

MEMBRO₃X, a Novel Combination of a Membrane Contactor with Advanced Oxidation (O₃/H₂O₂) for Simultaneous Micropollutant Abatement and Bromate Minimization

Tony Merle,[†] Wouter Pronk,[†] and Urs von Gunten^{*,†,‡,§}

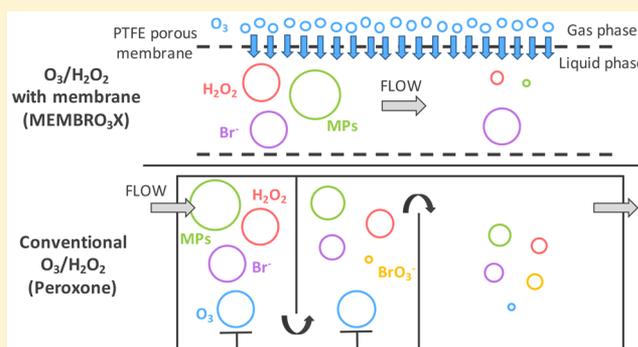
[†]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, 8600 Duebendorf, Switzerland

[‡]School of Architecture, Civil and Environmental Engineering, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

[§]Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, 8092 Zurich, Switzerland

Supporting Information

ABSTRACT: Ozonation is a water treatment process for disinfection and/or micropollutant abatement. However, ozonation of bromide-containing water leads to bromate (BrO₃⁻) formation, a potential human carcinogen. A solution for mitigating BrO₃⁻ formation during abatement of micropollutants is to minimize the ozone (O₃) concentration. This can be achieved by dosing ozone in numerous small portions throughout a reactor in the presence of H₂O₂. Under these conditions, O₃ is rapidly consumed to form hydroxyl radical (•OH), which will oxidize micropollutants. To achieve this goal, a novel process (“MEMBRO₃X”) was developed in which ozone is transferred to the water through the pores of polytetrafluoroethylene (PTFE) hollow fiber membranes. When compared to the conventional peroxone process (O₃/H₂O₂), the MEMBRO₃X process shows better performance in terms of micropollutant abatement and bromate minimization for groundwater and surface water treatment. For a groundwater containing 180 μg/L bromide, a 95% abatement of the ozone-resistant probe compound *p*-chlorobenzoic acid yielded <0.5 μg/L BrO₃⁻, whereas in the conventional peroxone process, 8 μg/L BrO₃⁻ was formed. In addition, the efficacy of the MEMBRO₃X process was demonstrated with river water and lake water.



INTRODUCTION

Ozonation has been applied for decades for disinfection and oxidation of drinking waters and to a lesser extent for wastewater treatment.¹ Bromate (BrO₃⁻) is potentially carcinogenic and regulated in drinking water.^{2,3} Therefore, ozonation of bromide-containing waters has to be optimized for maximal disinfection and/or micropollutant abatement while mitigating bromate formation.^{4–6} The level of bromate formation can be reduced during disinfection with ozone by pH depression, ammonia addition, or prechlorination followed by ammonia addition.^{6,7}

To reduce the level of bromate formation during oxidation of micropollutants, the peroxone process (O₃/H₂O₂) is a possible solution because it accelerates the transformation of ozone (O₃) to hydroxyl radical (•OH) reacting fast with most micropollutants.^{1,4,8} Moreover, hydrogen peroxide (H₂O₂) can reduce hypobromous acid (HOBr), an important bromate formation intermediate, to bromide (Br⁻).⁹ However, in the peroxone process, the oxidation of bromide is controlled by •OH and the further oxidation of Br• to BrO• by O₃ is critical for bromate formation (Figure 1).¹ Bromate cannot be entirely suppressed during the peroxone process; however, because of

the short lifetime of ozone, BrO• and hence bromate formation can be minimized.¹⁰

To further minimize bromate formation during the peroxone process, reactors were developed in which O₃ is injected in small quantities by numerous injection valves/static mixtures to minimize the dissolved ozone concentration.^{11–13} This distribution of very small O₃ doses in combination with H₂O₂ leads to very low dissolved ozone concentrations, which in turn minimizes BrO₃⁻ formation according to the mechanism shown in Figure 1. However, the number of dosing points is limited in the current systems because of system complexity and process control. The number of dosing points can be increased almost infinitely by using membrane pores. Ozone transfer through filtration membranes was previously examined with polymeric,^{14–17} ceramic,^{18–21} or glass membranes.²² However, these previous studies aimed to optimize

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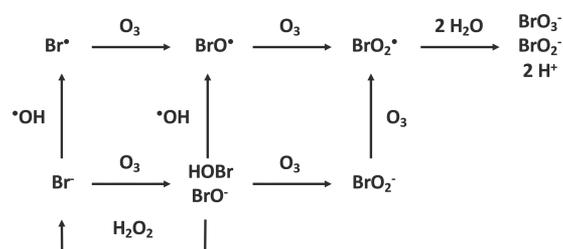


Figure 1. Simplified bromate formation pathway during ozonation and ozone-based advanced oxidation processes (AOPs) adapted from ref 1. Bromate formation in AOPs is controlled by an initial oxidation of bromide by $\bullet\text{OH}$ followed by the oxidation of $\text{Br}\bullet$ by ozone. If the ozone concentration is low as in the peroxone process or even lower as in the MEMBRO₃X process, the level of bromate formation can be significantly reduced.

the O_3 transfer for disinfection or for maximal abatement of micropollutants without considering bromate formation.

The objective of this study was to investigate the efficiency of the peroxone process in a novel membrane ozone contactor for micropollutant abatement and bromate minimization. A laboratory-scale reactor consisting of polytetrafluoroethylene (PTFE) hollow fiber membranes immersed in ozone gas was used to investigate the abatement of the ozone-resistant probe compound *p*-chlorobenzoic acid (*p*CBA) and bromate formation as a function of the ozone and H_2O_2 doses and compared to the conventional peroxone process in a batch reactor.

MATERIALS AND METHODS

Water Qualities. All experiments were performed with three natural waters, with differing dissolved organic carbon (DOC) concentrations and similar pHs and alkalinities (Table 1). The water samples were filtered through $0.45\ \mu\text{m}$ cellulose filters (Sartorius) and stored at $4\ ^\circ\text{C}$ before being used. Before the tests were performed, they were spiked with $100\ \mu\text{g L}^{-1}$ Br^- to simulate an elevated bromide level and with $0.5\ \mu\text{M}$ *p*CBA as a target compound to assess $\bullet\text{OH}$ reactions.

Table 1. Characteristics of the Waters Tested with MEMBRO₃X and the Conventional Peroxone Processes

	pH	DOC (mg of C L ⁻¹)	Br ⁻ ($\mu\text{g L}^{-1}$)	alkalinity (mM HCO ₃ ⁻)
Groundwater (Hardwald)	8.1	0.48	180 ± 4	3.1
River water (River Rhine)	8.1	1.47	205 ± 4	3.3
Lake water (Lake Greifensee)	8.4	3.60	140 ± 8	4.0

Analytical Methods. *p*CBA and bromate were measured by liquid chromatography/diode array detection and ion chromatography/mass spectrometry methods, respectively (see Text S1 for more details).

Tests with the MEMBRO₃X Process. The experimental setup consists of PTFE hollow fiber membranes (Polymem) immersed in a glass reactor continuously flushed with an ozone/oxygen gas mixture (Figure 2). Because of the hydrophobic character of the membranes, water flows only inside the membrane fibers (i.e., without permeation) and the membrane pores are filled with ozone gas. Ozone transfer through the membrane to the liquid phase is controlled by

chemical reactions occurring at the gas–liquid interface. Experiments were performed with ozone gas concentrations of $\leq 10\ \text{g Nm}^{-3}$, and the feed solutions were spiked with bromide and H_2O_2 ($0.35\text{--}5.67\ \text{mg L}^{-1}$) prior to entering the membranes. To achieve ozone gas concentrations of $< 5\ \text{g Nm}^{-3}$, dilution with pure oxygen was necessary. A concentrated solution of Na_2SO_3 was continuously injected downstream from the reactor to quench residual ozone. More specifications about the differing parts of this setup are given in Text S2.

Tests with the Peroxone Process ($\text{O}_3/\text{H}_2\text{O}_2$). Conventional peroxone experiments were performed in glass vials filled with 20 mL solutions containing H_2O_2 ($0.35\text{--}5.67\ \text{mg L}^{-1}$) prior to injection of an ozone stock solution²³ ($60 \pm 5\ \text{mg L}^{-1}$), yielding ozone doses of $0.2\text{--}2\ \text{mg L}^{-1}$. The vials were stirred during ozone addition and then stored in the dark at ambient temperature for $\geq 12\ \text{h}$ until ozone had been completely depleted. Samples were stored at $4\ ^\circ\text{C}$ afterwards prior to analyses.

RESULTS AND DISCUSSION

Effect of $[\text{O}_3]_g$, $[\text{H}_2\text{O}_2]$, and Residence Time on MEMBRO₃X Performance for Groundwater Treatment.

To understand the efficacy of the MEMBRO₃X process in terms of $\bullet\text{OH}$ production, *p*CBA was selected as a target compound because of its high reactivity with $\bullet\text{OH}$ ($k_{\bullet\text{OH}} = 5 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$) and low reactivity with O_3 ($k_{\text{O}_3} \leq 0.15\ \text{M}^{-1}\ \text{s}^{-1}$).²⁴

Figure 3 shows the abatement of *p*CBA and BrO_3^- formation for differing liquid residence times, differing O_3 gas concentrations, and two H_2O_2 doses (i.e., 0.71 and $5.67\ \text{mg L}^{-1}$). The extent of *p*CBA abatement increased from 36 to 75% with contact times from 7 to 48 s, respectively, for an O_3 gas concentration of $1.0\ \text{g Nm}^{-3}$ and a H_2O_2 dose of $0.71\ \text{mg L}^{-1}$ (Figure 3a). The enhanced abatement for longer residence times is caused by higher extents of $\bullet\text{OH}$ exposure. In parallel, the extent of O_3 exposure also increased, which is reflected by increasing BrO_3^- concentrations from 0.2 to $2.3\ \mu\text{g L}^{-1}$ for the same conditions (Figure 3b). The level of BrO_3^- formation increases to $59\ \mu\text{g L}^{-1}$ for an O_3 gas concentration of $10\ \text{g Nm}^{-3}$ and the longest residence time. Under these conditions, the drinking water standard for BrO_3^- ($10\ \mu\text{g L}^{-1}$) was even exceeded for the shortest residence time.

For contact times of $\leq 37\ \text{s}$, a 90% abatement of *p*CBA was observed for a H_2O_2 dose of $5.67\ \text{mg L}^{-1}$ and an O_3 gas concentration of $\geq 1\ \text{g Nm}^{-3}$ (Figure 3c), while at least $5\ \text{g Nm}^{-3}$ was necessary to achieve the same abatement with $0.71\ \text{mg L}^{-1}$ H_2O_2 (Figure 3a). Unexpectedly, higher concentrations of BrO_3^- were observed for all treatment conditions at the higher H_2O_2 level (Figure 3d). Because the MEMBRO₃X process does not require pressure, O_3 transfer is controlled by only diffusion and the reaction near the surface inside the membrane. Thus, if the concentration of one reactant (e.g., H_2O_2) increases in the aqueous phase, the consumption of O_3 at the gas–liquid interface becomes more important, thereby enhancing O_3 transfer. This leads to better *p*CBA abatement and enhanced bromate formation. Comparable results leading to the same conclusions were obtained for H_2O_2 concentrations of 0.35 and $1.42\ \text{mg L}^{-1}$ (Figure S1).

Overall, an O_3 gas concentration of $0.5\ \text{g Nm}^{-3}$ was optimal. BrO_3^- concentrations were below the LOQ for all contact times, and the level of *p*CBA abatement was $\sim 95\%$ for a contact time of 290 s (Figures 3c, d). For an O_3 gas concentration of $0.5\ \text{g Nm}^{-3}$, the maximal O_3 concentration in the water at 20

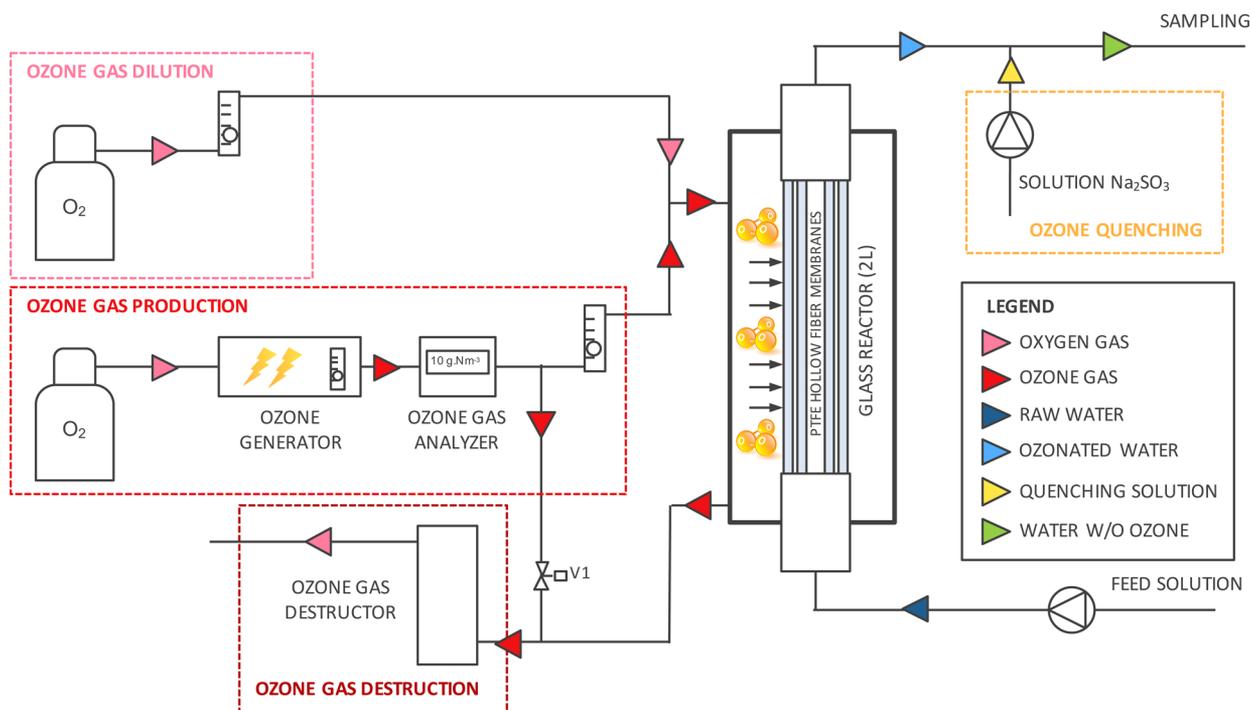


Figure 2. Scheme of the MEMBRO₃X process at laboratory scale. PTFE hollow fiber membranes were placed in a glass reactor fed with an ozone/oxygen gas mixture. The water flows inside the fibers without permeation through the membranes, while ozone gas diffuses through the membranes by a chemically driven transfer. Downstream from the reactor, residual ozone is quenched with SO₃²⁻.

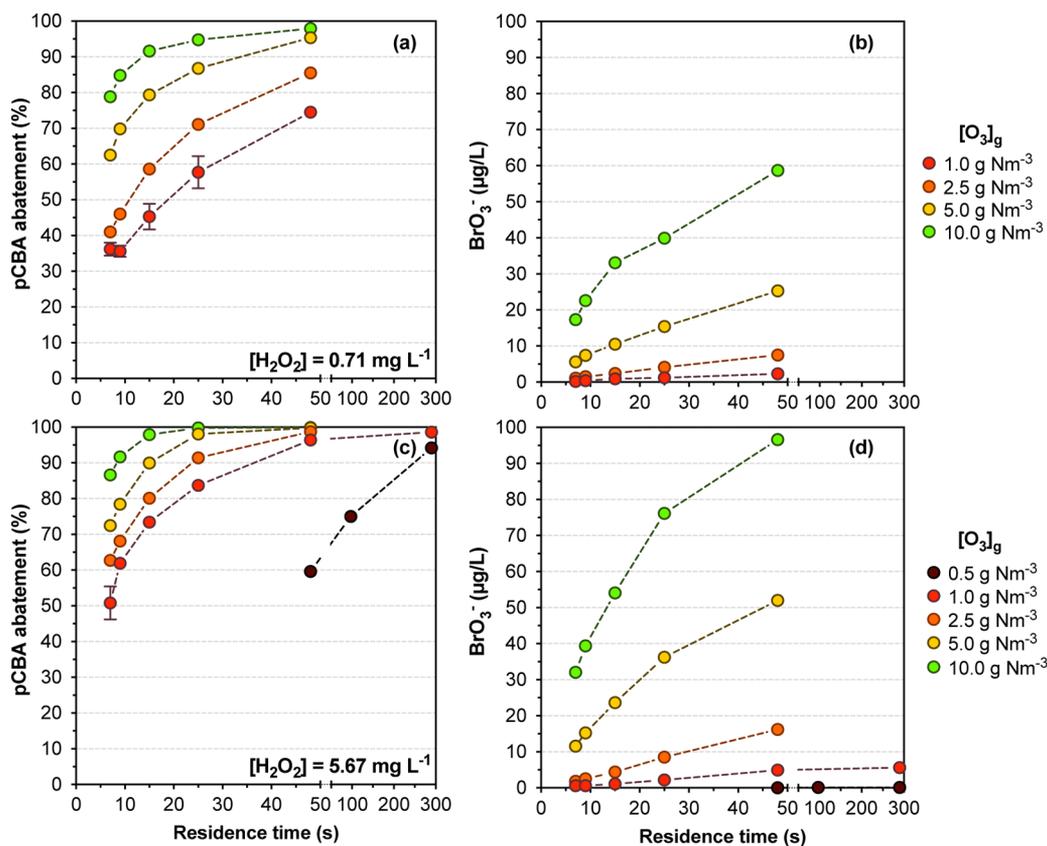


Figure 3. Treatment of groundwater (pH 8.1, [DOC] = 0.48 mg of C L⁻¹, [Br⁻] = 180 ± 4 µg L⁻¹, [HCO₃⁻] = 3.1 mM) by the MEMBRO₃X process. Effect of the residence time and the ozone gas concentration on (a and c) abatement of pCBA and (b and d) bromate formation. Conditions: 20 °C, [O₃]_g = 0.5, 1.0, 2.5, 5.0, and 10 g Nm⁻³, [H₂O₂] = 0.71 (a, b) or 5.67 mg L⁻¹ (c, d).

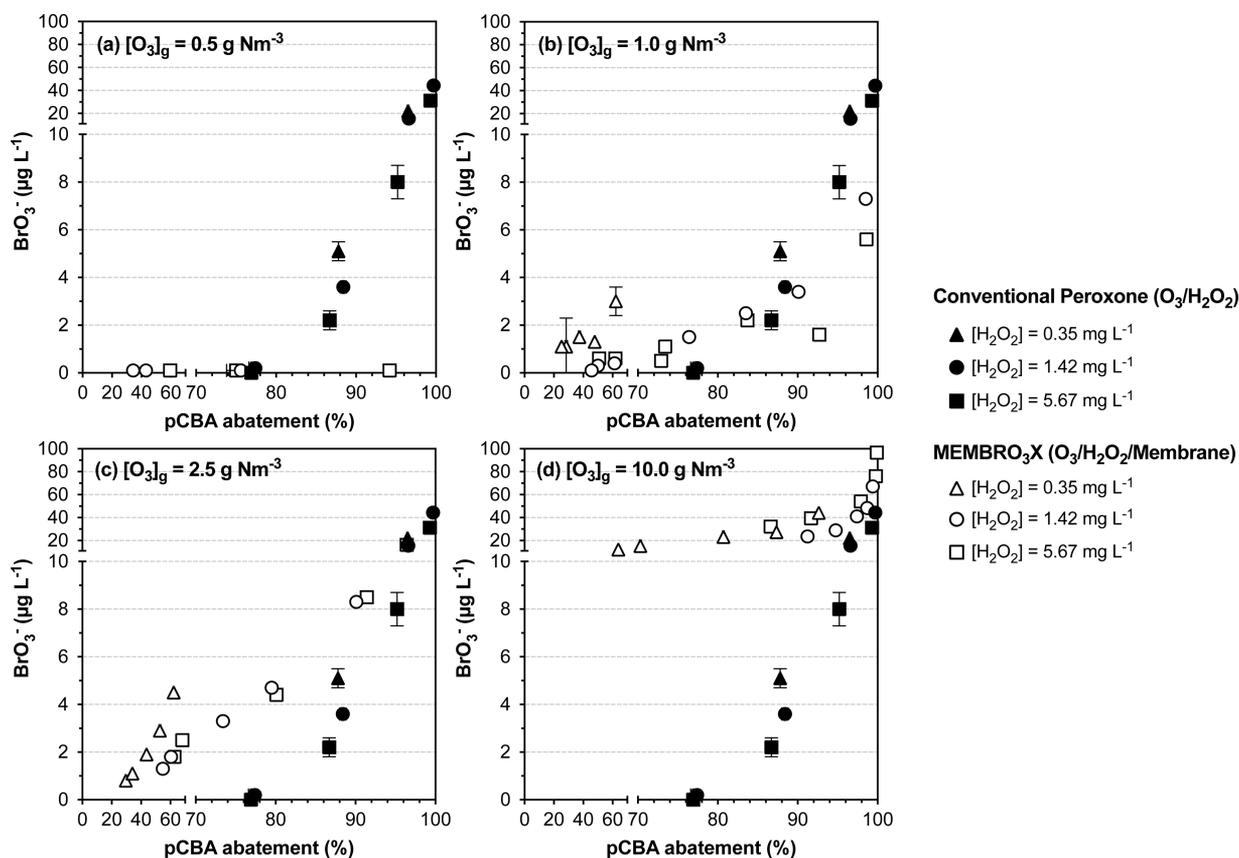


Figure 4. Comparison of the efficacy of the MEMBRO₃X and the conventional peroxide (O₃/H₂O₂) processes for *p*CBA abatement and bromate formation. Conditions: groundwater (pH 8.1, [DOC] = 0.48 mg of C L⁻¹, [Br⁻] = 180 ± 4 µg L⁻¹, [HCO₃⁻] = 3.1 mM), 20 °C, [H₂O₂] = 0.35, 1.42, and 5.67 mg L⁻¹. For the MEMBRO₃X process, [O₃]_g = (a) 0.5, (b) 1.0, (c) 2.5, and (d) 10.0 g Nm⁻³. For the conventional peroxide process, the ozone doses were 0.2, 0.5, 1.0, and 2.0 g Nm⁻³.

°C is ≤0.12 mg of O₃ L⁻¹.²⁵ The steady-state ozone concentration at the boundary layer near the membrane surface becomes even lower because of its H₂O₂-induced transformation to •OH. While these treatment conditions require the longest contact times for abatement of *p*CBA (300 s), the level of bromate formation can be kept very low. Therefore, the extent of micropollutant abatement could be adjusted by the liquid residence time with an upper limit of 10 min.

Comparison between the MEMBRO₃X and Conventional Peroxide Processes for Groundwater. MEMBRO₃X performance was compared to that of the conventional peroxide process (O₃/H₂O₂) as a benchmark. Because the transferred ozone dose through the membrane cannot be quantified from the liquid phase (because of the chemical reactions) or from the gas phase (because of an excess of O₃ gas), *p*CBA abatement was plotted versus bromate formation to assess the overall process performance for differing reaction times, ozone doses, and H₂O₂ concentrations for both processes (Figure 4). For the conventional peroxide process, the overall performances improved with larger H₂O₂ doses. For a 90% *p*CBA abatement, 10.3, 5.9, and 4.5 µg L⁻¹ BrO₃⁻ were formed for H₂O₂ doses of 0.35, 1.42, and 5.67 mg L⁻¹, respectively.

Paired *p*CBA–BrO₃⁻ concentration plots for the MEMBRO₃X process showed that large H₂O₂ doses (5.67 mg L⁻¹) were required because the *p*CBA abatement was less efficient for smaller H₂O₂ doses (e.g., 0.35 mg L⁻¹) (Figure 4). Because the ozone transfer in the MEMBRO₃X process is chemically

driven, it is expected to be higher for higher H₂O₂ concentrations, yielding an improved *p*CBA abatement. Overall, levels of BrO₃⁻ formation for comparable *p*CBA abatements were significantly lower than those of the conventional peroxide process for O₃ gas concentrations of ≤1.0 g Nm⁻³ (Figure 4a). For an O₃ concentration of 1.0 g Nm⁻³ and a H₂O₂ dose of 5.67 mg L⁻¹ (Figure 4b), the MEMBRO₃X process achieved 98% *p*CBA abatement with a formation of ~6 µg L⁻¹ BrO₃⁻, whereas ~29 µg L⁻¹ BrO₃⁻ was formed via the conventional peroxide process. However, for <85% *p*CBA abatement, the level of BrO₃⁻ formation was lower with the conventional peroxide process. When the O₃ gas concentration was increased to 10.0 g Nm⁻³, the level of diffusion of O₃ through the membrane was too high and the conventional peroxide process provided better performances for any conditions (Figures 4c, d). These process limitations must be taken into account for practical applications.

MEMBRO₃X Process Performance with River and Lake Water. The MEMBRO₃X performance was also tested with a river water and a lake water (Table 1) to elucidate the influence of the water matrix [mainly dissolved organic matter (DOM)].

Figure 5 shows a better performance of the MEMBRO₃X process (H₂O₂ dose of 5.67 mg L⁻¹) for the river water compared to the conventional peroxide process for >80% *p*CBA abatement. This corresponds to a residence time of >20 s. For H₂O₂ doses ≤1.42 mg L⁻¹, there is a smaller treatment range, for which the MEMBRO₃X process is beneficial. Only treatment conditions with >90% *p*CBA abatement lead to lower

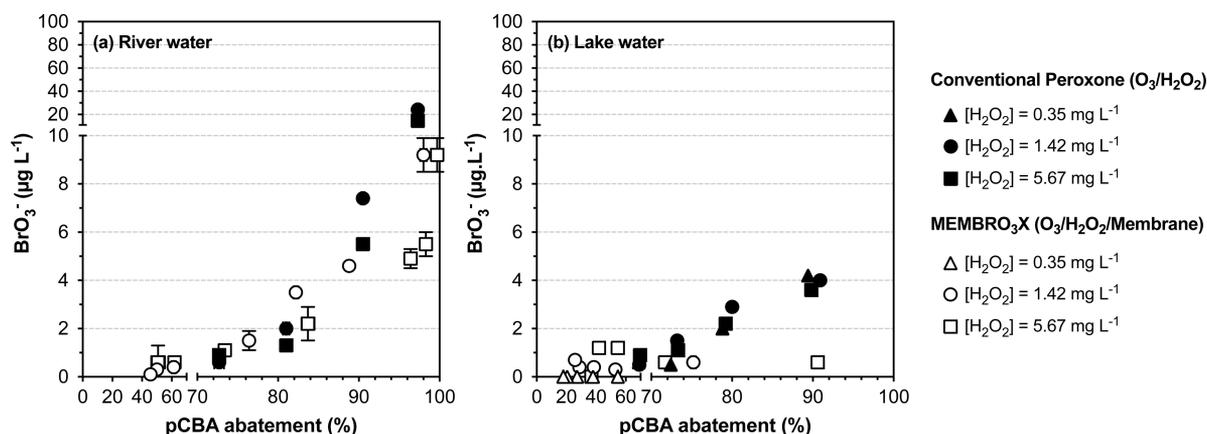


Figure 5. Performances of the MEMBRO₃X and the conventional peroxone (O₃/H₂O₂) processes for pCBA abatement and bromate formation for (a) river water (pH 8.1, [DOC] = 1.47 mg of C L⁻¹, [Br⁻] = 205 ± 4 µg L⁻¹, [HCO₃⁻] = 3.3 mM) and (b) lake water (pH 8.4, [DOC] = 3.6 mg of C L⁻¹, [Br⁻] = 140 ± 8 µg L⁻¹, [HCO₃⁻] = 4.0 mM). Conditions: 20 °C, [H₂O₂] = 0.35, 1.42, and 5.67 mg L⁻¹. For the MEMBRO₃X process: [O₃]_g = 1.0 g Nm⁻³. For the conventional peroxone process, ozone doses of 0.2, 0.5, 1.0, and 2.0 mg L⁻¹.

BrO₃⁻ levels compared to those observed for the conventional peroxone process (i.e., for a residence time of >190 s). Nevertheless, the BrO₃⁻ concentrations never exceeded 10 µg L⁻¹ for the MEMBRO₃X process for any conditions, while up to ~20 µg L⁻¹ was formed in the conventional peroxone process. In addition, the MEMBRO₃X process provided similar results for the river water and the groundwater (Figure 5a), though the DOC concentration in river water was almost 3 times higher than in groundwater. For the conventional peroxone process, the level of BrO₃⁻ formation was lower for river water than for groundwater for a similar pCBA abatement. As shown previously,²⁶ ozone stability and its transient concentration are lower for higher DOC concentrations. Consequently, the level of BrO₃⁻ formation is lower because of a lower level of ozone exposure, whereas the abatement of micropollutants, controlled by •OH, is still significant. This effect is further demonstrated by the data obtained for the lake water for which ≤4 µg L⁻¹ BrO₃⁻ was observed for the conventional peroxone process (Figure 5b). Nevertheless, treatment with the MEMBRO₃X process for 90% pCBA abatement led to an even lower level of BrO₃⁻ formation of 0.5 µg L⁻¹. The MEMBRO₃X process for the lake water is also limited to ozone gas concentrations of ≤5 g Nm⁻³ for a performance that is better than that of the conventional peroxone process (Figure S2).

The key feature of the MEMBRO₃X process is the distribution of the ozone dose over multiple injection points. In ozone-based AOPs, the •OH oxidation of bromide is followed by reaction of Br• with O₃ (Figure 1), which is decisive for BrO₃⁻ formation. Therefore, BrO₃⁻ formation can be limited by keeping the O₃ concentration low, which is achieved by dosing it in small quantities over a membrane contactor and transforming it by H₂O₂- and/or DOM-induced reactions to •OH, reacting with micropollutants.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00061.

A detailed description of analytical methods and setup as well as additional results for the MEMBRO₃X process (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +41 58 765 5270. Fax: +41 58 765 5802. E-mail: vongunten@eawag.ch.

ORCID

Tony Merle: 0000-0002-3051-6249

Notes

The authors declare no competing financial interest.

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