Options and limitations of hydrogen peroxide addition to enhance radical formation during ozonation of secondary effluents

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ABSTRACT

The oxidation of secondary effluent with ozone and O₃/H₂O₂ (peroxone) was evaluated in batch experiments as pre-treatment for soil aquifer treatment for non-potable reuse purposes. The addition of hydrogen peroxide improved the reduction of ozone-resistant compounds with an optimized radical formation at 0.5 mol H₂O₂/mol O₃. However, the improvement of radical formation was shown to be limited to approximately 30–40% independent from ozone dosage. Also a preozonation step did not accelerate efficiency of subsequent peroxone treatment. Thus, other treatment options, such as an increase of ozone dosages, need to be considered for more efficient removal of ozone-resistant compounds. However, the peroxone process might still be a promising option for oxidation of bromide containing effluents, since a reduction of bromate formation can allow the application of higher ozone dosages.

Key words | OH radicals, ozonation, peroxone process, pharmaceuticals

INTRODUCTION

Conventional wastewater treatment plants (WWTPs) are not designed for efficient removal of trace organic compounds (TrOCs). Several TrOCs, such as pharmaceuticals and personal care products, persist during wastewater treatment and have been detected in secondary effluents and receiving surface waters (Ternes 1998; Kolpin et al. 2002; Reemtsma et al. 2006). Advanced treatment of WWTP effluent is needed to minimize the discharge of these compounds into the aquatic environment. Ozonation is a promising tool for tertiary treatment of wastewater. Several studies have demonstrated efficient transformation of many relevant TrOCs by ozone (Huber et al. 2005; Bahr et al. 2007; Hollender et al. 2009).

Ozone is an electrophilic oxidant which selectively reacts with compounds containing electron-rich moieties, such as amines, activated aromatic rings (e.g., phenols), sulphur-containing compounds and olefins (von Sonntag & von Gunten 2002). Thus, reaction rates of organic compounds with ozone are highly variable. For the transformation of compounds with low reactivity (i.e., ozone-resistant compounds), the indirect reaction via OH-radicals plays an important role. These highly reactive and nonselective radicals can be formed from the reaction of ozone in aqueous solution. The formation of hydroxyl radicals from the hydroxide ion is described in reactions 1–5 (Merenyi et al. 2010a, b).

\[
\begin{align*}
\text{OH}^- + \text{O}_3 & \rightarrow \text{HO}_4^- \leftrightarrow \text{HO}_2^+ + \text{O}_2^{2-} \\
\text{HO}_2^+ & \rightarrow \text{O}_2^{2-} + \text{H}^+ \\
\text{O}_2^{2-} + \text{O}_3 & \rightarrow \text{O}_2 + \text{O}_3^{2-} \\
\text{O}_3^{2-} & \leftrightarrow \text{O}_2 + \text{O}^{2-} \\
\text{O}^{2-} + \text{H}^+ & \leftrightarrow \cdot\text{OH}
\end{align*}
\]
However, due to the slow reaction of OH with ozone ($k = 70 \text{ M}^{-1} \text{s}^{-1}$), it only plays a minor role for ozonation of wastewater. During ozonation of natural waters with high content of natural organic matter, radicals are mainly produced from reactions of ozone with phenols and amines described in reactions 6 and 7, respectively (Buffle & Von Gunten 2006). It has been reported that high formation of radicals by ozonation of secondary effluents had an OH-radical yield near 13% (Noethe et al. 2009) leading to a significant transformation of many ozone-resistant compounds (e.g., Huber et al. 2005; Hollender et al. 2009).

$$\text{PhO}^- + \text{O}_3 \rightarrow \text{PhO}^+ + \text{O}_3^- \quad (6)$$

$$\text{R}_2\text{NH} + \text{O}_3 \rightarrow \text{R}_2\text{NO}^+ + \text{H}^+ + \text{O}_2^- \quad (7)$$

The advanced oxidation process (AOP) O$_3$/H$_2$O$_2$, also called peroxone-process, involves the formation of OH-radicals from the reaction of ozone with hydrogen peroxide (reaction 8). The formed radicals are reacting to OH-radicals according to reactions 2–5. For a detailed mechanistic description of the peroxone process see Merenyi et al. (2010a). Peroxide can be formed from reactions of ozone with the water matrix but its contribution to overall OH-radical formation during wastewater ozonation is not significant (Noethe et al. 2009).

$$\text{HO}_2^- + \text{O}_3 \leftrightarrow \text{HO}_2 \leftrightarrow \text{HO}_2^+ + \text{O}_3^- \quad (8)$$

Many authors have reported an increasing reduction of ozone-resistant compounds, such as X-ray contrast media, by addition of hydrogen peroxide during ozonation of ground and surface waters (Duguet et al. 1985; Prados et al. 1995; Zwiener & Frimmel 2000). In contrast, the benefits of peroxone treatment for oxidation of secondary effluents are less pronounced. Several authors showed only little improvement of the transformation of ozone-resistant compounds by H$_2$O$_2$ addition (Buffle et al. 2006a; Wert et al. 2007; Katsoyiannis et al. 2011). This was also confirmed by Pocostales et al. (2010), who explained the little effect of H$_2$O$_2$-addition on radical formation by its competition with highly reactive organic substances in the effluents. However, most studies only tested the peroxone process by adding a limited number of peroxide dosages before oxidation.

Ozone depletion in secondary effluents can be described as a reaction in two phases: a very fast depletion from 0 to 20 seconds, operationally defined as instantaneous ozone demand (IOD), followed by first order ozone depletion (Schumacher 2005). Later quench flow experiments demonstrated that the IOD can also be described as two reaction stages with first order ozone depletion (Noethe et al. 2009). The fact that the reaction of H$_2$O$_2$ with ozone competes with ozone consumption by organic and inorganic compounds raises the question whether H$_2$O$_2$ addition at a later stage of the reaction when highly reactive compounds are already oxidized, can be a promising option to reduce hydrogen peroxide demand.

The objectives of this study were to analyse and quantify advantages and limitations of the peroxone process for the treatment of secondary effluents. Batch experiments with molar ratios of 0–1 mol H$_2$O$_2$/mol O$_3$ were conducted to evaluate the optimum H$_2$O$_2$ dosage to enhance radical exposure. In addition, peroxone treatment after preozonation of secondary effluent was tested.

**EXPERIMENTS**

**Description of oxidation experiments**

Batch ozonation experiments were conducted with secondary effluent from Berlin Ruhleben in 500 mL Duran bottles on magnetic stirrers. 20–50 mL of an ozone stock solution was added to 200 mL of secondary effluent and sample volume was adjusted to 250 mL with ultrapure water. The ozone stock solution of approximately 70 mg/L was produced in a 4-L semi-batch stirred tank reactor (cooled to 0°C). Gaseous ozone was produced from pure oxygen using a Modular 8 HC generator (Wedeco, Germany). Concentration of dissolved ozone in the stock solution was measured directly before ozonation in each experiment using the Indigo method (Bader & Hoigne 1982). In addition, dissolved ozone was measured in several experiments after 20 seconds of the reaction to determine the IOD. Ozonated samples
were analysed for bulk parameters and TrOCs after complete reaction with ozone.

Experiments were repeated in three different sampling events (see Table 1 for details). In every event perozone treatment was evaluated: (i) with moderate ozone dosage of $8.5 \pm 0.2 \text{ mg/L}$, (ii) with high ozone dosage of $14.0 \pm 0.3 \text{ mg/L}$ and (iii) with moderate ozone dosage after preozonation of secondary effluent. During two sampling events (February 13; April 13) two additional ozonation experiments (without H$_2$O$_2$ addition) with $5.8 \pm 0.3 \text{ mg/L}$ and $11.4 \pm 0.3 \text{ mg/L}$ were conducted. Molar hydrogen peroxide to ozone ratios of 0, 0.1, 0.3, 0.5 and 1 were applied with an error of approximately 10% caused by variations of stock solution concentration.

Preozonation was conducted in a 4-L semi-batch stirred tank reactor, where gaseous ozone is introduced into the sample batch via a ring pipe. Ozone concentration in the in- and off-gas, dissolved ozone and gas flow rate were measured continuously using BMT 964 and BMT 961 TPC (BMT, Germany), Orbisphere 31331.1 (Orbisphere, Germany) and 807 MFM O2 (Bürkert, Germany), respectively. In order to set up a complete mass balance to calculate ozone consumption, all off-gas ozone was stripped with pure oxygen.

**Analytical methods**

Temperature and pH were measured directly after experiments using a WTW 357 pH meter (WTW, Germany). Samples for analysis of bulk parameters were filtered through a 0.45 μm cellulose nitrate filter (Sartorius, Germany). Dissolved organic carbon (DOC) and total inorganic carbon (TIC) were measured on a varioTOC and a highTOC II analyser (Elementar, Germany), respectively. Analysis for UV absorbance at 254 nm was conducted on a Lambda 12 photometer (Perkin-Elmer, Germany). Residual H$_2$O$_2$ was measured on February 5, 2013 and April 30, 2013 by the KI-thiosulphate method described by Klassen et al. (1994).

For measurement of bromate, the method described by Snyder et al. (2005) was adapted. Product ions with m/z 110.9 and 112.9 were detected as quantifier and qualifier, respectively. Ninety-eight per cent $^{18}$O-labelled potassium bromate with a chemical purity of 90–95% (LGC Standards, Germany) was added as internal standard and calibration ranged from 0.2 to 50 μg/L.

Eleven TrOCs were analysed during experiments. TrOCs can be categorized by their reactivity with ozone in three groups: fast reacting compounds ($k_{O3} > 10^4 \text{ M}^{-1} \text{s}^{-1}$) are mainly oxidized by ozone; moderately reacting TrOCs ($10 \text{ M}^{-1} \text{s}^{-1} < k_{O3} < 10^4 \text{ M}^{-1} \text{s}^{-1}$) are oxidized by both, ozone and OH-radicals; and slowly reacting compounds ($k_{O3} < 10 \text{ M}^{-1} \text{s}^{-1}$), which are not significantly oxidized by direct reaction with ozone (Hübner et al. 2015). To ensure detection before and after ozonation, several TrOCs were spiked before starting the experiments. Spiking concentrations, rate constants and analytical data are summarized in Table 2.

Determination of pCBA was conducted on a HPLC Series 1100 system (Hewlett Packard, USA) equipped with a Micromass Quattro LC 9037 (Waters, USA) without additional sample preparation. Separation was achieved on a 3 μm Luna C18 column (150 × 2.0 mm, Phenomenex, USA) at a flow rate of 250 μL/min with a gradient programme with ultrapure water (A) and acetonitrile (B), both acidified with 0.25% of formic acid. B was increased from 25 to 95% within 6 min, held for 2 min, reduced back to 25% within 4 min and stabilized for an additional 10 min. 50 μg/L of 2,4-di-CBA was added prior to analysis as internal standard.

| Table 1 | Water quality parameters and ozone dosages at different sampling events |
|--------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Date   | Ozone stock solution [mg/L] | Preozonation [mg/L] | DOC [mg/L] | TIC [mg/L] | UVA [1/m] | pH |
|--------|---------------------|---------------------|---------------------|---------------------|---------------------|
| November 12 | 71.9 ± 2.6 | 6.3 | 12.2 | 41.1 | 31.5 | n.a. |
| February 13 | 70.8 ± 3.6 | 7.5 | 8.6 | 40.7 | 22.2 | 7.2 |
| April 13 | 72.1 ± 2.1 | 7.8 | 11.9 | n.a. | 29.5 | 7.4 |

n.a. not analysed.
The acidic pharmaceuticals diclofenac, clofibric acid, ibuprofen, ketoprofen, naproxen and bezafibrate were analysed on a TSQ Vantage (Thermo Scientific, USA) in negative mode after online extraction on a 1.9 μm Hypersil Gold aQ precolumn (20 × 2.1 mm, Thermo Scientific, USA). 1 mL sample was loaded with water (1% MeOH, 0.1% HCOOH) for 1 min at a flow rate of 1,000 μL/min onto the column. Elution and separation on a Hypersil Gold aQ analytical column (50 × 2.1 mm × 1.9 μm, Thermo Scientific, USA) was conducted with ultrapure water with 2 mmol/L ammonium acetate (A) and methanol (B) at a flow rate of 250 μL/min. The gradient programme was as follows: B was increased from 30 to 50% after 5 min and to 80% after 8 min, held for 30 s, decreased back to 30% after 9 min and stabilized for 6 min. D4-diclofenac was spiked at 25 ng/L and used as internal standard for all compounds.

The other compounds (iopromide, primidone, benzotriazole and carbamazepine) were directly injected onto the column without additional sample pretreatment. Separation of analytes was achieved on a Hypersil Gold aQ column (50 × 2.1 mm × 1.9 μm, Thermo Scientific, USA) with ultrapure water containing 0.5% formic acid (A) and methanol (B). B was increased from 10 to 100% within 10 min, held for 30 s, reduced back to 10% after 11 min and stabilized for 5 min. Deuterated internal standards were added at a concentration of 100 ng/L and electron spray ionization was operated in positive mode.

### RESULTS

#### Characterization of ozonation

##### Ozone depletion

Previous studies revealed a very fast depletion of ozone during ozonation of secondary effluents (Buffé et al. 2006b; Noethe et al. 2009). Ozone depletion was not analysed during experiments but the IOD, operationally defined as the amount of ozone consumed in the first 20 seconds of the reaction, was determined in experiments with high ozone dosage. Calculated IOD ranged from 8.1 to 8.6 mg/L, which is in agreement with results from a different secondary effluent (Noethe et al. 2009). The quick consumption is mainly attributed to fast reacting organic compounds in the water, but also inorganic compounds, such as nitrite, Fe(II) and Mn(II) can contribute to the IOD. Unfortunately, these parameters were not analysed during experiments. A more detailed description of ozone depletion in secondary effluents can be found elsewhere (Schumacher 2005; Buffé et al. 2006b; Noethe et al. 2009).

#### Removal of TrOCs

Removal of TrOCs by ozone in different experiments (without peroxide addition) is compared in Figure 1.

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**Table 2** Analytical data and rate constants for analysed TrOCs

<table>
<thead>
<tr>
<th>Compound</th>
<th>LOQ [μg/L]</th>
<th>Spiking [μg/L]</th>
<th>c0 [μg/L]</th>
<th>MS fragmentation</th>
<th>Coll. energy [eV]</th>
<th>kO3 [M⁻¹ s⁻¹]</th>
<th>kOH [10⁹ M⁻¹ s⁻¹]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>pCBA</td>
<td>2</td>
<td>200/300⁻</td>
<td>317.1 ± 98.8</td>
<td>155/111</td>
<td>0/12</td>
<td>0.15</td>
<td>5.2</td>
<td>1</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>0.1</td>
<td>10</td>
<td>14.6 ± 4.4</td>
<td>209</td>
<td>13</td>
<td>0.4</td>
<td>8.4</td>
<td>2</td>
</tr>
<tr>
<td>Iopromide</td>
<td>0.1</td>
<td>20/50⁻</td>
<td>41.0 ± 13.7</td>
<td>559/572.8</td>
<td>24/24</td>
<td>0.8</td>
<td>3.3</td>
<td>3</td>
</tr>
<tr>
<td>Primidone</td>
<td>0.2</td>
<td>50</td>
<td>51.1 ± 1.7</td>
<td>91/162</td>
<td>30/13</td>
<td>1</td>
<td>6.7</td>
<td>2</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>0.05</td>
<td>10</td>
<td>17.0 ± 3.0</td>
<td>161</td>
<td>22</td>
<td>9.1</td>
<td>7.4</td>
<td>3</td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>0.1</td>
<td>10</td>
<td>12.8 ± 0.9</td>
<td>127/129</td>
<td>17/19</td>
<td>20</td>
<td>4.7</td>
<td>3, 4</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>0.1</td>
<td>–</td>
<td>7.2 ± 1.2</td>
<td>65/92</td>
<td>24/16</td>
<td>230</td>
<td>9.9</td>
<td>5</td>
</tr>
<tr>
<td>Bezafibrate</td>
<td>0.05</td>
<td>10</td>
<td>10.5 ± 5.0</td>
<td>154/274</td>
<td>30/21</td>
<td>590</td>
<td>7.4</td>
<td>3</td>
</tr>
<tr>
<td>Naproxen</td>
<td>0.02</td>
<td>10</td>
<td>14.6 ± 4.4</td>
<td>169</td>
<td>37</td>
<td>2 × 10⁵</td>
<td>9.6</td>
<td>3, 4</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>0.05</td>
<td>–</td>
<td>1.5 ± 0.3</td>
<td>194/237</td>
<td>20/2</td>
<td>3 × 10⁵</td>
<td>8.8</td>
<td>3</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>0.02</td>
<td>–</td>
<td>3.2 ± 0.7</td>
<td>254/256</td>
<td>14/14</td>
<td>1 × 10⁶</td>
<td>7.5</td>
<td>3</td>
</tr>
</tbody>
</table>

*Lower spiking concentration on November 21, 2013.*

References: ¹Yao & Haag (1991); ²Real et al. (2009); ³Huber et al. (2003); ⁴Packer et al. (2003); ⁵Leitner & Roshani (2010).
The results confirm that the specific ozone consumption (normalization of ozone consumption by DOC) is a good parameter to compare efficiency of compound removal by ozone in experiments with different water quality. The removal of TrOCS from secondary effluents is in line with results from previous studies (Huber et al. 2005; Hollender et al. 2009). Whereas fast reacting compounds ($k_{O3} > 10^4$ M$^{-1}$ s$^{-1}$) diclofenac, carbamazepine and naproxen were removed below limit of quantitation (LOQ) with $Z_{spec} = 0.6$ mgO$_3$/mg DOC$_0$, higher ozone dosages are needed for $>80\%$ transformation of slow and moderately reacting compounds. The partial removal of ozone-resistant compounds ($k_{O3} < 10$ M$^{-1}$ s$^{-1}$) indicates a significant formation of OH-radicals during ozonation of secondary effluent.

Formation of OH-radicals

In this study, OH-radical exposures are calculated from relative residual concentrations of all five ozone-resistant compounds using second order rate kinetics (Reaction (9)) and shown as average values. The OH-radical exposure is a simple parameter to characterize the oxidation of a type of water as it includes initiation, promotion and scavenging capacity of the water matrix. Results from ozonation experiments without peroxide addition are shown in Figure 2.

\[
\int (\cdot \text{OH}) \, dt = -\ln \frac{S}{S_0} \div k_{C\cdot \text{OH}} \quad (9)
\]

OH-radical formation from different experiments linearly correlated with the specific ozone consumption. This has been reported previously (Lee et al. 2013) and is also known from ozonation of ground and surface waters (Hoigne & Bader 1979). The linear correlation is characterized by an initial ozone consumption without radical formation. This is likely caused by reactions with reduced inorganic compounds (Fe$^{2+}$, Mn$^{2+}$, NO$_2^-$) and olefins, which do not produce significant amounts of radicals in side reactions. These compounds were quickly removed in a preozonation step resulting in significantly higher radical formation in subsequent ozonation.

Effects of hydrogen peroxide addition on radical formation

Ozone and H$_2$O$_2$ depletion

During experiments with high ozone dosages, the IOD was measured as ozone consumption within the first 20 seconds of reaction. With increasing H$_2$O$_2$ dosages, IOD
increases from 8.4 mg/L to approximately 13.2 mg/L (Figure 3) showing that H$_2$O$_2$ addition can significantly reduce ozone exposure and reaction time. Only 30–35% from applied H$_2$O$_2$ was consumed during oxidation, which demonstrates the strong competition with effluent organic matter. At a H$_2$O$_2$/O$_3$ ratio of 1, the consumption decreased to 20%. Preozonation can be applied to reduce competition for perozone reactions by removing fast-reacting compounds. Oxidation after preozonation showed significantly enhanced H$_2$O$_2$ consumption of approximately 50% at applied ratios of 0.1, 0.3 and 0.5 mol/mol (data not shown).

**OH-radical formation**

To characterize the formation of OH-radicals in different experiments, a new parameter, the transformation efficiency of ozone to OH-radicals ($T_{OH}$), was adapted from Schumacher (2005). The $T_{OH}$ is calculated by relating the OH-radical exposure to the specific ozone consumption $Z_{spec}$. Results from perozone experiments demonstrate that an increase of overall OH-radical exposures (in comparison to ozone treatment) is limited to a maximum of approximately 40% in both moderate and high ozone dosages (Figures 4 and 5). This is in agreement with literature data (Pocostales et al. 2010) and can be explained by the strong competition of H$_2$O$_2$ with effluent organic matter especially at low and moderate ozone dosages and the fact that ozonation alone can already be described as effective AOP. Although H$_2$O$_2$ consumption could be enhanced by preozonation the efficiency of radical formation was not improved in comparison to experiments without preozonation (Figure 6).

It is assumed that the positive effect of preozonation on H$_2$O$_2$ consumption is compensated by the higher radical formation during the second ozonation step (see Figure 2). All experiments revealed maximum exposures at H$_2$O$_2$/O$_3$ ratios of 0.3–0.5 mol/mol. At higher concentrations H$_2$O$_2$ also significantly contributes to the scavenging of OH-radicals ($k_{OH} = 2.7 \times 10^7 \text{M}^{-1} \text{s}^{-1}$). This effect might explain the decreased OH-radical exposures at H$_2$O$_2$/O$_3$ ratios of 1.0 mol/mol.

The maximum effect of a 30–40% increase of radical exposures on transformation of ozone-resistant compounds
can be easily calculated from second order rate kinetics (shown in Figure 7 for 30%). Results demonstrate a rather limited enhancement of compound elimination. Similar results were reported by different authors (Buffle et al. 2006a; Wert et al. 2007; Pocostales et al. 2010; Katsoyiannis et al. 2011). Although addition of peroxide can accelerate O₃ depletion, formation of radicals in wastewater only changes marginally.

Effect of H₂O₂ on other water quality parameters

Besides the increase of radical formation, addition of hydrogen peroxide during ozonation induces a reduction of ozone exposure, which might affect direct reactions of compounds with ozone. However, fast reacting compounds were completely removed independent from H₂O₂ addition and effects on the removal of moderately reacting compounds were found to depend on rate constants. Whereas clofibric acid (kₒ₃ = 20 M⁻¹ s⁻¹) was more efficiently oxidized by peroxide treatment, no significant effect was observed for bezafibrate (kₒ₃ = 590 M⁻¹ s⁻¹). Reduction of UV absorbance, which is often used as an indicator for electrophilic ozone reactions, appeared to be less efficient with H₂O₂, but a correction by the UV absorbance of residual peroxide almost fully compensated this effect.

Disinfection was not an objective of this study. The negative effect of H₂O₂ addition on disinfection efficiency in drinking water treatment is well known. However, whether these adverse effects are also relevant for wastewater treatment is not clear and needs to be evaluated in additional tests.

Bromate minimization

Bromate was analysed in the experiments from February 2013. Previous experiments with secondary effluent from Berlin Ruhleben showed a formation of 11 μg/L at $Z_{\text{spec}} = 0.8$ mgO₃/mg DOC₀ (Bahr et al. 2007). Similar bromate formation (10.2 μg/L) was observed during preozonation with $Z_{\text{spec}} = 0.87$ mgO₃/mg DOC₀. In batches with
higher ozone dosages (1.2 and 2.0 mg O₃/mg DOCₐ mg) bromate concentrations reached 21.8 and 50.7 µg/L. The addition of H₂O₂ at a molar ratio of 0.5 reduced bromate formation by approximately 15%. Besides the reduction of ozone exposure, bromate control might occur by the reaction of H₂O₂ with hypobromic acid, a major intermediate during bromate formation. Further minimization at higher H₂O₂/O₃ ratios (up to 35%) can also be attributed to the scavenging effect of hydrogen peroxide since bromate formation is also initiated by OH-radicals.

**CONCLUSIONS**

Different options for the application of perozone treatment (H₂O₂/O₃) of secondary effluents were studied. Independent from ozone dosage the enhancement of OH-radical exposures by perozone addition during ozonation is limited to a maximum of approximately 30–40% with stable ozone dosage and molar H₂O₂/O₃ ratios of 0.5. Also a pre-treatment of effluent with ozone did not enhance radical formation efficiency in subsequent AOP. Calculations from second order rate kinetics showed that even the observed enhancement of radical formation only slightly improves transformations of ozone-resistant compounds. For a more efficient removal of these compounds other measures, for example an increase of ozone dosage or the application of different AOP techniques need to be considered.

The limited effect of the perozone process on radical formation can be attributed to the strong competition of H₂O₂ with the highly reactive organic matter in secondary effluent. This could be supported by low consumption and relatively high residual H₂O₂ after oxidation. In addition, radical formation from reactions of ozone with effluent organic matter is already high reducing the potential improvement by perozone treatment.

Besides enhancement of radical formation, addition of perozone increases ozone depletion and thereby reduces ozone exposure. This resulted, together with the scavenging of hypobromic acid, in a reduction of bromate formation by approximately 15–20%. Therefore, H₂O₂/O₃ might still be a promising option for the treatment of bromide containing effluents in order to optimize ozone dose with minimum formation of bromate.

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