATEC BVP-Z pump) from a jacketed vessel (20 ± 1 °C) into the reactor inlet. At the same time, the $O_3$ gas stream was introduced by the lumen side of the membrane, permeating the membrane pores, and the gas-water contact occurred on the membrane shell side surface. All experiments were performed in continuous mode and, except for specific cases, with the gas flow rate ($Q_G$) of 0.75 $Ndm^3$ $min^{-1}$, natural pH of the UWW (7.7 ± 0.3), and a liquid flow rate ($Q_L$) of 100 L $h^{-1}$, corresponding to a residence time (τ) of 5.8 s. First, with the UWW1, the efficiency of the ozonation process (standalone) in the degradation of the 19 target CECs, under steady-state conditions was assessed for different: (i) $O_3$ doses ($D_{O3}$ of 6, 12, 15, and 18 g $m^{-3}$), (ii) residence times (5.8 or 60 s), (iii) UWW pH value (5.0 ± 0.2 or 9.0 ± 0.2) and, (iv) $O_3$ concentrations in the inlet gas stream ($[O_3]_{G,inlet}$ of 30, 40 and 200 g $Nm^{-3}$, 20 °C, 1 bar). Photocatalytic ozonation ($O_3$/UVC/$TiO_2$) tests were also performed for $[O_3]_{G,inlet}$ of 40 and 200 g $Nm^{-3}$ and maintaining the other operational conditions as the tests with only $O_3$. For the ozonation tests with the residence time of 60 s, and in order to keep the remaining operating conditions unchanged, a column with a capacity of 1.5 L was coupled downstream of the membrane reactor. At the end of these tests, and based on the results, some operational conditions were chosen to be replicated for the treatment of UWW2.

For each test, samples were collected before treatment and at least three times at steady-state conditions for CECs analysis. When applicable, samples were also collected before and after ozonation treatment in sterile vials for microbiological analysis or flasks for toxicology bioassays. A subsequent adsorption step using GAC was also carried out for the treatment test selected for toxicological assessment (the adsorption procedure is described in Text S1 and the schematic in Fig. S1 of the *Supplementary Material* file). The operational details for all ozonation experiments are summarized in Table 3 and further information on the procedure and membrane properties can be found in a previous study (Presumido et al., 2022).

The applied ($D_{A\text{-}O3}$), transferred ($D_{T\text{-}O3}$) and consumed ozone dose ($D_{C\text{-}O3}$), all expressed in g $O_3$ $m^{-3}$, were calculated following Eqs. (1)–(3), and the ozone transfer yield (%) from Eq. (4):

$$D_{A-O_3} = \frac{Q_G \times [O_3]_{G,Inlet}}{Q_L} \tag{1}$$

$$D_{T-O_3} = \frac{\left([O_3]_{G,Inlet} - [O_3]_{G,Outlet}\right) \times Q_G}{Q_L} \tag{2}$$

$$D_{C-O_3} = D_{T-O_3} - [O_3]_L \tag{3}$$

$$\text{Transfer yield } (\%) = \frac{D_{T-O_3}}{D_{A-O_3}} \times 100 \tag{4}$$

Furthermore, the specific transferred ozone dose (g $O_3$ $g^{-1}$ $DOC_0$) was also calculated (nitrite correction was not required as it was not detected in both UWW, Table 2).

## *2.5. Quantification of contaminants of emerging concern*

An Acquity UPLC® liquid chromatography interfaced to a XEVO TQD® triple quadrupole mass spectrometer (LC-MS/MS) equipped with an electrospray interface (ESI) (Waters, USA) was used for the determination of the CECs concentrations. The quantification was performed by the standard addition method using standards prepared in UWW and direct injection of the samples. More detailed information about chromatograms and method performance parameters can be found in our previous study (Presumido et al., 2022). The performance of the analytical method was reevaluated with the matrix of this study, see performance figures in Table S3.

## *2.6. Enumeration of culturable microorganisms*

One millilitre of the serially 10-fold diluted sample, or up to 100 mL of sample, was filtered through cellulose nitrate membrane filters (0.22 μm porosity; Whatman, UK) in triplicate. Afterwards, the filtering membranes were placed onto the appropriate culture media of the target microbial group: Plate Count Agar [PCA; VWR International (Pennsylvania, USA); 30 °C, 48 h] for culturable heterotrophs, m-Faecal Coliform Agar [mFC;

**Table 3**
Experimental conditions employed for each test.

| Matrix[a] | # | $Q_L$ ($Lh^{-1}$) | τ (s) | $Q_G$ ($Ndm^3\ min^{-1}$) | $[O_3]_{G,inlet}$ ($g\ Nm^{-3}$) | $D_{A\text{-}O3}$ ($g\ m^{-3}$) | $D_{T\text{-}O3}$ ($g\ m^{-3}$) | $D_{C\text{-}O3}$ ($g\ m^{-3}$) | Radiation[d] | Evaluated parameters[e] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | CECs | M | MR | ARB | T |
| UWW1 | 1 | 100 | 5.8 | 0.75 | 14 | 6 | 2.4 | 2.3 | – | × | – | – | – | – |
| UWW1 | 2 | 100 | 5.8 | 0.75 | 26 | 12 | 4.5 | 4.1 | – | × | – | – | – | – |
| UWW1 | 3 | 100 | 5.8 | 0.75 | 34 | 15 | 4.8 | 4.3 | – | × | – | – | – | – |
| UWW1 | 4 | 100 | 5.8 | 0.75 | 40 | 18 | 6.8 | 5.6 | – | × | × | – | – | – |
| UWW1 | 5 | 100 | 60 | 0.75 | 26 | 12 | 4.6 | 4.6 | – | × | – | – | – | – |
| UWW1 | 6 | 100 | 60 | 0.75 | 40 | 18 | 5.9 | 5.8 | – | × | – | – | – | – |
| UWW1 | 7[b] | 100 | 5.8 | 0.75 | 40 | 18 | 5.8 | 5.7 | – | × | × | – | – | – |
| UWW1 | 8[c] | 100 | 5.8 | 0.75 | 40 | 18 | 6.8 | 6.8 | – | × | × | – | – | – |
| UWW1 | 9 | 100 | 5.8 | 1.00 | 30 | 18 | 4.8 | 3.4 | – | × | × | – | – | – |
| UWW1 | 10 | 100 | 5.8 | 0.15 | 200 | 18 | 15.8 | 6.8 | – | × | × | – | – | – |
| UWW1 | 11 | 100 | 5.8 | 0.75 | 40 | 18 | 5.9 | 5.7 | UVC | × | × | – | – | – |
| UWW1 | 12 | 100 | 5.8 | 0.15 | 200 | 18 | 15.8 | 6.8 | UVC | × | – | – | – | – |
| UWW2 | 13 | 100 | 5.8 | 1.00 | 30 | 18 | 6.6 | 4.2 | – | × | × | × | × | – |
| UWW2 | 14 | 100 | 5.8 | 0.75 | 40 | 18 | 8.0 | 6.3 | – | × | × | × | × | – |
| UWW2 | 15 | 100 | 5.8 | 0.15 | 200 | 18 | 16.0 | 8.6 | – | × | × | × | × | × |

[a] Wastewater collected in the winter (UWW1) and summer (UWW2) period.
[b] Adjusted pH to 5.0 ± 0.2.
[c] Adjusted pH to 9.0 ± 0.2.
[d] Photonic flux of 2.89 ± 0.08 W.
[e] CECs – CECs removal; M – enumeration of culturable microorganisms; MR – microbiological regrowth; ARB – antibiotic-resistant bacteria; T – toxicity screening with zebrafish embryo bioassays.

Thermo Fisher Scientific (Massachusetts, USA); 37 °C, 24 h] for enterobacteria, and Slanetz Bartley Agar (mENT; Thermo Fisher Scientific (Massachusetts, USA); 37 °C, 48 h) for enterococci. Additionally, m-Faecal Coliform Agar supplemented with 32 mg $L^{-1}$ amoxicillin (AMX), 4 mg $L^{-1}$ cefotaxime (CTX) or 350 mg $L^{-1}$ sulfamethoxazole (SUL) were used to assess resistance prevalence before and after treatment. These antibiotic concentrations were based on previous studies (Marano et al., 2020; Novo et al., 2013). Results were expressed as colony forming units (CFU) per 100 mL of sample.

### 2.7. Toxicity screening using zebrafish embryo bioassay

Zebrafish embryo bioassays were carried out based on the OECD Fish Embryo Acute Toxicity (FET) Test 236 (OECD, 2013; Barros et al., 2018) to evaluate the toxicity of UWW fortified with the 19 CECs before and after ozonation treatment, and also after adsorption by GAC. The zebrafish embryo bioassay involved four different conditions: control (dechlorinated water – CTRL), real matrix (UWW2) fortified with 19 target CECs before and after the ozonation treatment (UWW + CECs and UWW + CECs + $O_3$, respectively), and after ozonation plus GAC adsorption (UWW + CECs + $O_3$ + GAC). Each treatment condition was tested without dilution and with dilutions factors of 2 and 4 with dechlorinated water.

#### 2.7.1. Zebrafish maintenance and embryos collection

A stock of adult zebrafish was maintained in dechlorinated water at 28 ± 1 °C, under a photoperiod of 14:10 h (light:dark). The animals were fed twice a day with commercial fish diet Zebrafeed (Sparos, Olhão, Portugal) supplemented with live *Artemia* spp. (OECD, 2013). For the zebrafish reproduction, in the afternoon before breeding, a group of males and females in a proportion of 2:1, respectively, were isolated in a breeding box under the same water and photoperiod conditions as the stock. At the following day, 1.5 h after the beginning of the light period, the eggs were collected, cleaned and selected for the zebrafish embryo bioassays.

#### 2.7.2. Zebrafish embryo bioassays

After observation in a magnifying glass, cleaned fertilized embryos were randomly allocated into 24-well plates (one embryo per well). All the plates were incubated with 2 mL sample of each treatment the day before and renewed at the beginning of the assay. Treatment solutions were renewed daily in order to maintain oxygen saturation and the integrity of the solutions. Each plate was assigned a condition, consisting of 20 embryos plus an internal control (4 embryos), which were randomly maintained in an incubator at 26 °C ± 0.5 for 96 h under the same photoperiod as the adults.

Embryos were checked at 24-, 48-, 72- and 96-h post-fertilization (hpf), under an inverted microscope (Nikon Eclipse 5100 T), for mortality (dead embryos were removed), morphological abnormalities on eyes, head, tail or yolk-sac and pericardial oedema and recorded as present or absent. The different abnormalities were grouped at each observation time point and presented as total abnormalities. Heart rate (cardiac frequency) was also evaluated every day ($n$ = 6–8), during 15 s using a stopwatch (OECD, 2013; Barros et al., 2018).

#### 2.7.3. Statistical analysis

Data were first checked for homogeneity of variances (Levene's test) and subsequently analyzed by one-way ANOVA followed by Fisher's least significant difference test (LSD) or nonparametric analysis (Kruskall-Wallis ANOVA by ranks followed by multiple comparisons of mean ranks) if the homogeneity of variances was not achieved after data transformation. The significance threshold was set at $p < 0.05$. All statistics were computed with Statistica 12 (Stat-soft, USA).

## 3. Results and discussion

### 3.1. Efficiency of the ozone membrane contactor for CECs removal

#### 3.1.1. Effect of ozone dose and residence time

The efficiency of tertiary treatment applying the ozone membrane contactor was first evaluated for UWW1 spiked with the 19 target CECs. As expected, the application of higher doses of $O_3$ (tests #1 to #4, with $D_{A\text{-}O3}$ of 6, 12, 15 and 18 g $m^{-3}$) increased the removal of the target CECs (Fig. 2a). The higher specific transfer $O_3$ dose, ranging from 0.18 to 0.44 g $O_3$ $g^{-1}$ DOC in these tests, explain these results. The target CECs also showed different levels of degradation, which is related to the reactivity of the compound to the oxidizing species present, given by second-order rate constants with $O_3$ ($k_{O3}$) and OH• ($k_{HO•}$). According to Hollender et al. (Hollender et al., 2009), compounds with $k_{O3}$ >$10^4$ $M^{-1}$ $s^{-1}$ require low delivered $O_3$ doses (easily degraded). CECs with $k_{O3}$ < $10^4$ $M^{-1}$ $s^{-1}$ are more persistent to treatment with $O_3$, and their degradation can occur mainly by reaction with OH•. For $D_{A\text{-}O3}$ > 12 g $m^{-3}$ (or > 0.34 g $O_3$ $g^{-1}$ DOC), it was observed (Fig. 2a) that compounds highly reactive with $O_3$, such as CBZ, E2, EE2, DCF, and LSTN ($k_{O3} \geq 10^5$ $M^{-1}$ $s^{-1}$, Table 1), reached removal values below the limit of quantification (LOQ). These compounds are known to contain functional groups that react quickly with $O_3$, such as aniline (e.g., DCF), olefins (e.g., CBZ), phenol (e.g., E2, EE2), and benzene ring (e.g., CBZ, LSTN) (Li et al., 2021). In contrast, beta-blockers ATNL and BSPL (with $10^3 \leq k_{O3} \leq 10^4$ $M^{-1}$ $s^{-1}$, Table 1), as well as ISTN and DRN (both with $k_{O3} = 10^1$ $M^{-1}$ $s^{-1}$, Table 1) presented removal levels between 60 % and 80 % only for the highest $O_3$ dose (test #4, $D_{A\text{-}O3}$ of 18 g $m^{-3}$ and specific dose of 0.44 g $O_3$ $g^{-1}$ DOC), while the remaining target CECs (with $k_{O3} \leq 10^1$ $M^{-1}$ $s^{-1}$, Table 1) had low or null removals (Fig. 2a). Levels of oxidation >90 % for CBZ, CBZ-EPX, DCF (in common with the present study) were also reported for full-scale ozonation plants in Sweden and Denmark (Kharel et al., 2021) applying a $D_{A\text{-}O3}$ between 4 and 28.6 g $m^{-3}$ and a residence time between 10 and 30 min. Other pertinent works (Gorito et al., 2021; Dogruel et al., 2020; Lee et al., 2012), with $D_{A\text{-}O3}$ ranging from 3 to 8 g $m^{-3}$ and residence times from 4 to 15 min, also observed high removal efficiencies (>80 %) for several CECs, including CBZ, DCF, PFOA, ATNL, DEET.

Considering the short residence time applied in these tests ($Q_L$ of 100 L $h^{-1}$, corresponding to 5.8 s), and that most of the ozonation treatments applying similar $D_{A\text{-}O3}$ are carried out with residence times of a few minutes (from 4 to 30 min) (Dogruel et al., 2020; Ashauer, 2016), tests with $D_{A\text{-}O3}$ of 12 and 18 g $m^{-3}$ were performed for a residence time of 60 s (tests #5 and #6, Table 3). Improvements in the removal efficiency of several CECs were evidenced for $D_{A\text{-}O3}$ of 12 g $m^{-3}$ (Fig. 2b), with increases of 1.3-fold for LSTN, VSTN and AC-K, ~2-fold for DRN, DEET, BSPL and CBZ-EPX, and 3.8-times for ATNL and ISTN. These better results are related to the total consumption of dissolved $O_3$ verified in test #5 ($D_{T\text{-}O3} = D_{C\text{-}O3} = 4.6$ g $m^{-3}$, Table 3), which did not occur when the contact time was only 5.8 s ($D_{T\text{-}O3} > D_{C\text{-}O3} = 4.1$ g $m^{-3}$, Table 3). In turn, for a $D_{A\text{-}O3}$ of 18 g $m^{-3}$, the difference between the $O_3$ consumed for the tests with 5.8 s and 60 s was smaller ($D_{C\text{-}O3}$ of 5.6 and 5.8 g $m^{-3}$, respectively, Table 3), so improvements were verified only for ATNL (1.3-fold) and AC-K (2-fold) (Fig. 2b).

### 3.1.2. Effect of wastewater pH

The $O_3$ stability in water strongly depends on the pH value, while under acidic conditions, the rate of $O_3$ self-decomposition is slow (higher $O_3$ concentration in the liquid phase), alkaline conditions promote $O_3$ decay reactions (and the generation of OH•) (Ling et al., 2019). This is in line with the observed drop in dissolved $O_3$ concentration (from 3.2 g $m^{-3}$ to 0.6 g $m^{-3}$) when the pH value was increased (from 3 to 9) in the ozone mass transfer assays reported for this membrane contactor by Presumido et al. (Presumido et al., 2022), indicating greater $O_3$ decomposition at higher pH values. Taking this, when operating under acidic conditions, the main oxidation pathway for CECs is expected to be the direct reaction with dissolved $O_3$, whereas, under alkaline conditions, the indirect oxidation pathway (i.e., CECs reacting with OH•) becomes predominant. In this way, for the ozonation treatment at pH 5.0 (test #7, Table 3), the target CECs with $k_{O3} \geq 10^5$ $M^{-1}$ $s^{-1}$ maintained high levels of oxidation and reached concentrations below the LOQ (Fig. 2c). On the other hand, when compared to ozonation at the natural pH of the UWW1 (test #4, pH of 7.7), the lower OH• generation at pH 5.0 led to a decrease in the removal of several CECs such as DRN and DEET (~1.4 times lower) and BSPL, ATNL and ISTN (~2 times lower). This shows the importance of the indirect reaction pathway for those CECs that react poorly with $O_3$ ($k_{O3} \leq 10^5$ $M^{-1}$ $s^{-1}$). In turn, no significant differences in performance were observed between ozonation at pH 7.7 and 9.0 (tests #4 vs. #8, Fig. 2c). The lack of improvement in oxidation ability at pH 9.0 may be related to inorganic species associated with the alkalinity of the effluent (carbonates/bicarbonates) that are affected by pH adjustment, which act as OH• scavengers and inhibitors of the chain reaction of $O_3$ decomposition. This was also observed in other studies (Dogruel et al., 2020; Cuervo Lumbaque et al., 2020) and perceived by the increase in the concentration of inorganic carbon when the pH of the UWW1 was adjusted to 9.0 (from 46.7 mg $L^{-1}$ to 66.7 mg $L^{-1}$). The opposite trend was also observed, with decreasing concentration of inorganic carbon in the UWW when the pH was adjusted to 5.0.

### 3.1.3. Effect of ozone inlet concentration and flow rate

Keeping the natural pH, a $D_{A\text{-}O3}$ of 18 g $m^{-3}$, and a residence time of 5.8 s (selected according to the results presented above), the $[O_3]_{G,inlet}$ was then varied (tests #4, #9 and #10, Table 3). A substantial improvement in the CECs removal was observed for the highest $[O_3]_{G,inlet}$ (test #10; 200 g $Nm^{-3}$), with 13 of the 19 CECs removed >80 % or below the LOQ and one CEC >50 % (SCH) (Fig. 3). These results can be explained by the ozone transfer yield observed in these experiments (Fig. 3a inset), while only 30 % ± 3 % of the delivered $O_3$ was effectively transferred in tests #4 and #9 ($[O_3]_{G,inlet}$ of 40 and 30 g $Nm^{-3}$, respectively), this value increased to 88 % in test #10 ($[O_3]_{G,inlet}$ of 200 g $Nm^{-3}$). This is consistent with the mass-transfer theory, where for increasing $O_3$ concentrations in the gas phase (driving force), a higher $O_3$ diffusion rate is expected; thus, more $O_3$ is transferred from the gas to the liquid phase (Hanh Le et al., 2021; Ren et al., 2012) and available to react with the target CECs. Furthermore, to keep the hydrodynamic conditions and attain the same $D_{A\text{-}O3}$ while increasing the $[O_3]_{G,inlet}$ for test #10, it was required to decrease the inlet gas flow rate (see Table 3). For this membrane ozone contactor, it was verified that for the same liquid flow rate, mass transfer efficiency increases with the decrease in the gas flow rate due to the higher contact time between the gas and the liquid phase (Presumido et al., 2022). Therefore, although the same $D_{A\text{-}O3}$ was applied in tests #4, #9 and #10, the ozone transfer yield increased and, consequently, the specific ozone dose obtained for test #10 was ~3-fold higher than for tests #4 and #9 (1.17 vs. 0.44 and 0.36 g $O_3$ $g^{-1}$ DOC, respectively, Fig. 3a inset).

Beyond the expected good removal performance for the CECs with $k_{O3} \geq 10^5$ $M^{-1}$ $s^{-1}$, very interesting removals (58–96 %) were also observed in test #10 for compounds with low ozone reactivity, as CBZ-EPX, DEET, VSTN, ISTN, DRN, and AC-K, which can be ascribed as a result of their oxidation by the OH• radical ($k_{HO\bullet} > 10^9$ $M^{-1}$ $s^{-1}$, Table 1) produced by ozone's decomposition. Literature reports a lack of comprehensive data on the reaction rate between $O_3$ and CBZ-EPX. However, Rosal et al. (Rosal et al., 2010) and Zoumpouli et al. (Zoumpouli et al., 2020) indicated that CBZ-EPX exhibits low $k_{O3}$ values. Furthermore, according to Kharel et al. (Kharel et al., 2021), CBZ-EPX behaved similarly to *Rac trans 10,11 dihydro 10,11 dihydroxy carbamazepine* (another CBZ metabolite), but it is less reactive with ozone than CBZ. The lower ozone reactivity of the metabolites can be explained by the missing double bond (Kharel et al., 2021). The only CECs that persisted without any sign of oxidation, even when applying the highest $[O_3]_{G,inlet}$, were the four short-chain perfluoroalkyl substances (PFAS) and MLN (Fig. 3a). These organic compounds are highly stable and expected to be resistant to degradation by both $O_3$ and OH• radical ($k_{O3}$ unknown and $k_{HO\bullet} < 10^5$ $M^{-1}$ $s^{-1}$, Table 1). A possible explanation for the non-removal of PFAS with $O_3$ may be the presence of strong and stable carbon-fluorine bonds in the alkyl carbon chain, which agrees with other studies (Kaiser et al., 2021; Trojanowicz et al., 2018; Franke et al., 2019). Regarding MLN, a previous study has demonstrated that a $D_{A\text{-}O3}$ of 10 g $m^{-3}$ and a reaction time of 20 min was required to achieve ~65 % removal (Sangjung and Ihnsup, 2015). Maurino et al. (Maurino et al., 2016) also indicated that among the oxidative processes, only photocatalysis and the generation of sulfate radicals ($SO_4^{\bullet-}$) were able to transform MLN efficiently.

### 3.1.4. Photocatalytic ozonation

The combination of ozonation and photocatalysis for water treatment is currently reported to have increased oxidation efficiency (synergy) compared to the sum of the oxidation efficiencies of these two oxidation systems separately (Mehrjouei et al., 2015). Beyond oxidation by $O_3$ and/or the OH• naturally generated from the reaction of $O_3$ with the wastewater matrix, it is expected that complementary mechanisms for CECs degradation to be simultaneously triggered by $O_3$/UVC/$TiO_2$, namely (i) direct photolysis, (ii) indirect oxidation by reactive oxygen species yielded from $O_3$ photolysis, $TiO_2$ photoactivation, and photo-oxidation/reduction interaction between $O_3$ and $TiO_2$ electron/holes ($e^-/h^+$). Therefore, aiming at the removal of MLN and the four PFAS compounds, the combined $O_3$/

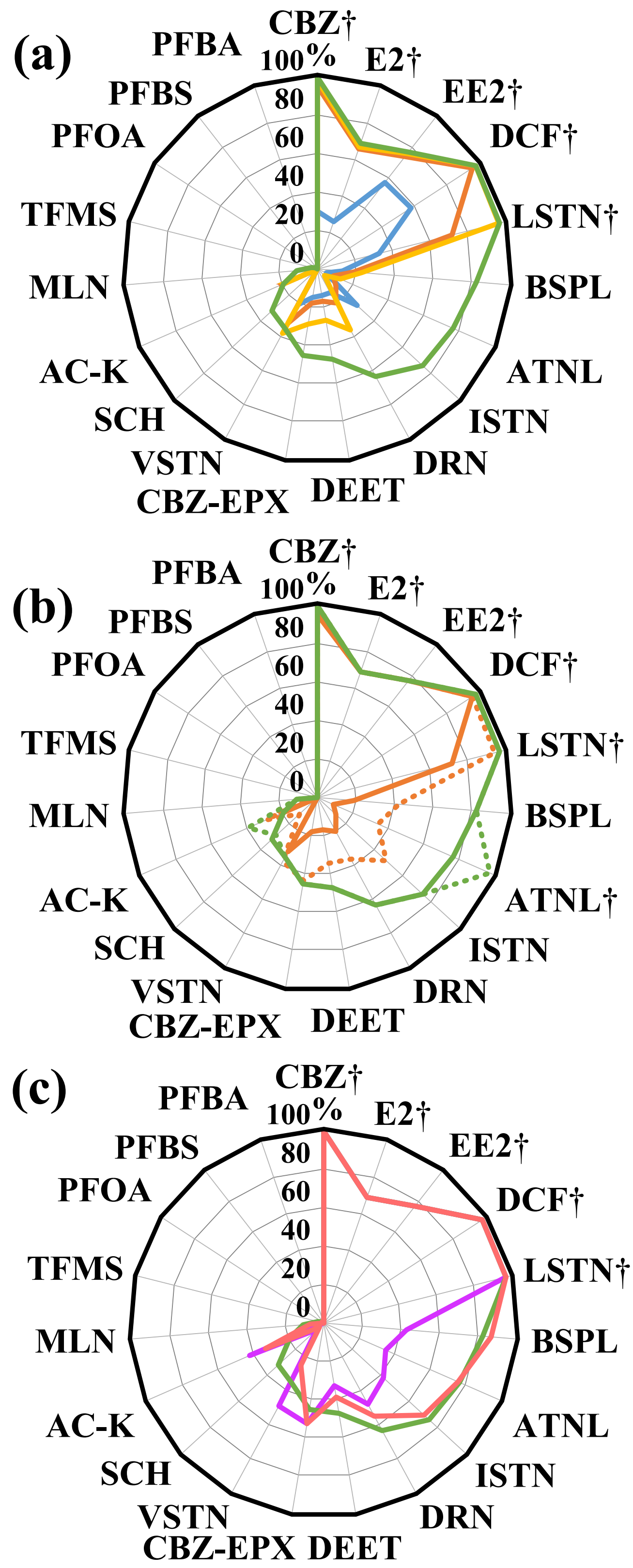


**Fig. 2.** Removal efficiency (%) of the 19 target CECs spiked in UWW1 ($[CECs]_0$ = 10 μg $L^{-1}$) after a treatment time of 5.8 s under different (a) ozone doses (—) $D_{A\text{-}O3}$ = 6 g $m^{-3}$ (test #1), (—) $D_{A\text{-}O3}$ = 12 g $m^{-3}$ (test #2), (—) $D_{A\text{-}O3}$ = 15 g $m^{-3}$ (test #3), and (—) $D_{A\text{-}O3}$ = 18 g $m^{-3}$ (test #4); (b) contact time of 60 s (– –) $D_{A\text{-}O3}$ = 12 g $m^{-3}$ (test #5) and (– –) $D_{A\text{-}O3}$ = 18 g $m^{-3}$ (test #6); and (c) pH values (—) pH = 5.0 ± 0.2 (test #7), (—) pH = 7.7 ± 0.3 (test #4) and (—) pH = 9.0 ± 0.2 (test #8). NOTE: For details on operational conditions of each test, please refer to Table 3. †Limit of quantification, Table S3.

UVC/$TiO_2$ process was evaluated for a $[O_3]_{G,inlet}$ of 40 and 200 g $Nm^{-3}$ (tests #11 and #12, from Table 3). For both cases, photocatalytic ozonation showed no significant differences in the removal efficiency of the target CECs when compared to ozonation treatments under similar operational conditions (tests #4 vs #11 and #10 vs #12, Fig. 3b). An explanation for these results may be the low UVC dose provided (0.10 kJ $L^{-1}$) due to the short residence time (5.8 s) of the treatment tests. This hypothesis is supported by the lack of significant removal of the 19 CECs in the UVC/$TiO_2$ test (<10 % for all targets, data not shown).

### 3.1.5. Effect of wastewater characteristics

To represent typical variations observed in the main traditional characteristics of effluent quality that are known to occur due to seasonal fluctuations, secondary-treated UWW2 was collected in the summer period, contrary to UWW1, which was collected in the winter. For a better insight into the ozonation efficiency, three treatments were selected for UWW2 (tests #13 to #15, Table 3) repeating operational conditions that were used for UWW1 (tests #4, #9 and #10, Table 3). Apart from the CECs highly reactive with $O_3$ ($k_{O3} \geq 10^5$ $M^{-1}$ $s^{-1}$, Table 1), which presented concentrations below the LOQ for the two treated wastewaters (Fig. 4), the removal of target CECs for UWW2 was globally lower for all compounds. Collected in the dry season, UWW2 presented a higher organic and inorganic load compared to UWW1 (Table 2), which can be verified by the higher values for COD (2.1-fold), DOC (1.7-fold), DIC (1.5-fold) and TSS (5.1-fold). Thus, despite the operational conditions being similar to those previously applied for UWW1, in fact, there was a considerable decrease in the specific ozone dose in the treatments with UWW2, which affected the abatement of the CECs. The specific ozone doses for UWW2 were 0.29, 0.35, and 0.70 g $O_3$ $g^{-1}$ DOC (tests #13, #14 and #15, respectively), which in relation to analogous tests with UWW1 represents a decrease of about 20 % for tests with $[O_3]_{G,inlet}$ of 30 and 40 g $Nm^{-3}$ and 40 % for $[O_3]_{G,inlet}$ of 200 g $Nm^{-3}$. Typically, the specific ozone dose used in WWTPs is between 0.1 and 1.7 g $O_3$ $g^{-1}$ DOC (Kharel et al., 2021), which is within the range of doses applied for both wastewaters tested in this work.

After ozonation, some physicochemical parameters of UWW1 and UWW2 were also improved (Table 2). DOC was reduced by 25 % and 31 %, COD by 43 % and 56 %, and TSS by 49 % and 66 % for UWW1 (1.17 g $O_3$ $g^{-1}$ DOC) and UWW2 (0.70 g $O_3$ $g^{-1}$ DOC), respectively. In this regard, von Gunten (von Gunten, 2018) indicates that the natural organic matter (NOM) is usually the main consumer of $O_3$ in wastewater, which justifies the differences between the results obtained for the two UWW. However, the DOC removal and the modification of chemical structures by ozonation greatly depend on the composition of the NOM (Phan et al., 2022), but generically results in NOM becoming more bioavailable and that can be subsequently biodegraded or removed by a simpler process (Zhang et al., 2019). The mineralization degree obtained in this work was higher than that indicated by Sauter et al. (Sauter et al., 2021), with DOC decreasing around 5 % when applying 0.65 g $O_3$ $g^{-1}$ DOC, and Nöthe et al. (Nöthe et al., 2009), who showed an average DOC decrease between 4 and 10 % after ozonation with 0.4–0.8 g $O_3$ $g^{-1}$ DOC. Differences in the wastewater matrices can lead to variations in the mineralization degree since it will influence the amount of OH• produced and scavenger effects.

Among the micronutrients analyzed (Table 2), the vast majority had concentrations similar to those found before the ozonation treatment. For UWW2, it was possible to observe that ozonation promoted an increase in nitrate concentration (Table 2); this may be attributed to ammonia consumption. According to Singer and Zilli (Singer and Zilli, 1975), ammonia is oxidized completely to nitrate by ozone ($NH_3 + 4O_3 \rightarrow NO_3^- + 4O_2 + H_2O + H^+$). The oxidation process is first-order in terms of ammonia concentration, and the rate increases with pH in the range of pH 7–9 (Singer and Zilli, 1975). Furthermore, several studies using ozone microbubbles (Singer and Zilli, 1975; Yang et al., 1999; de Vera et al., 2017) concluded that the increase in nitrate concentration is related to the oxidation of ammonia by ozone.

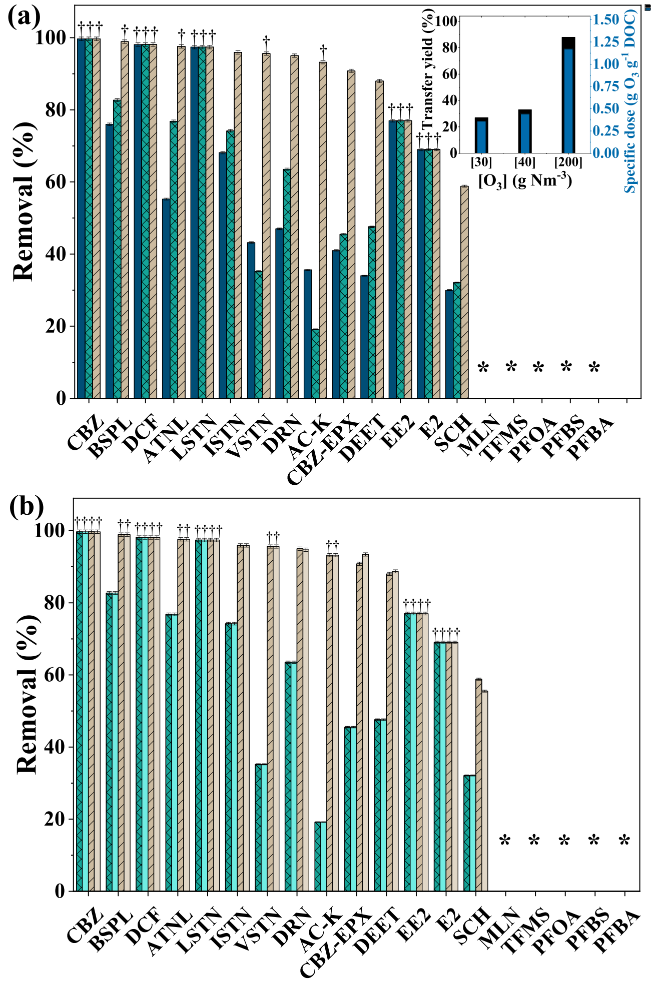


**Fig. 3.** Removal efficiency (%) of the 19 target CECs spiked in UWW1 ($[CECs]_0$ = 10 μg $L^{-1}$) applying a $D_{A\text{-}O3}$ of 18 g $m^{-3}$ under (a) different ozone inlet concentrations ( ) $[O_3]_{G,inlet}$ = 30 g $Nm^{-3}$ (test #9), ( ) $[O_3]_{G,inlet}$ = 40 g $Nm^{-3}$ (test #4) and ( ) $[O_3]_{G,inlet}$ = 200 g $Nm^{-3}$ (test #10); and (b) photocatalytic ozonation of ( ) $[O_3]_{G,inlet}$ = 40 g $Nm^{-3}$ + UVC/$TiO_2$ (test #11) and ( ) $[O_3]_{G,inlet}$ = 200 g $Nm^{-3}$ + UVC/$TiO_2$ (test #12). The inset of Fig. 3a shows the ozone transfer yield (%) and specific ozone dose (g $O_3$ $g^{-1}$ DOC) employed. NOTE: For details on operational conditions of each test, please refer to Table 3. * No removal. † Limit of quantification, Table S3.

### 3.2. Efficiency of ozone membrane contactor for microbiological inactivation

#### 3.2.1. Total heterotrophs, enterobacteria and enterococci

The performance of ozonation in terms of bacterial inactivation greatly depends on the susceptibility of the target bacterium to $O_3$, the $O_3$ concentration, wastewater pH and NOM content (Iakovides et al., 2021). Therefore, the total heterotrophs, enterobacteria and enterococci were enumerated before and immediately after some selected ozonation (standalone process) treatments for UWW1 (tests #4, #7 to #11, Fig. 5a) and UWW2 (tests #13 to #15, Fig. 5b). All the selected tests applied a $D_{A\text{-}O3}$ of 18 g $m^{-3}$, which is in line with the $D_{A\text{-}O3}$ between 1 and 35 g $m^{-3}$ use in WWTPs for disinfection purposes (Xu et al., 2002). There was no need to enrich the wastewater with microorganisms, as the original untreated UWW samples showed the presence of target bacteria at quantifiable levels: UWW1 ($Log_{10}$ CFU/100 mL) – 6.93 ± 0.02, 6.45 ± 0.02, 1.71 ± 0.02, and UWW2 ($Log_{10}$ CFU/100 mL) - 8.33 ± 0.03, 6.01 ± 0.08, 4.96 ± 0.02, for total heterotrophs, enterobacteria and enterococci, respectively.

For UWW1, a good removal of the target bacterial groups was globally observed after ozonation (Fig. 5a), with log reductions >4 units for total heterotrophs (test #10, $[O_3]_{G,inlet}$ of 200 g $Nm^{-3}$) and values below the limit of detection (LOD of 0.33 × $10^{-2}$ CFU $mL^{-1}$) for enterobacteria (from $[O_3]_{G,inlet}$ ≥ 40 g $Nm^{-3}$; test #4) and enterococci (from $[O_3]_{G,inlet}$ ≥ 30 g $Nm^{-3}$; test #9). The total heterotrophs were not completely removed even when the highest $[O_3]_{G,Inlet}$ was applied (Fig. 5a.1), being quantified at approximately $10^3$ CFU 100 $mL^{-1}$ (10 CFU $mL^{-1}$).

Several studies have regarded pH as the main effective parameter of $O_3$ efficiency for microorganisms inactivation (Foroughi et al., 2022). It is well-known that the effect of pH on the disinfection performance of $O_3$ is multi-faceted, as the influence of pH is a trade-off status (Pak et al., 2016); high pH values reduce the concentration of $O_3$, but on the other hand, it generates more OH• radical species. The present study observed that the lower the pH, the greater the removal efficiency of total heterotrophs (test #7, Fig. 5a.1). It suggests that ozonation is efficient against total heterotrophs inactivation at low pH conditions (pH = 5.0) where molecular $O_3$ is the predominant species. In another study, Zuma et al. (Zuma et al., 2009) described that the kinetics of *E. coli* removal occurred twice as fast at acidic pH (pH 4.9) than at basic pH (pH 9.2). Also, Pak et al. (Pak et al., 2016) reported that the ARB removal efficiencies at pH 6 were higher than those at pH 9. It is possible to hypothesize that OH• scavengers, such as bicarbonate ions in microbial cells, may quench the free radical reaction (Zuma et al., 2009).

The inactivation of microorganisms can be further enhanced using the synergic effect of $O_3$ and UVC. This was verified in test #11, where the addition of UVC radiation led to a further ~1.3 log decrease on the concentration of the total heterotrophs (Fig. 5a.1). Microbial inactivation depends on the effect of irradiation and the interaction of the oxidant with the carbohydrates present in the cell of the microorganism (Yadav et al., 2021). Furthermore, the germicidal effects of UVC are related with DNA damage, and UVC wavelength in the range of 260–270 nm is sufficient for the inactivation of the microorganism even at low residence times (Yadav et al., 2021). So, although there was no improvement regarding the removal of the target CECs for test #11 (as discussed in Section 3.1.4), a clear enhancement of disinfection ability was observed, even with a low residence time and UVC dose.

For UWW2, the highest inactivation values were obtained applying a $[O_3]_{G,inlet}$ of 200 g $Nm^{-3}$ (test #15), where heterotrophs were reduced >5 log units, enterobacteria and enterococci reduced >3 log units (Fig. 5b). As mentioned previously, for similar operational conditions, the specific ozone dose applied in UWW2 was lower than when treating UWW1, globally hindering the treatment efficiency. Furthermore, the microbial load before ozonation was considerably higher for UWW2 when compared to UWW1.

#### 3.2.2. Microbiological regrowth and antibiotic resistance

Another important indicator to assess the efficiency of wastewater disinfection is the regrowth of microorganisms, which is particularly relevant for cases where the treated UWW is stored until reuse. Due to the distinct characteristics of the studied wastewaters and from a conservative perspective, UWW2 was chosen to be tested for microbial regrowth. In agreement with other works (Ribeirinho-Soares et al., 2022; Moreira et al., 2021), the storage for 3 days of $O_3$-treated UWW2 (from test #15) promoted regrowth (Fig. 5b), with a decrease in the regrowth rate with increasing $[O_3]_{G,inlet}$. This result is justified, as disinfection is a process that eliminates only part of the microorganisms or harms some cells, allowing later regrowth, which, in the case of ozonation, may be mainly due to the availability of assimilable organic carbon resulting from the partial degradation of complex organic compounds (Sousa et al., 2017). Indeed, in stored $O_3$-treated UWW2, total heterotrophs, enterobacteria and enterococci density was similar to- or above the pre-treatment levels. This reflects the inability of ozone to provide a residual disinfection effect, which is paramount when reuse for agricultural purposes is intended. Studies showcasing different treatment methods, including UV/$H_2O_2$, UV/chlorine, and solar photo Fenton (Malvestiti and Dantas, 2018; Wang et al., 2014; Ahile et al., 2021), also reported microbial regrowth after treatment. Malvestiti and Dantas (Malvestiti and Dantas, 2018) indicated the occurrence of microbial

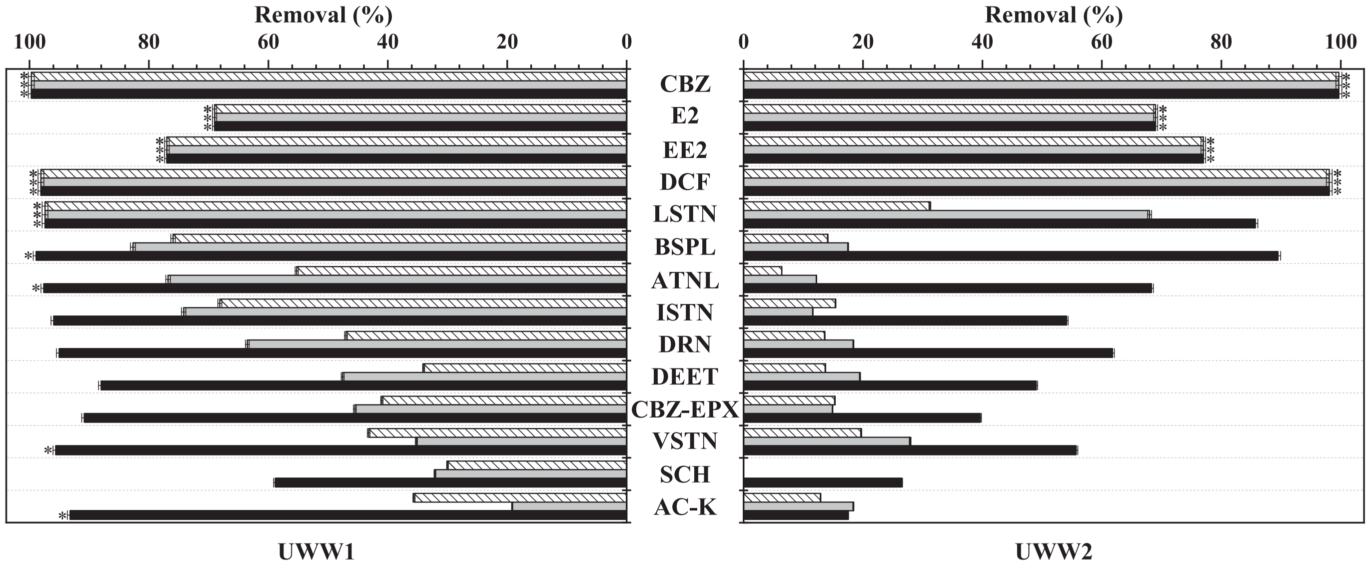


**Fig. 4.** Removal efficiency (%) for target CECs spiked ($[CECs]_0$ = 10 μg $L^{-1}$) in UWW1 and UWW2 applying a $D_{A\text{-}O3}$ of 18 g $m^{-3}$ and different ozone inlet concentrations (■) $[O_3]_{G,inlet}$ = 30 g $Nm^{-3}$ (test #9 and #13), (▒) $[O_3]_{G,inlet}$ = 40 g $Nm^{-3}$ (test #4 and #14) and (▨) $[O_3]_{G,inlet}$ = 200 g $Nm^{-3}$ (test #10 and #15). NOTE: For details on operational conditions of each test, please refer to Table 3. ∗Limit of quantification, Table S3.

regrowth after treatments with $O_3$, $O_3/H_2O_2$, and $UV/H_2O_2$, although ozonation yielded greater regrowth compared to the last two treatments. It is widely acknowledged that bacteria possess repairing mechanisms, which means that they can reactivate themselves even after being inactivated due to damages inflicted on their structure by the treatments.

The removal of enterobacteria harboring resistance to three antibiotics (amoxicillin (AMX), cefotaxime (CTX) and sulfamethoxazole (SUL)) was observed immediately after treatment for the tested $O_3$ concentrations, with log reduction values ranging from 2.6 for AMX to 3.1 for SUL (Fig. 5c). Some authors observed ARB inactivation values below the LOD using ozonation or other AOPs, but these works presented contact times much higher than the present study (≥15 min) (Iakovides et al., 2021; Czekalski et al., 2016). For example, Czekalski et al. (Czekalski et al., 2016) demonstrated that the concentration of total heterotrophs carrying resistance to SUL, trimethoprim (TMP), and tetracycline (TC) in effluents treated with conventional activated sludge and subjected to bench-scale ozonation (specific ozone dose: >0.5 g $O_3$ $g^{-1}$ DOC; contact time: >30 min) was below the LOD. Zheng et al. (Zheng et al., 2017) explored the effectiveness of bench-scale ozonation in batch mode to inactivate total heterotrophs carrying resistance to TC and SUL. Their findings showed that a $D_{A\text{-}O3}$ of 2 g $m^{-3}$ and contact time of 10 min resulted in a significant reduction of TC- and SUL -resistant bacteria, while higher $D_{A\text{-}O3}$ were required for efficient inactivation of total cultivable bacteria. Ahmed et al. (Ahmed et al., 2021) conducted a study on a modified photo-Fenton process that utilized ethylenediamine-N,N′-disuccinic acid (EDDS) to chelate iron(III) and maintain a neutral pH range during the simultaneous removal of ARB, ARG, and CECs. Their results demonstrated that a small dosage of 0.1 mM Fe(III), 0.2 mM EDDS and 0.3 mM $H_2O_2$ effectively reduced ARB by 6-log within 30 min and e-ARGs by 6-log within 10 min.

### 3.3. Toxicity screening with zebrafish embryo bioassays

All the zebrafish embryo bioassays met the OECD FET test 236 criteria: overall survival and hatching rate in the control at 96 hpf were ≥ 90 % (OECD, 2013). Mortality, total abnormalities, and heart rate were determined in zebrafish embryos exposed to the three conditions – UWW2 fortified with the 19 CECs before ozonation (UWW + CECs), after ozonation test #15 (UWW + CECs + $O_3$) and after ozonation test #15 followed by GAC (UWW + CECs + $O_3$ + GAC) - with undiluted samples (Table S4) and with dilution factors of 2 and 4 (Fig. 6).

The undiluted samples showed high toxicity to zebrafish embryos, with significant mortality and total abnormalities observed in all three conditions (Table S4). In the case of the samples with the dilution factor of 2, significant mortality and a substantial decrease in the heart rate were observed in UWW + CECs and UWW + CECs + $O_3$ treatments after 72 hpf exposure. Moreover, a significant increase in total abnormalities was recorded for the UWW + CECs and UWW + CECs + $O_3$ treatments from 24 hpf and 72 hpf of exposure, respectively (Fig. 6b.1). Even though the ozonation process was effective in eliminating the parental compounds added to the effluent, as described in Section 3.1, the toxicity observed in the UWW + CECs + $O_3$ treatment is potentially related to the generation of toxic transformation products resulting from the degradation of the CECs. Regarding dilution factor 4, the toxicity was substantially reduced in all conditions, only the UWW + CECs condition showed a significant decrease of heart rate at 72 and 96 hpf (Fig. 6b.2). It should be mentioned that a fixed standard dilution factor of 10 is frequently used in risk assessment studies for effluents entering in the receiving waters (European Chemicals Bureau, 2003). Notwithstanding, it has been verified that this may not be the case for many locations, so the chosen dilution factor in bioassays can many times lead to the underestimation of environmental risks, especially during low flow conditions of receiving water (Link et al., 2017).

Considering that in WWTPs a post-treatment stage is currently applied after ozonation (Kienle et al., 2022), an adsorption step with GAC was used to complement the ozonation treatment (Fig. S1), targeting the removal of CECs recalcitrant to ozonation, degradation by-products and subsequent decrease of the effluent toxicity. As expected, all CECs after ozonation and GAC adsorption showed concentration values below the LOQ (Table S3). The characterization of the ozonated UWW2 after GAC also shows a good reduction in the organic load (Table 2; 56 % for DOC, 61 % for $SUVA_{254}$, 80 % for COD, 72 % for TSS compared to UWW2 after ozonation). Regarding the toxicity results, all the endpoints mentioned above returned to control levels after the ozonation was coupled with the GAC adsorption process, so no significant differences were observed between the control and the UWW + CECs + $O_3$ + GAC treatment in all observation time points (Fig. 6). Therefore, ozonation coupled with GAC adsorption increased the fitness of zebrafish embryos leading to a significant decrease of the toxicity.

## 4. Conclusions

A low-footprint tubular membrane ozonation contactor system, operated in continuous mode, was applied for the tertiary treatment of UWW

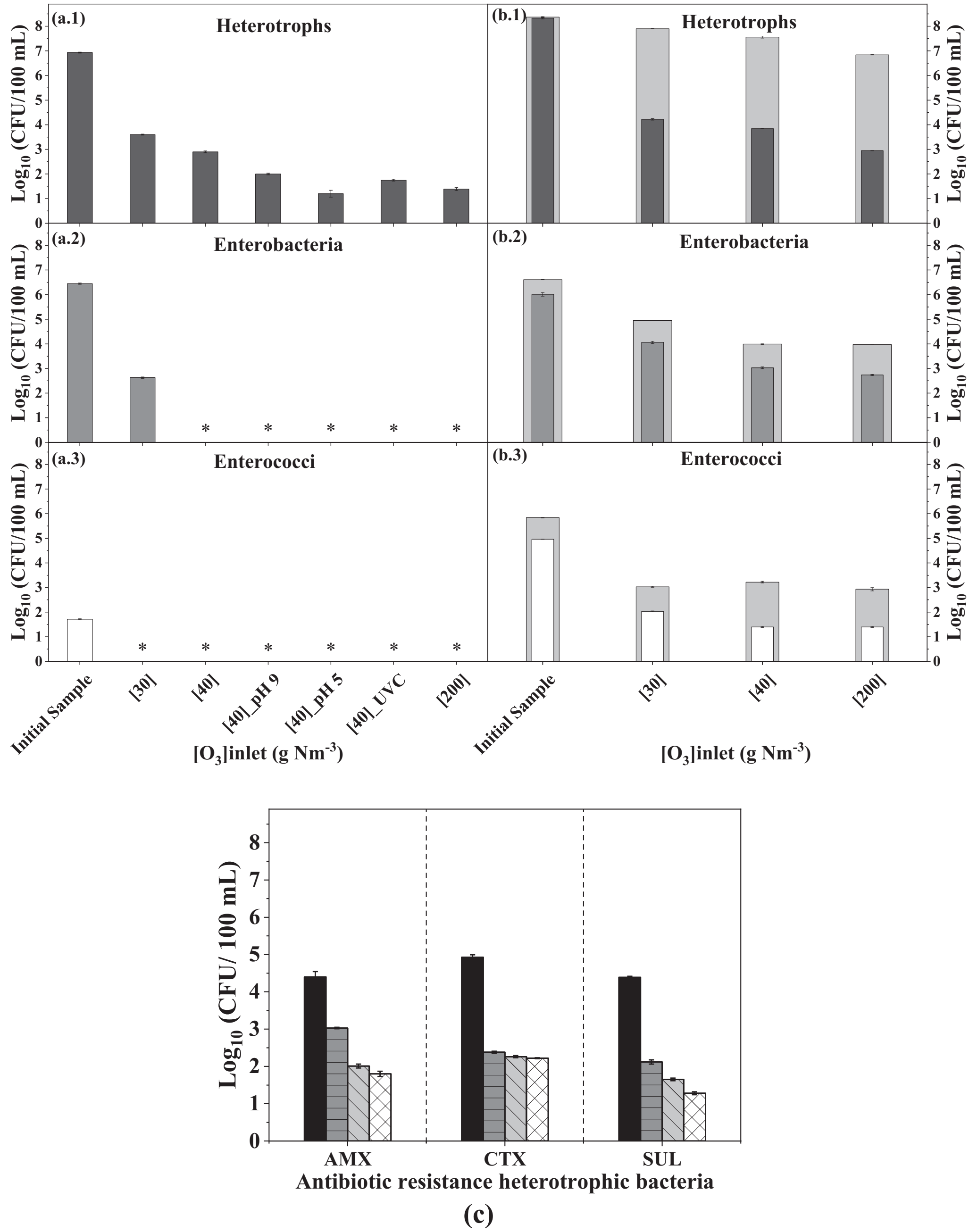


**Fig. 5.** Quantification in (a) UWW1 and (b) UWW2 of total heterotrophs (.1), enterobacteria (.2) and enterococci (.3), before and after selected ozonation tests, and (c) quantification of antibiotic resistant enterobacteria (AMX – Amoxicillin; CTX – Cefotaxime; SUL – Sulfamethoxazole) for ozonation tests with UWW2 (▬ - initial sample) applying a $D_{A\text{-}O3}$ of 18 g $m^{-3}$ and different ozone inlet concentrations (▤) $[O_3]_{G,inlet}$ = 30 g $Nm^{-3}$ (test #13), (▨) $[O_3]_{G,inlet}$ = 40 g $Nm^{-3}$ (test #14) and (▩) $[O_3]_{G,inlet}$ = 200 g $Nm^{-3}$ (test #15). In graph (b) the bars in the background refer to the regrowth test. *Below the detection limit (3.3 × $10^{-3}$ CFU $mL^{-1}$).

and demonstrated the ability to significantly reduce CECs and bacterial contamination, improving the overall physicochemical quality of the effluent. The best performance for this system was obtained for the highest $O_3$ concentration in the gas and lowest gas/liquid volumetric ratio, providing the highest ozone transfer yield (88 %) and, thus, higher specific ozone dose (g $O_3$ per g dissolved organic carbon) boosting the oxidation of the target CECs and disinfection. The seasonal fluctuation of the wastewater characteristics has shown to have an impact on the ozonation treatment efficiency, indicating the importance of adjusting the specific transfer ozone dose, as it considers the organic load of the effluent. Of the 19 target CECs, the four perfluoroalkyl substances and melamine proved to be highly resistant to ozonation. The inclusion of a small dose of UVC radiation (0.10 kJ $L^{-1}$) showed no impact on the oxidation of CECs but led to improvements in the reduction of microbial contamination. Despite the high reductions in total heterotrophs, enterobacteria, and enterococci, this effect was transient, and cells that survived ozonation were able to regrowth back to their initial concentrations, hindering the possible reuse of the $O_3$-treated UWW for irrigation purposes. Ozonation with the present membrane contactor also reduced the abundance but not the presence of ARB in the effluent immediately after treatment. After ozonation, a dilution factor of 4 was shown to be required for no toxic effects to occur on zebrafish embryos, being reduced to a dilution factor of 2 if a post-treatment by GAC adsorption is coupled. Future studies are still in demand to establish the cost and life cycle assessment associated with this membrane ozonation system

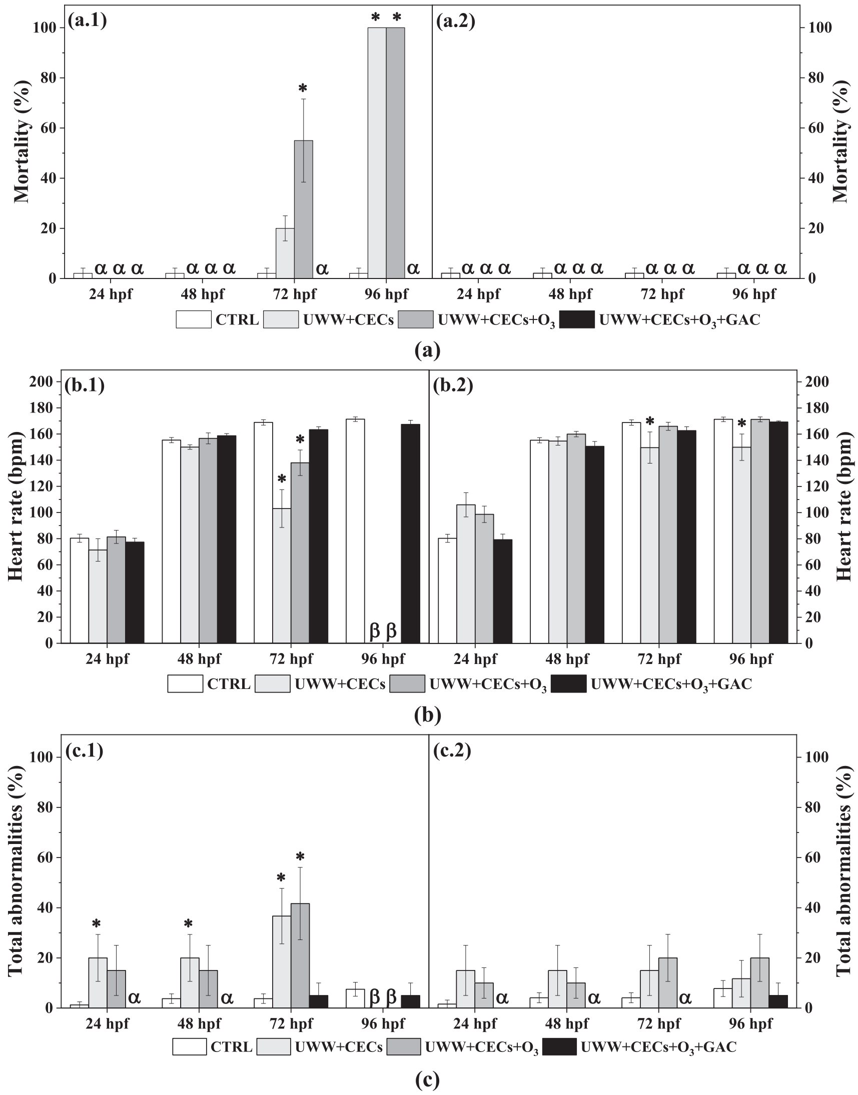


**Fig. 6.** Toxicological effects observed in zebrafish embryos exposed to three conditions with a dilution factor of 2 (.1) and 4 (.2): UWW2 fortified with 19 CECs before and after the ozonation process (UWW + CECs and UWW + CECs + $O_3$, respectively), and UWW + CECs after ozonation plus GAC adsorption process (UWW + CECs + $O_3$ + GAC). (a) Mortality (%), (b) Total abnormalities (%) and (c) Heart rate (bpm). Significant differences from control ($p \leq 0.05$) are marked with a symbol (*). The symbol β was used to indicate 100 % mortality (so it was not possible to determine abnormalities) and α to indicate 0 % mortality. Results are expresses as mean ± SE ($n = 10$ for the control and $n = 5$ for the other treatments).

and the best strategy to ensure long-term disinfection. Finally, this ozone membrane reactor allows for the use of other catalysts, including those that can be photo- or ozone-activated to enhance photocatalytic activity.

## CRediT authorship contribution statement

**Pedro H. Presumido:** Conceptualization, Methodology, Investigation, Writing – original draft. **Sara Ribeirinho-Soares:** Methodology, Writing – review & editing. **Rosa Montes:** Methodology, Writing – review & editing. **José Benito Quintana:** Resources, Writing – review & editing. **Rosario Rodil:** Resources, Writing – review & editing. **Marta Ribeiro:** Methodology, Writing – review & editing. **Teresa Neuparth:** Methodology, Writing – review & editing. **Miguel M. Santos:** Resources, Writing – review & editing. **Manuel Feliciano:** Supervision, Writing – review & editing. **Olga C. Nunes:** Methodology, Writing – review & editing. **Ana I. Gomes:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Vítor J.P. Vilar:** Conceptualization, Methodology, Resources, Supervision, Writing – review & editing.

## Data availability

Data will be made available on request.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.164492.

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