

Optimization of Ozonation and Peroxone Process for Simultaneous Control of Micropollutants and Bromate in Wastewater

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Abstract: The study aims to simultaneously control micropollutants and bromate formations by using ozonation and peroxone process. The batch experiments were run with variations in specific ozone dose (SOD) and hydrogen peroxide-to-ozone (H_2O_2/O_3) ratio. Based on the removal by ozonation and peroxone, micropollutants were categorized to 3 groups: non-reactive compounds (i.e., amidotriazole), moderately reactive compounds (i.e., metoprolol, acesulfame potassium, bezafibrate, and benzotriazole), and highly reactive compounds (i.e., carbamazepine and diclofenac). For ozonation and peroxone process, the removals for highly reactive compounds and moderately reactive compounds were 82-99% and 29-99%, respectively. The removal of amidotriazole was not observed in this study. The effect of ozonation on micropollutant removals was similar to the peroxone process. However, differences in bromate formation were observed. Bromate formation depended on the SOD, while addition of hydrogen peroxide suppressed the bromate formation. The peroxone process at the H_2O_2/O_3 ratio of 0.3 was recommended to bromide-containing water below $100 \mu g.L^{-1}$ for simultaneous control of micropollutants and bromate. Enhancement in micropollutant removals, except for the non-reactive groups was achieved with either higher SOD or addition of hydrogen peroxide to ozonation. The micropollutant removal predicted from the second-order kinetic reaction with ozone and $\bullet OH$ exposures was higher than the observed data.

Keywords: ozonation; peroxone; micropollutants; hydroxyl radical; bromate

Introduction

Occurrence of micropollutants in surface water has led to concern in ecological effects since these compounds are principally made for specific reactivity and functionality to biological system (Schwarzenbach et al., 2006; Ternes and Joss, 2006). Regarding emerging pollutants, an important group is pharmaceuticals such as pain killers, anti-inflammatories or even antibiotics. A removal of pharmaceuticals by a conventional wastewater treatment process (i.e., physical separation and biological treatment process) is ineffective due to the physical and chemical properties and some of them are not susceptible to biodegradation (Reemtsma et al., 2006; Kasprzyk-Hordern et al., 2009). Therefore, an additional treatment technology is necessary for the removal of residual micropollutants.

Ozonation and peroxone process have been known as effective processes to remove recalcitrant compounds (Ikehata et al., 2006). The major reactive oxidants are ozone molecules (O_3) and hydroxyl radicals ($\bullet OH$). For advanced treatment of municipal wastewater, ozonation is usually effective enough for removal of non-biodegradable compounds, while the peroxone process can be used as an additional technique for bromate control (Hübner et al., 2015). Because major oxidant consumers in wastewater are organic compounds, a specific ozone dose (SOD), a ratio between ozone dose and dissolved organic carbon (O_3/DOC), is recommended for a comparison between waters with different DOC concentrations (Reungoat et al., 2012; Lee et al., 2013). Lower SOD may result in an inadequate removal of organic compounds, while higher SOD can cause undesired byproducts (e.g., bromate) (Lee et al., 2016). Bromate ion, a carcinogenic compound, forms when bromide-containing water is ozonated (von Gunten, 2003a; Wildhaber et al., 2015). Thus, identifying an optimum SOD for both control of recalcitrant compounds and bromate is an important step. Bromate formation can be inhibited

1 by hydrogen peroxide (H₂O₂) addition. H₂O₂ rapidly reacts and converts hypobromous acid
 2 (HOBr), the major intermediate for bromate formation, to bromide (von Gunten and Oliveras,
 3 1998). In addition, H₂O₂ can retard a formation of other intermediates (e.g., BrO⁻ and BrO[•]) by
 4 increase in ozone depletion rate (von Gunten, 2003b). Although H₂O₂ is provided during
 5 ozonation, bromate can form through a reaction of •OH with bromide and HOBr (von Gunten,
 6 2003b). Lee et al (2016) reported that H₂O₂ addition generally decreased bromate formation.
 7 Unexpectedly, an increase in bromate formation was observed in some cases, depending on a
 8 molar ratio between H₂O₂ and ozone (H₂O₂/O₃). To minimize bromate exposure, it raises the
 9 question that what H₂O₂/O₃ ratio can be used for bromate suppression? Addition of H₂O₂
 10 benefits not only suppression of bromate, but also enhancement of •OH formation (von Gunten,
 11 2003b). However, an excessive H₂O₂ may exhibit as scavengers for •OH, leading to lower
 12 oxidation capability (Hübner et al., 2015). To provide adequate amount of H₂O₂ for bromate
 13 suppression and maintaining oxidation capability, optimizing the H₂O₂/O₃ ratio is another
 14 solution for achieving simultaneous control of micropollutants and bromate.

15 The objective of the study is to simultaneously control micropollutants and bromate in
 16 wastewater by using ozonation and peroxone process. To determine the optimum SOD, the
 17 SOD was varied between 0, 0.5, 0.7 and 1.0 mgO₃.mgDOC⁻¹. At a SOD of 0.7 mgO₃.mgDOC⁻¹,
 18 various H₂O₂ concentrations were added for studying effect of different H₂O₂/O₃ ratios. The
 19 findings can be used as an operating guideline for controlling micropollutants and bromate at
 20 the same time.

21 22 **Material and Methods**

23 *Chemicals and wastewater*

24 Seven model compounds (metoprolol, benzotriazole, diclofenac, carbamazepine,
 25 acesulfame potassium, amidotrizoate and bezafibrate) were used for representing
 26 micropollutants with different ozone reactivity (Table 1). Amidotrizoate, benzotriazole,
 27 bezafibrate, carbamazepine, and diclofenac were purchased from Sigma-Aldrich. Metoprolol
 28 was purchased from RTC chemical, and acesulfame potassium was supplied from Supelco. All
 29 compounds were dissolved in ethanol and then in deionized water for the preparation of the
 30 calibration curves.
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 32

33 Table 1 Model compounds

Compound	CAS	Company	Formula	MW
Acesulfame potassium	55589-62-3	Supelco	C ₄ H ₄ KNO ₄ S	201,2
Bezafibrate	41859-67-0	Sigma-Aldrich	C ₁₉ H ₂₀ ClNO ₄	361,8
Benzotriazole	95-14-7	Sigma-Aldrich	C ₆ H ₅ N ₃	119,1
Carbamazepine	298-46-4	Sigma-Aldrich	C ₁₅ H ₁₂ N ₂ O	236,3
Amidotrizoate	50978-11-5	Sigma-Aldrich	C ₁₁ H ₉ I ₃ N ₂ O ₄	649,9
Diclofenac	15307-79-6	Sigma-Aldrich	C ₁₄ H ₁₀ C ₁₂ NO ₂ Na	318,1
Metoprolol	37350-58-6	RTC	C ₁₅ H ₂₅ NO ₃ ·C ₄ H ₆ O ₆	267,4

34 Three effluent samples were collected from two different municipal wastewater
 35 treatment plants (A and B) and transported with a 20 L-polyethylene tank. Water characteristics
 36 are presented in Table 2. After collection, they were immediately stored in a refrigerator. Water
 37 was placed at room temperature (23 ± 2 °C) for at least 3 hours to increase temperature before
 38 starting the experiment.
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Table 2 Water characteristics

Parameter	A1	A2	B
pH	7.09	6.95	7.14
DOC (mg.L ⁻¹)	7.1	4.6	4.5
UV254 (cm ⁻¹)	0.195	0.112	0.131
Bromide (µg.L ⁻¹)	246	94	99
Bromate (µg.L ⁻¹)	0	2	1

The ozonation and peroxone process were accessed with batch experiments. A 3-L glass bottle was used for the preparation of the ozone solution. The glass bottle was put in an ice bucket to reduce the water temperature. Ozone stock solution was prepared by injecting ozone gas in deionized water. Ozone gas was produced from an ozone generator (OZ500/5, Fischer Technology) fed with ultrapure oxygen (>99%), and it was continuously injected at the bottom of the ozone stock reactor. At steady state conditions, the ozone concentration was in the range of 39 - 43 mg.L⁻¹. Various volumes of ozone solution were mixed with the water sample in order to adjust the specific ozone doses (O₃/DOC) at 0, 0.5, 0.7 and 1.0 mgO₃.mgDOC⁻¹ (coded as Control, SOD0.5, SOD0.7 and SOD1.0, respectively). For the peroxone process, H₂O₂ was added to the samples before injecting ozone solution, and the O₃/DOC was controlled at 0.7 mgO₃.mgDOC⁻¹. H₂O₂/O₃ ratios were tested at 0.3, 0.5 and 1.0 (coded as AOP0.3, AOP0.5 and AOP1.0, respectively). In addition, the samples were mixed with H₂O₂ solution at the same testing peroxone ratios, but without adding ozone solution (coded as H0.3, H0.5 and H1.0, respectively). The ozone and •OH exposures were examined in ozonation trials. Ozone solution was mixed with the waters in a dispenser bottle, and the first sample was immediately collected after 10 sec. All testing conditions were duplicated.

The dissolved ozone concentration was measured by the indigo colorimetric method (DIN 38408-3). Bromate ion and the seven model compounds were analysed with a high performance liquid chromatograph (Primaide 1210 Auto Sampler, Hitachi High Technologies, USA) combined with a hybrid triple quadrupole/linear trap ion trap mass spectrometer (3200 Q Trap LC/MS-MS, Applied Biosystems, Foster City, CA, USA). The electrospray ionization (ESI) source was operated in a negative and positive-ion mode. *Para*-chlorobenzoic acid (pCBA), a probe compound for •OH, was determined via LC/UV. The •OH exposure was calculated from degradation of pCBA (Equation 1). DOC concentrations were determined in a DOC analyzer (TOC-L CPH, Shimadzu). Ammonium, nitrite and nitrate ions were measured via the continuous flow analyzer-SAN Plus System (Skalar). The absorbance at the wavelength of 254 nm (UV254), an indicator for unsaturated and reactive aromatic bonds, was measured by a UV-Vis spectrophotometer (Dr. Lange – Cadas 100). The oxidation capability for •OH and ozone exposures was calculated from Equation 2. It is worth noting that changes in DOC concentrations after treatment with various SODs and H₂O₂/O₃ ratios were negligible.

$$\frac{d[pCBA]}{dt} = -k_{\bullet OH/pCBA}[pCBA][\bullet OH] \quad (1)$$

$$-\ln \frac{MP}{MP_0} = k_{\bullet OH} \int [\bullet OH] dt + k_{O_3} \int [O_3] dt \quad (2)$$

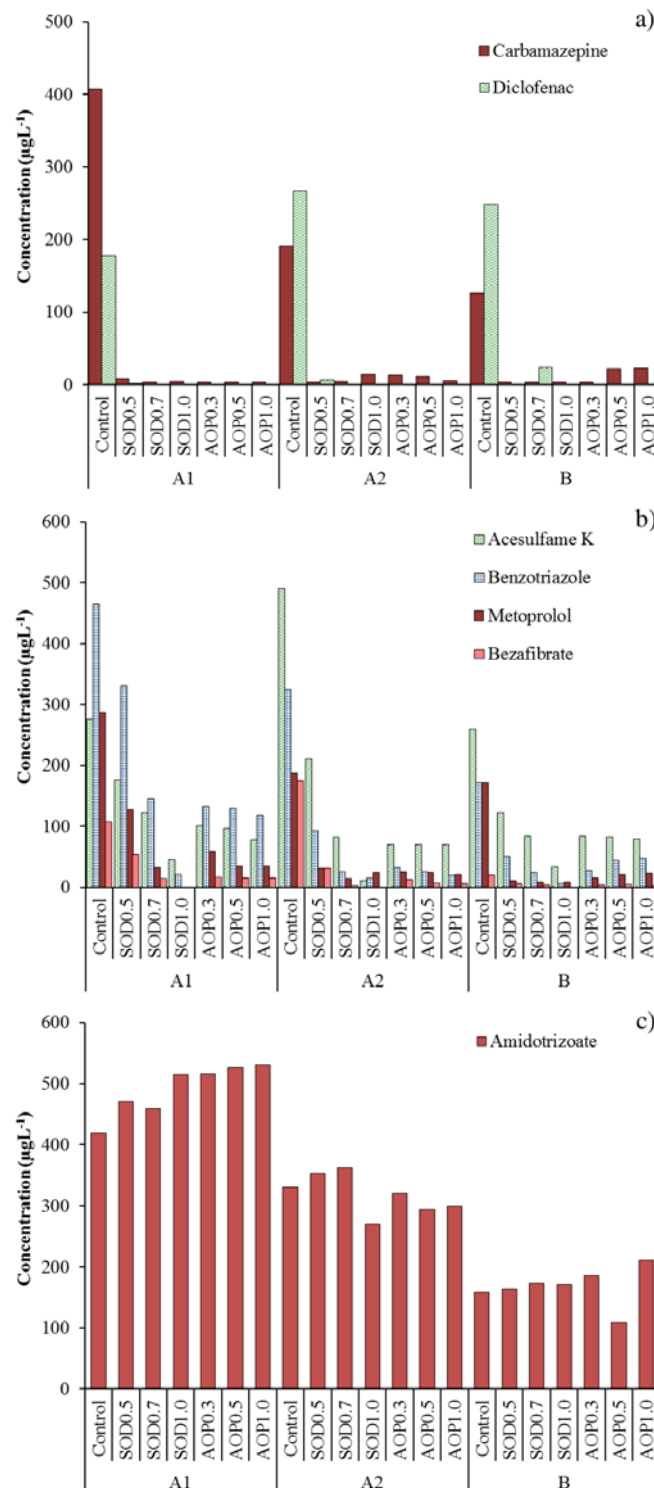
With: MP and MP_0 = a concentration of micropollutant at t time and initial time,
 $k_{\bullet OH/pCBA} = 5 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ (Elovitz and von Gunten, 1999),
 $k_{\bullet OH}$ and k_{O_3} = a reaction constant for ozone and $\bullet OH$, respectively.

Results and Conclusions

Effects of ozonation and peroxone process on micropollutant removal

Most of micropollutants were oxidized after ozonation. Carbamazepine and diclofenac were highly reactive compounds since their removal rate was above 90% (Figure 1a). Previous studies reported that carbamazepine and diclofenac were fast reactive compounds to ozone and $\bullet OH$ (Andreozzi et al., 2002; Ikehata et al., 2006). Their second-order rate constants were reported between 5 and 9 orders of magnitude for the reactions with ozone and $\bullet OH$, respectively (Andreozzi et al., 2002; Huber et al., 2003; Vogna et al., 2004). This highly reactive property resulted in the indifferent removal for high and low DOC waters (i.e; A1, A2, and B). Metoprolol, acesulfame potassium, bezafibrate, and benzotriazole were partially removed by ozonation. Their reaction rate constants with ozone and $\bullet OH$ are 2-4 and 9 orders of magnitude, respectively (Huber et al., 2003; Benner et al., 2008; Leitner und Roshani, 2010; Kaiser et al., 2013). Higher SOD ratios induced a greater reduction of metoprolol, acesulfame potassium, bezafibrate, and benzotriazole, which is the typical pattern for moderately reacting substances. The removals of these compounds were in the range of 29-94% ($\bar{X} \pm SD = 65 \pm 18$), 55-98% ($\bar{X} \pm SD = 82 \pm 12$) and 82-99% ($\bar{X} \pm SD = 92 \pm 7$) for the SOD of 0.5, 0.7 and 1.0 $\text{mgO}_3 \cdot \text{mgDOC}^{-1}$, respectively (Figure 1b). Interference of DOC concentrations on the removal of moderately reactive groups was observed. The removal of moderately reactive compounds in A1 water (high DOC) varied between 29-99% for the applied SOD at 0.5-1.0 $\text{mgO}_3 \cdot \text{mgDOC}^{-1}$, while that in A2 and B water were 53-99%. Specifically, a high DOC concentration (A1) seemed to interfere with the removal of benzotriazole, acesulfame potassium and bezafibrate, compared to low DOC water (A2 and B). The presence of DOC had less impact on the removal of metoprolol since its degradation constant with ozone (k_{O_3}) was as high as 4 orders of magnitude (Benner et al., 2008). Among the used model compounds, the most resistant compound was amidotriazole since the removal was not observed during ozonation at the SOD of 0.5-1.0 $\text{mgO}_3 \cdot \text{mgDOC}^{-1}$. This result was consistent with previous studies who reported the low reactivity of amidotriazole toward ozone molecule and $\bullet OH$ (Ternes et al., 2003; Huber et al. 2005; Kovalova et al., 2013). Interestingly, the amidotriazole concentration increased after the ozonation instead (Figure 1c). The increase in amidotriazole may result from a degradation of conjugate compounds. Based on treatment performance of the ozonation, the targeted compounds were categorized into 3 groups: highly reactive compounds (i.e., carbamazepine and diclofenac), moderately reactive compounds (i.e., metoprolol, acesulfame potassium, bezafibrate, and benzotriazole), and non-reactive compounds (i.e., amidotriazole) (Figure 2).

1 This categorization was similar to several references that use the second-order rate constants
 2 with ozone to group micropollutants (von Gunten, 2003a; Wert et al., 2009; Lee et al., 2013).
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7 **Figure 1** Concentration of micropollutants after ozonation and peroxone process: highly
 8 reactive compounds (a), moderately reactive compounds (b), and non-reactive compounds (c)

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2 The removal of micropollutants by the peroxone process was similar to ozonation. The highly
3 reactive groups were greatly removed by the peroxone process (Figure 1a). The removal for
4 carbamazepine and diclofenac was in the range of 82-99% and over 99%, respectively. For the
5 moderately reactive compounds (i.e., metoprolol, acesulfame potassium, bezafibrate, and
6 benzotriazole), the peroxone process slightly enhanced the reduction by 10-20%, compared to
7 the ozonation at the same SOD ($0.7 \text{ mgO}_3.\text{mgDOC}^{-1}$) (Figure 1b). Variation in $\text{H}_2\text{O}_2/\text{O}_3$ ratios
8 did not significantly change the removal of moderately reactive compounds. The percent
9 reduction of moderately reactive compounds ranged from 61-92% ($\bar{X} \pm \text{SD} = 80 \pm 10$), 65-95%
10 ($\bar{X} \pm \text{SD} = 80 \pm 10$) and 69-96% ($\bar{X} \pm \text{SD} = 89 \pm 9$) for AOP0.3, AOP0.5 and AOP1.0,
11 respectively. Although the reaction rate constant for ozone (k_{O_3}) is much lower than the reaction
12 rate constant for $\bullet\text{OH}$ ($k_{\bullet\text{OH}}$), the ozone exposure is generally predominant in the reaction. Lee
13 et al. (2013) reported that the effect of H_2O_2 addition on micropollutant removals was minor
14 (<10%). The treatability for the peroxone process (AOP0.3-1.0) was lower than the ozonation
15 with the SOD of $1.0 \text{ mgO}_3.\text{mgDOC}^{-1}$. This result was plausibly explained by the high ozone
16 stability in the SOD of $1.0 \text{ mgO}_3.\text{mgDOC}^{-1}$ that induced the greater removal for these
17 moderately reactive compounds since they were reactive to both ozone and $\bullet\text{OH}$. Variations in
18 DOC concentrations seemed to have less effect on the removal of moderately reactive
19 compounds by the peroxone process. This advantage of peroxone process possibly resulted
20 from the fast decomposition of ozone, leading to greater $\bullet\text{OH}$ production. The peroxone process
21 occasionally increased the amidotriazole concentration (Figure 1c). Peroxonation of water with
22 high DOC concentrations (A1) clearly increased the concentration of amidotriazole by 10-23%.
23 For low DOC water (A2 and B), the effect of peroxone process on amidotriazole was ambiguous.
24 This result may be attributed to differences in water characteristics since A2 and B water were
25 collected from different sources.

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27 The removal of micropollutants by H_2O_2 oxidation was minor. H_2O_2 oxidation partially
28 removed both highly-reactive and moderately-reactive compounds (i.e., carbamazepine,
29 diclofenac, metoprolol, acesulfame potassium and bezafibrate). For highly reactive compounds,
30 carbamazepine and diclofenac were removed by 1-12% and 2-13%, respectively. Metoprolol,
31 acesulfame potassium and bezafibrate were depleted by 1-31%, 2-20% and 1-20%, respectively.
32 Although the removal of highly reactive groups was greatly achieved by ozonation and
33 peroxone process, its removal by H_2O_2 oxidation was likely less than the removal of moderately
34 reactive compounds. Only the result of non-reactive compounds was similar to the effect of
35 ozonation and peroxone process. Amidotriazole increased significantly up to 63% after H_2O_2
36 oxidation. These results indicated that H_2O_2 oxidation was ineffective for removals of
37 micropollutant.

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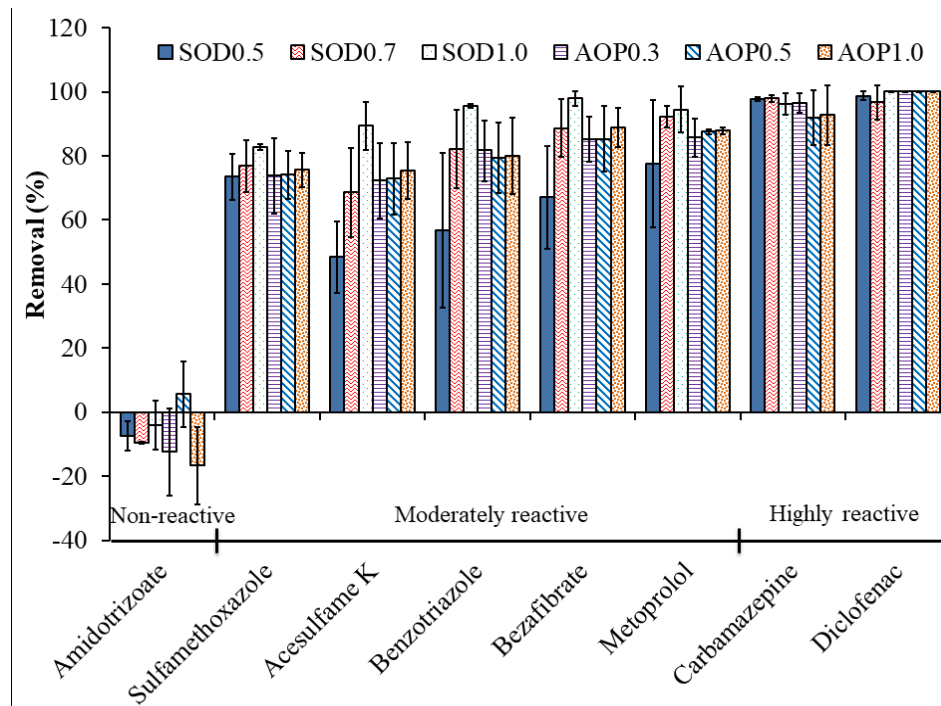
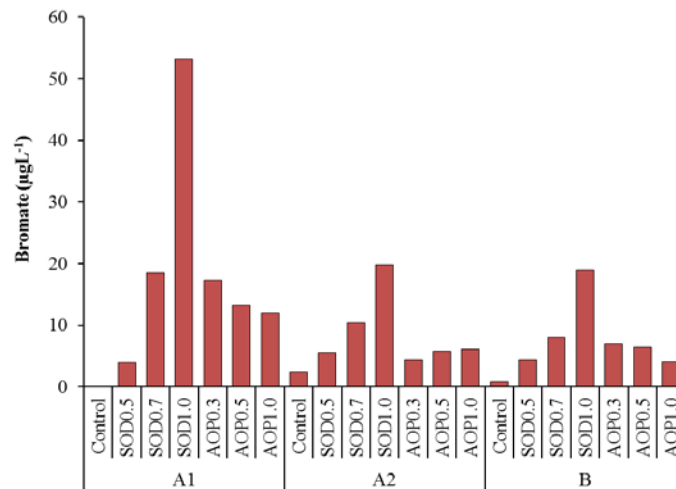


Figure 2 Percent removals of micropollutants during ozonation and peroxone process (n = 3)

Effects of ozonation and peroxone process on bromate formation

Ozonation elevated the bromate formation. A higher SOD resulted in a higher formation of bromate. For A1 water with excessive bromide concentrations ($246 \mu\text{g.L}^{-1}$), the ozonation with the SOD at 0.5, 0.7 and 1.0 $\text{mgO}_3.\text{mgDOC}^{-1}$ considerably increased bromate levels to 4, 18 and 53 $\mu\text{g.L}^{-1}$, respectively (Figure 3). The bromate formation in A2 water was similar to B water as the bromide concentrations were alike. Bromate formed in A2 and B water was in the range of 4-6, 8-10 and 19-20 $\mu\text{g.L}^{-1}$ for the SOD at 0.5, 0.7 and 1.0 $\text{mgO}_3.\text{mgDOC}^{-1}$, respectively. When water was ozonated at the SOD of 1.0 $\text{mgO}_3.\text{mgDOC}^{-1}$, the bromate concentration was 2-5 folds higher than the guideline value of the drinking water standard (10 $\mu\text{g.L}^{-1}$) (WHO, 2011). To avoid adverse effects from bromate, the use of SOD at 1.0 $\text{mgO}_3.\text{mgDOC}^{-1}$ is not recommended albeit its performance on the removal of moderately reactive compounds was highest (Figure 2). The addition of H_2O_2 suppressed the bromate formation, compared with the standalone ozonation at the same SOD (0.7 $\text{mgO}_3.\text{mgDOC}^{-1}$). For the bromide-rich water (A1), AOP0.3, AOP0.5 and AOP1.0 inhibited bromate formations by 7%, 28% and 35%, respectively. However, the bromate concentration did not meet the guideline value, even when the highest dose of H_2O_2 (AOP1.0) was applied. Implementation of peroxone process with highly bromide-containing water may require a higher $\text{H}_2\text{O}_2/\text{O}_3$ ratio than 1.0. Overall, AOP0.3, AOP0.5 and AOP1.0 decreased bromate formations by 7-57%, 20-44% and 35-49%, respectively. Effect of H_2O_2 addition on the bromate reduction was in agreement with several studies. Hübner et al (2015) showed that the bromate formation was reduced by 15% and 35% for the $\text{H}_2\text{O}_2/\text{O}_3$ ratio of 0.5 and 1.0, respectively. From a test with nine wastewater effluents, the bromate reduction from eight wastewater sources varied from 13-37% and 8-48% for the $\text{H}_2\text{O}_2/\text{O}_3$ ratio of 0.5 and 1.0 (with the SOD of 1.0 $\text{mgO}_3.\text{mgDOC}^{-1}$), respectively (Lee et al., 2016). It was interesting to note that one of wastewater samples likely exhibited ineffectiveness of H_2O_2 addition for the bromate suppression. Since the

1 micropollutant removals obtained from AOP0.3, AOP0.5 and AOP1.0 were comparable,
 2 AOP0.3 is recommended to water with bromide concentrations of less than $100 \mu\text{g.L}^{-1}$ for
 3 simultaneous control of micropollutants and bromate. Addition of higher concentrations of
 4 H_2O_2 is needed if water with higher bromide concentrations is used.
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 7 **Figure 3** Bromate formations during ozonation and peroxone processes
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9 *Comparison of micropollutant removal between predicted data and observed data*
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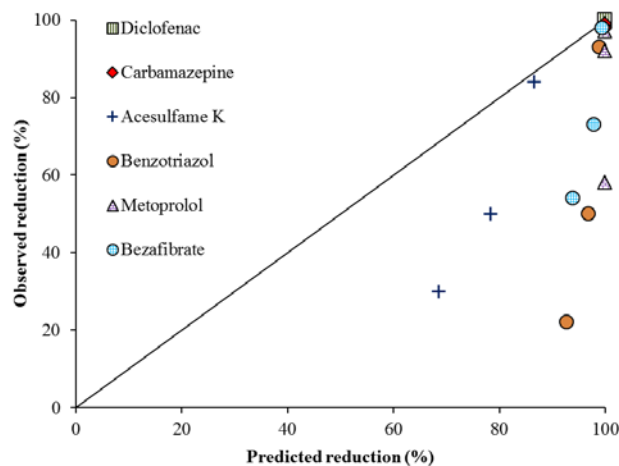
11 The prediction of micropollutant removal was calculated from the multiplication of
 12 ozone and $\bullet\text{OH}$ exposures with a reaction kinetic constant (equation 2). The kinetic constants
 13 used in this study are summarised in Table 3. Amidotrizoate was excluded due to its low
 14 reactivity with both ozone and $\bullet\text{OH}$. The comparison between predicted data and observed data
 15 revealed that the predicted data were mostly higher than the observed data (Figure 4). This does
 16 not align with several studies who found that the prediction by the use of $\bullet\text{OH}$ exposure
 17 correlated well with the observed data for the removal of ozone-resistant compounds ($k_{O_3} < 10$
 18 $\text{M}^{-1}.\text{s}^{-1}$) (Lee et al., 2013; Wildhaber et al., 2015; Lee et al., 2016). In our case, the ozone
 19 exposure was included in the prediction since the direct ozone reaction could not be neglected
 20 for the compounds with the high k_{O_3} values ($> 10 \text{M}^{-1}.\text{s}^{-1}$). The differences between predicted
 21 data and observed data in this study may result from competitiveness between the targeted
 22 compounds and the effluent organic matters (EfOM). The presence of EfOM can decrease the
 23 ozone exposure (Wert et al., 2009). In addition, EfOM is considered as an important scavenger
 24 to $\bullet\text{OH}$ since the second-order reaction rate constant ($k_{\bullet\text{OH}}$) can be up to $35 \times 10^8 \text{M}_\text{C}^{-1}.\text{s}^{-1}$ (units
 25 of per molar carbon concentration per second), depending on the molecular size (Dong et al.,
 26 2010). A smaller molecular size of EfOM promoted greater $k_{\bullet\text{OH}}$ values (Dong et al., 2010).
 27 Since ozone could cause dissociation of large-molecular EfOM into smaller ones (Wert et al.,
 28 2009; Rodriguez et al., 2012), the lower removal in the observed data possibly resulted from an
 29 in-situ increase in the $k_{\bullet\text{OH}}$ value, leading to an overestimation of $\bullet\text{OH}$ exposure in the prediction.
 30 In contrast, Lee and von Gunten (2010) reported that the $k_{\bullet\text{OH}}$ value with the parent EfOM was
 31 similar to the oxidation product of EfOM, leading to a constant consumption rate of $\bullet\text{OH}$ during
 32 the entire oxidation process. Generally, the recommended $\bullet\text{OH}$ consumption rate constant by
 33 EfOM is $2.5 \times 10^4 \text{L}.\text{mg}^{-1}.\text{s}^{-1}$ (Westerhoff et al., 2007; Lee and von Gunten, 2010). This
 34 contradiction in the $k_{\bullet\text{OH}}$ values with EfOM possibly occurs since the $\bullet\text{OH}$ consumption rate is

1 source-dependent (Lee et al., 2013). To provide more elaborately data, a further study on effect
 2 of EfOM on the $k_{\bullet OH}$ value should be carried out.

3
 4 Table 3 Kinetic constants for micropollutants

Micropollutant	k_{O_3} [M ⁻¹ .s ⁻¹]	$k_{\bullet OH}$ [M ⁻¹ .s ⁻¹]	References
Diclofenac	1×10^6	7.5×10^9	Huber et al. (2003)
Carbamazepine	3×10^5	8.8×10^9	Huber et al. (2003)
Metoprolol	4×10^4	7.3×10^9	Benner et al. (2008)
Bezafibrate	590	7.4×10^9	Huber et al. (2003)
Benzotriazole	230	9.9×10^9	Leitner and Roshani (2010)
Acesulfame potassium	88	4.5×10^9	Kaiser et al. (2013)

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Figure 4 Comparison of micropollutant removal between predicted data and observed data

10 **Conclusions**

11 The major findings of the study are presented below:

- 12 • Micropollutants used in this study can be categorized to 3 groups: non-reactive
 13 compounds (i.e., amidotriazole), moderately reactive compounds (i.e., metoprolol,
 14 acesulfame potassium, bezafibrate, and benzotriazole), and highly reactive compounds
 15 (i.e., carbamazepine and diclofenac).
- 16 • For ozonation and peroxone process, the removal for highly reactive compounds and
 17 moderately reactive compounds were 82-99% and 29-99%, respectively. The removal
 18 of amidotriazole was not observed in this study.
- 19 • Higher SOD increased the formation of bromate. At the SOD of 1.0 mgO₃.mgDOC⁻¹,
 20 the bromate concentration was 2-5 folds higher than the guideline value for drinking
 21 water. The addition of hydrogen peroxide with a SOD of 0.7 mgO₃.mgDOC⁻¹ could
 22 suppress the bromate formation to values lower than the guideline value, when the
 23 bromide concentration in the water was less than 100 µg.L⁻¹. A higher H₂O₂/O₃ ratio
 24 than 1.0 is needed if high bromide-containing water is treated.
- 25 • The removal of micropollutants by ozonation with a SOD of 0.5-1.0 mgO₃.mgDOC⁻¹
 26 was likely similar to the peroxone process. The peroxone process at the H₂O₂/O₃ ratio

1 of 0.3 is suggested for water with bromide concentrations below 100 µg.L⁻¹ in order
2 to control micropollutants and bromate at the same time.

- 3 • The prediction of micropollutants elimination by using the ozone and •OH exposures
4 was higher than observed data for moderately reactive compounds.

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11 **References**

- 12 - Androzzi, R., Marotta, R., Pinto, G., Pollio, A. 2002. Carbamazepine in water: persistence
13 in the environment, ozonation treatment and preliminary assessment on algal toxicity. *Water*
14 *Research* 36, 2869-2877.
- 15 - Benner, J., Salhi, E., Ternes, T., von Gunten, U. 2008. Ozonation of reverse osmosis
16 concentrate: kinetics and efficiency of beta blocker oxidation. *Water Research* 42, 3003–
17 3012.
- 18 - Dong, M.M., Mezyk, S.P., Rosario-Ortiz, F.L. 2010. Reactivity of effluent organic matter
19 (EfOM) with hydroxyl radical as a function of molecular weight. *Environmental Science and*
20 *Technology* 44, 5714-5720.
- 21 - Elovitz, M.S., and von Gunten, U. 1999. Hydroxyl radical/ozone ratios during ozonation
22 processes. I. The R_{ct} concept. *Ozone: Science and Engineering* 21, 239-260.
- 23 - Huber, M.M., Canonica, S., Park, G.Y., von Gunten, U. 2003. Oxidation of pharmaceuticals
24 during ozonation and advanced oxidation processes. *Environmental Science and Technology*
25 37, 1016-1024.
- 26 - Huber, M.M., Gobel, A., Joss, A., Hermann, N., Löffler, D., McArdell, C.S., Ried, A., Siegrist,
27 H., Ternes, T.A., von Gunten, U. 2005. Oxidation of pharmaceuticals during ozonation of
28 municipal wastewater effluents: a pilot study. *Environmental Science and Technology* 39,
29 4290-4299.
- 30 - Hübner, U., Zucker, I., Jekel, M. 2015. Options and limitations of hydrogen peroxide addition
31 to enhance radical formation during ozonation of secondary effluents. *Journal of Water Reuse*
32 *and Desalination* 05.1, 8–16.
- 33 - Ikehata, K., Naghashkar, N.J., El-din, M.G. 2006. Degradation of aqueous pharmaceuticals
34 by ozonation and advanced oxidation processes: a review. *Ozone: Science and Engineering*
35 28, 353-414.
- 36 - Kaiser, H.P., Köster, O., Gresch, M., Perisset, P.M.J., Jäggi, P., Salhi, E., von Gunten, U.
37 2013. Process control for ozonation systems: a novel real-time approach. *Ozone: Science and*
38 *Engineering* 35, 168–185.
- 39 - Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J. 2009. The removal of pharmaceuticals,
40 personal care products, endocrine disruptors and illicit drugs during wastewater treatment and
41 its impact on the quality of receiving waters. *Water Research* 43, 363–380.
- 42 - Kovalova, L., Seigrist, H., von Gunten, U. Eugster, J., Hagenbuch, M., Wittmer, A., Moser,
43 R., McArdell C.S. 2013. Elimination of micropollutants during post-treatment of hospital
44 wastewater with powdered activated carbon, ozone, and UV. *Environmental Science and*
45 *Technology* 47, 7899-7908.
- 46 - Lee, Y., Gerrity, D., Lee, M., Bogeat, A.E., Salhi, E., Gamage, S., Trenholm, R.A., Wert,
47 E.C., Snyder, S.A., von Gunten, U. 2013. Prediction of Micropollutant Elimination during

- 1 Ozonation of Municipal Wastewater Effluents: Use of Kinetic and Water Specific
2 Information. *Environmental Science & Technology* 47, 5872–5881.
- 3 - Lee, Y., Gerrity, D., Lee, M., Gamage, S., Pisarenko, A., Trenholm, R.A., Canonica, S.,
4 Snyder, S.A., von Gunten, U. 2016. Organic contaminant abatement in reclaimed water by
5 UV/H₂O₂ and a combined process consisting of O₃/H₂O₂ followed by UV/H₂O₂: Prediction
6 of abatement efficiency, energy consumption, and byproduct formation. *Environmental
7 Science and Technology* 50, 3809-3819.
- 8 - Lee, Y., and von Gunten, U. 2010. Oxidative transformation of micropollutants during
9 municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine
10 dioxide, ferrate^{VI}, and ozone) and non-selective oxidants (hydroxyl radical). *Water Research*
11 44, 555-566.
- 12 - Leitner, N.K.V., Roshani, B., 2010. Kinetic of benzotriazole oxidation by ozone and hydroxyl
13 radical. *Water Research* 44, 2058–2066.
- 14 - Reemtsma, T., Weiss, S., Mueller, J., Petrovic, M., Gonzalez, S., Barcelo, D., Ventura, F.,
15 Knepper, T.P. 2006. Polar pollutants entry into the water cycle by municipal wastewater: a
16 European perspective. *Environmental Science and Technology* 40, 5451-5458.
- 17 - Reungoat, J., Escher, B.I., Macova, M., Argaud, F.X., Gernjak, W., Keller, J. 2012. Ozonation
18 and biological activated carbon filtration of wastewater treatment plant effluents. *Water
19 Research* 46, 863-872.
- 20 - Rodriguez, F.J., Marcos, L.A., Nunez, L.A., Garcia, M. 2012. Effects of ozonation on
21 molecular weight distribution of humic substances and coagulation processes-A case study:
22 The Uzquiza reservoir water. *Ozone: Science and Engineering* 34, 342-353.
- 23 - Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten,
24 U., Wehrli, B. 2006. The challenge of micropollutants in aquatic systems. *Science* 313, 1072-
25 1077.
- 26 - Ternes, T.A., Joss, A. 2006. Human pharmaceuticals, hormones and fragrance. The challenge
27 of micropollutants in urban water management. IWA Publishing: London.
- 28 - Ternes, T.A., Stuber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M., Teiser, B.
29 2003. Ozonation: A tool for removal of pharmaceuticals, contrast media and mushroom fragrances
30 from wastewater? *Water Research* 37, 1976-1982.
- 31 - von Gunten, U. 2003a. Ozonation of drinking water: Part I. Oxidation kinetics and product
32 formation. *Water Research* 37, 1443-1467.
- 33 - von Gunten, U. 2003b. Ozonation of drinking water: Part II. Disinfection and by-product
34 formation in presence of bromide, iodide or chlorine. *Water Research* 37, 1469-1487.
- 35 - von Gunten, U., and Oliveras, Y. 1998. Advanced oxidation of bromide-containing waters:
36 Bromate formation mechanisms. *Environmental Science and Technology* 32, 63-70.
- 37 - Vogna, D., Marotta, R., Andreozzi, R., Napolitano, A., d'Ischia, M. 2004. Kinetic and
38 chemical assessment of the UV/H₂O₂ treatment of antiepileptic drug carbamazepine.
39 *Chemosphere* 54, 497-505.
- 40 - Wert, E.C., Rosario-Ortiz, F.L., Snyder, S.A. 2009. Effect of ozone exposure on the oxidation
41 of trace organic contaminants in wastewater. *Water Research* 43, 1005-1014.
- 42 - Westerhoff, P., Mezyk, S.P., Cooper, W.J., Minakata, D. 2007. Electron pulse radiolysis
43 determination of hydroxyl radical rate constants with Suwannee river fulvic acid and other
44 dissolved organic matter isolates. *Environmental Science and Technology* 41, 4640-4646.
- 45 - World Health Organization (WHO), 2011. Guidelines for drinking-water quality. 4th edition.
- 46 - Wildhaber, Y.S., Mestankova, H., Schärer, M., Schirmer, K., Salhi, E., von Gunten, U. 2015.
47 Novel test procedure to evaluate the treatability of wastewater with ozone. *Water Research*
48 75, 324-335.