Optimization of ozonation and peroxone process for simultaneous control of micropollutants and bromate in wastewater

Songkeart Phattarapattamawong, Andreas Marius Kaiser, Ernis Saracevic, Heidemarie Paula Schaar and Jörg Krampe

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 into three groups: non-reactive compounds (i.e. amidotrizoate), 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 amidotrizoate 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 $\mu g \cdot L^{-1}$ for simultaneous control of micropollutants and bromate. Enhancement in micropollutant removals, except for the non-reactive groups, was achieved with either higher SOD or the addition of hydrogen peroxide to ozonation. The micropollutant removal predicted from the second-order kinetic reaction with ozone and •OH exposures was higher than the observed data.

Key words | bromate, hydroxyl radical, micropollutants, ozonation, peroxone

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INTRODUCTION

The 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 the biological system (Schwarzenbach *et al.* 2006; Ternes & 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 (•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 by hydrogen peroxide (H_2O_2) addition. H_2O_2 rapidly reacts and converts hypobromous acid (HOBr), the major intermediate for bromate formation, to bromide (von Gunten & Oliveras 1998). In addition, H_2O_2 can retard a formation of other intermediates (e.g. BrO^- and $BrO\bullet$) by increase in ozone depletion rate (von Gunten 2003b). Although H_2O_2 is provided during ozonation, bromate can form through a reaction of $\bullet OH$ with bromide and HOBr (von Gunten 2003b). Lee *et al.* (2016) reported that H_2O_2 addition generally decreased bromate formation. Unexpectedly, an increase in bromate formation was observed in some cases, depending on a molar ratio between H_2O_2 and ozone (H_2O_2/O_3). To minimize bromate exposure, it raises the question that what H_2O_2/O_3 ratio can be used for bromate suppression? Addition of H_2O_2 benefits not only suppression of bromate, but also enhancement of $\bullet OH$ formation (von Gunten 2003b). However, an excessive H_2O_2 may exhibit as scavengers for $\bullet OH$, leading to lower oxidation capability (Hübner *et al.* 2015). To provide an adequate amount of H_2O_2 for bromate suppression and maintaining oxidation capability, optimizing the H_2O_2/O_3 ratio is another solution for achieving simultaneous control of micropollutants and bromate.

The objective of the study is to simultaneously control micropollutants and bromate in wastewater by using ozonation and peroxone process. To determine the optimum SOD, the SOD was varied between 0, 0.5, 0.7 and 1.0 $mgO_3.mgDOC^{-1}$. At an SOD of 0.7 $mgO_3.mgDOC^{-1}$, various H_2O_2 concentrations were added for studying the

effect of different H_2O_2/O_3 ratios. The findings can be used as an operating guideline for controlling micropollutants and bromate at the same time.

MATERIAL AND METHODS

Chemicals and wastewater

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

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

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

Table 1 | Model compounds

Compound	CAS	Company	Formula	MW
Acesulfame potassium	55589-62-3	Supelco	$C_4H_4KNO_4S$	201,2
Bezafibrate	41859-67-0	Sigma-Aldrich	$C_{19}H_{20}ClNO_4$	361,8
Benzotriazole	95-14-7	Sigma-Aldrich	$C_6H_5N_3$	119,1
Carbamazepine	298-46-4	Sigma-Aldrich	$C_{15}H_{12}N_2O$	236,3
Amidotrizoate	50978-11-5	Sigma-Aldrich	$C_{11}H_9I_3N_2O_4$	649,9
Diclofenac	15307-79-6	Sigma-Aldrich	$C_{14}H_{10}Cl_2NO_2Na$	318,1
Metoprolol	37350-58-6	RTC	$C_{15}H_{25}NO_3 \cdot C_4H_6O_6$	267,4

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

39–43 mg·L^{-1}. Various volumes of ozone solution were mixed with the water sample in order to adjust the specific ozone doses (O$_3$/DOC) at 0, 0.5, 0.7 and 1.0 mgO$_3$·mgDOC^{-1} (coded as Control, SOD0.5, SOD0.7 and SOD1.0, respectively). For the peroxone process, H$_2$O$_2$ was added to the samples before injecting ozone solution, and the O$_3$/DOC was controlled at 0.7 mgO$_3$·mgDOC^{-1}. H$_2$O$_2$/O$_3$ 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 H$_2$O$_2$ 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 s. 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

H$_2$O$_2$/O$_3$ ratios were negligible.

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

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

With:

MP and MP_0 = a concentration of micropollutant at t time and initial time,

$k_{\bullet OH/pCBA} = 5 \times 10^9$ M^{-1}·s^{-1} (Elovitz & von Gunten 1999),

$k_{\bullet OH}$ and k_{O_3} = a reaction constant for ozone and ·OH, respectively.

RESULTS AND CONCLUSIONS

Effects of ozonation and peroxone process on micropollutant removal

Most micropollutants were oxidized after ozonation. Carbamazepine and diclofenac were highly reactive compounds since their removal rate was above 90% (Figure 1(a)). Previous studies reported that carbamazepine and diclofenac were fast reactive compounds to ozone and ·OH (Andreozzi *et al.* 2002; Ikehata *et al.* 2006). Their second-order rate constants were reported between five and nine orders of magnitude for the reactions with ozone and ·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 ·OH are 2–4 and nine orders of magnitude, respectively (Huber *et al.* 2003; Benner *et al.* 2008; Leitner & 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 mgO$_3$·mgDOC^{-1}, respectively (Figure 1(b)). 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 mgO$_3$·mgDOC^{-1}, while that in A2 and B water
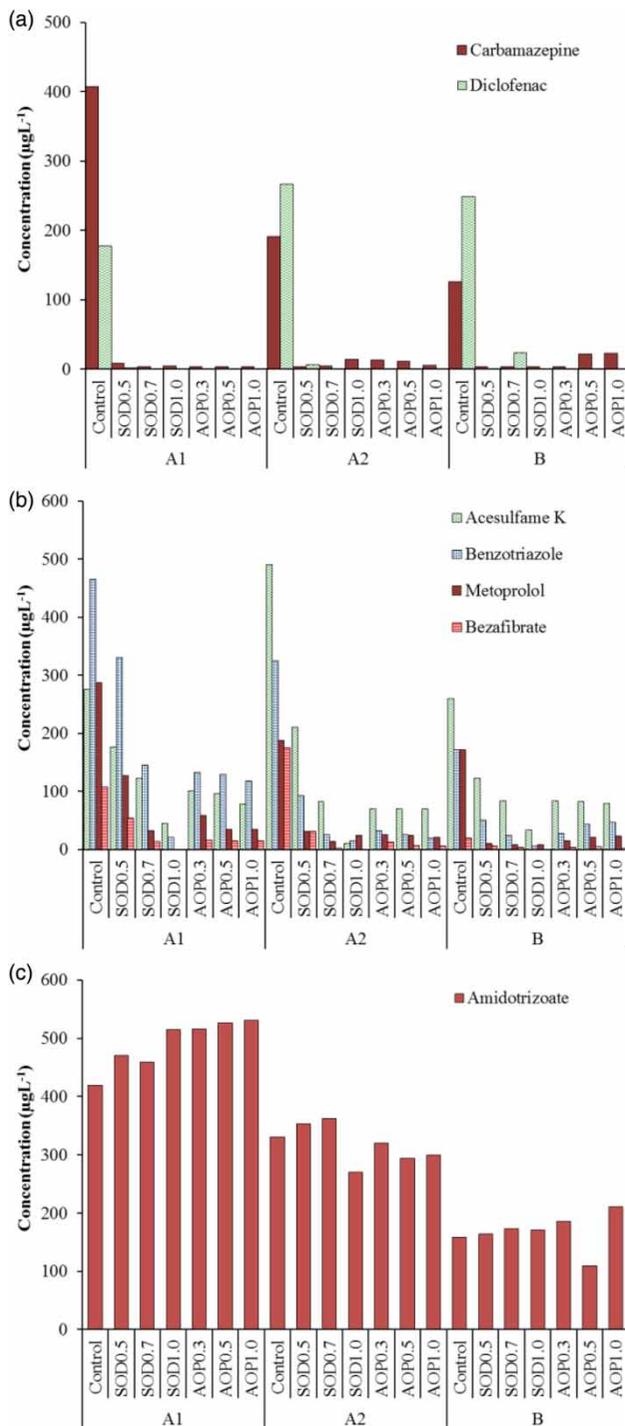
Figure 1 │ Concentration of micropollutants after ozonation and peroxone process: highly reactive compounds (a), moderately reactive compounds (b), and non-reactive compounds (c).

on the removal of metoprolol since its degradation constant with ozone (k_{O_3}) was as high as four orders of magnitude (Benner *et al.* 2008). Among the used model compounds, the most resistant compound was amidotrizoate since the removal was not observed during ozonation at the SOD of 0.5–1.0 $mgO_3 \cdot mgDOC^{-1}$. This result was consistent with previous studies who reported the low reactivity of amidotrizoate toward ozone molecule and $\cdot OH$ (Ternes *et al.* 2003; Huber *et al.* 2005; Kovalova *et al.* 2013). Interestingly, the amidotrizoate concentration increased after the ozonation instead (Figure 1(c)). The increase in amidotrizoate may result from a degradation of conjugate compounds. Based on treatment performance of the ozonation, the targeted compounds were categorized into three 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. amidotrizoate) (Figure 2). This categorization was similar to several references that use the second-order rate constants with ozone to group micropollutants (von Gunten 2003a; Wert *et al.* 2009; Lee *et al.* 2013).

The removal of micropollutants by the peroxone process was similar to ozonation. The highly reactive groups were greatly removed by the peroxone process (Figure 1(a)). The removal for carbamazepine and diclofenac was in the range of 82–99% and over 99%, respectively. For the moderately reactive compounds (i.e. metoprolol, acesulfame potassium, bezafibrate, and benzotriazole), the peroxone process slightly enhanced the reduction by 10–20%, compared to the ozonation at the same SOD (0.7 $mgO_3 \cdot mgDOC^{-1}$) (Figure 1(b)). Variation in H_2O_2/O_3 ratios did not significantly change the removal of moderately reactive
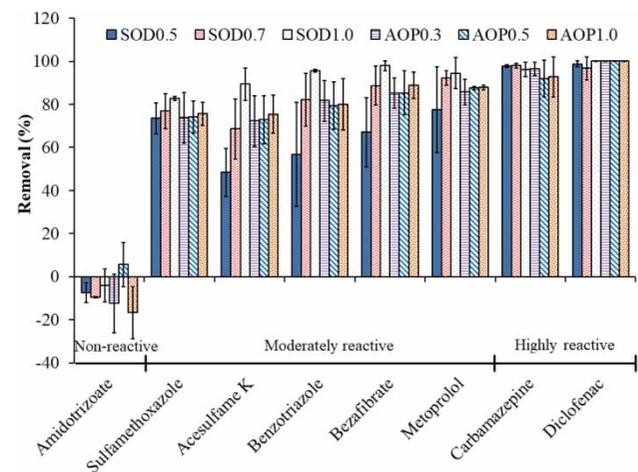

Figure 2 │ Percent removals of micropollutants during ozonation and peroxone process ($n = 3$).

were 53–99%. Specifically, a high DOC concentration (A1) seemed to interfere with the removal of benzotriazole, acesulface potassium and bezafibrate, compared to low DOC water (A2 and B). The presence of DOC had less impact

compounds. The percent reduction of moderately reactive compounds ranged from 61–92% ($\bar{X} \pm SD = 80 \pm 10$), 65–95% ($\bar{X} \pm SD = 80 \pm 10$) and 69–96% ($\bar{X} \pm SD = 89 \pm 9$) for AOP0.3, AOP0.5 and AOP1.0, respectively. Although the reaction rate constant for ozone (k_{O_3}) is much lower than the reaction rate constant for •OH ($k_{•OH}$), the ozone exposure is generally predominant in the reaction. Lee *et al.* (2013) reported that the effect of H_2O_2 addition on micropollutant removals was minor (<10%). The treatability for the peroxone process (AOP0.3-1.0) was lower than the ozonation with the SOD of 1.0 mgO$_3$·mgDOC^{-1}. This result was plausibly explained by the high ozone stability in the SOD of 1.0 mgO$_3$·mgDOC^{-1} that induced the greater removal for these moderately reactive compounds since they were reactive to both ozone and •OH. Variations in DOC concentrations seemed to have less effect on the removal of moderately reactive compounds by the peroxone process. This advantage of peroxone process possibly resulted from the fast decomposition of ozone, leading to greater •OH production. The peroxone process occasionally increased the amidotrizoate concentration (Figure 1(c)). Peroxonation of water with high DOC concentrations (A1) clearly increased the concentration of amidotrizoate by 10–23%. For low DOC water (A2 and B), the effect of peroxone process on amidotrizoate was ambiguous. This result may be attributed to differences in water characteristics since A2 and B water were collected from different sources.

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

Effects of ozonation and peroxone process on bromate formation

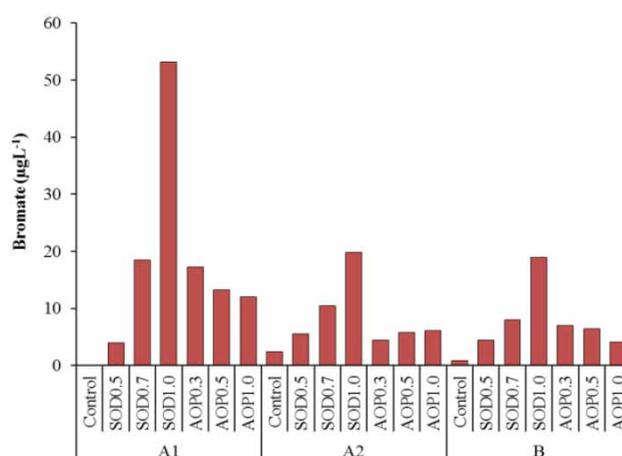Ozonation elevated the bromate formation. A higher SOD resulted in a higher formation of bromate. For A1 water

Figure 3 | Bromate formations during ozonation and peroxone processes.

with excessive bromide concentrations (246 µg.L^{-1}), the ozonation with the SOD at 0.5, 0.7 and 1.0 mgO$_3$·mgDOC^{-1} considerably increased bromate levels to 4, 18 and 53 µg·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 µgL^{-1} for the SOD at 0.5, 0.7 and 1.0 mgO$_3$·mgDOC^{-1}, respectively. When water was ozonated at the SOD of 1.0 mgO$_3$·mgDOC^{-1}, the bromate concentration was 2–5 folds higher than the guideline value of the drinking water standard (10 µg·L^{-1}) (WHO 2011). To avoid adverse effects from bromate, the use of SOD at 1.0 mgO$_3$·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 mgO$_3$·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 H_2O_2/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. The 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 H_2O_2/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 H_2O_2/O_3 ratio of 0.5 and 1.0

(with the SOD of 1.0 $mgO_3 \cdot mgDOC^{-1}$), 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 micropollutant removals obtained from AOP0.3, AOP0.5 and AOP1.0 were comparable, AOP0.3 is recommended to water with bromide concentrations of less than 100 $\mu g \cdot L^{-1}$ for simultaneous control of micropollutants and bromate. Addition of higher concentrations of H_2O_2 is needed if water with higher bromide concentrations is used.

Comparison of micropollutant removal between predicted data and observed data

The prediction of micropollutant removal was calculated from the multiplication of ozone and •OH exposures with a reaction kinetic constant (Equation (2)). The kinetic constants used in this study are summarized in Table 3. Amidotrizoate was excluded due to its low reactivity with both ozone and •OH. The comparison between predicted data and observed data revealed that the predicted data were mostly higher than the observed data (Figure 4). This does not align with several studies that found that the prediction by the use of •OH exposure correlated well with the observed data for the removal of ozone-resistant compounds ($k_{O_3} < 10\ M^{-1} \cdot s^{-1}$) (Lee et al. 2013, 2016; Wildhaber et al. 2015). In our case, the ozone exposure was included in the prediction since the direct ozone reaction could not be neglected for the compounds with the high k_{O_3} values ($>10\ M^{-1} \cdot s^{-1}$). The differences between predicted data and observed data in this study may result from competitiveness between the targeted compounds and the effluent organic matters (EfOM). The presence of EfOM can decrease the ozone exposure (Wert et al. 2009). In addition, EfOM is considered as an important scavenger to •OH since the second-order reaction rate constant ($k_{•OH}$) can be up to
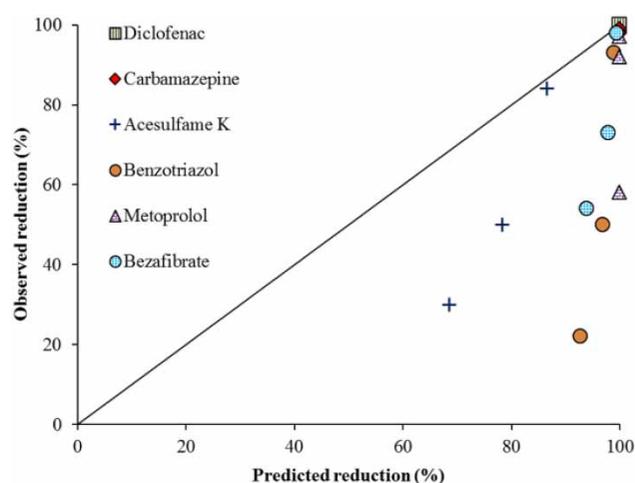

Figure 4 | Comparison of micropollutant removal between predicted data and observed data.

$35 \times 10^8\ M_C^{-1} \cdot s^{-1}$ (units of per molar carbon concentration per second), depending on the molecular size (Dong et al. 2010). A smaller molecular size of EfOM promoted greater $k_{•OH}$ values (Dong et al. 2010). Since ozone could cause dissociation of large-molecular EfOM into smaller ones (Wert et al. 2009; Rodriguez et al. 2012), the lower removal in the observed data possibly resulted from an in-situ increase in the $k_{•OH}$ value, leading to an overestimation of •OH exposure in the prediction. In contrast, Lee & von Gunten (2010) reported that the $k_{•OH}$ value with the parent EfOM was similar to the oxidation product of EfOM, leading to a constant consumption rate of •OH during the entire oxidation process. Generally, the recommended •OH consumption rate constant by EfOM is $2.5 \times 10^4\ L \cdot mg^{-1} \cdot s^{-1}$ (Westerhoff et al. 2007; Lee & von Gunten 2010). This contradiction in the $k_{•OH}$ values with EfOM possibly occurs because the •OH consumption rate is source-dependent (Lee et al. 2013). To provide more elaborately data, a further study on effect of EfOM on the $k_{•OH}$ value should be carried out.

CONCLUSIONS

The major findings of the study are presented below:

- Micropollutants used in this study can be categorized into three groups: non-reactive compounds (i.e. amidotrizoate), moderately reactive compounds (i.e. metoprolol, acesulfame potassium, bezafibrate, and benzotriazole), and highly reactive compounds (i.e. carbamazepine and diclofenac).

Table 3 | Kinetic constants for micropollutants

Micropollutant	k_{O_3} [$M^{-1} \cdot s^{-1}$]	$k_{•OH}$ [$M^{-1} \cdot s^{-1}$]	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 & Roshani (2010)
Acesulfame potassium	88	4.5×10^9	Kaiser et al. (2013)

- For ozonation and peroxone process, the removal for highly reactive compounds and moderately reactive compounds were 82–99% and 29–99%, respectively. The removal of amidotrizoate was not observed in this study.
- Higher SOD increased the formation of bromate. At the SOD of 1.0 $mgO_3 \cdot mgDOC^{-1}$, the bromate concentration was 2–5 folds higher than the guideline value for drinking water. The addition of hydrogen peroxide with an SOD of 0.7 $mgO_3 \cdot mgDOC^{-1}$ could suppress the bromate formation to values lower than the guideline value, when the bromide concentration in the water was less than 100 $\mu g \cdot L^{-1}$. A higher H_2O_2/O_3 ratio than 1.0 is needed if high bromide-containing water is treated.
- The removal of micropollutants by ozonation with a SOD of 0.5–1.0 $mgO_3 \cdot mgDOC^{-1}$ was likely similar to the peroxone process. The peroxone process at the H_2O_2/O_3 ratio of 0.3 is suggested for water with bromide concentrations below 100 $\mu g \cdot L^{-1}$ in order to control micropollutants and bromate at the same time.
- The prediction of micropollutants elimination by using the ozone and •OH exposures was higher than observed data for moderately reactive compounds.

ACKNOWLEDGEMENT

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