VARIABILITY IN REQUIRED OZONE DOES FOR REMOVING PHARMACEUTICALS FROM WASTEWATER EFFLUENTS

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Aim of study. The aim of the present study was to investigate the ozone dosage required to remove active pharmaceutical ingredients (APIs) from biologically treated wastewater of varying quality originating from different wastewater treatment processes.

Methods. Secondary effluents from six Swedish wastewater treatment plants (WWTP) were spiked with 42 APIs (nominal concentration 1μg/L) and treated with different O₃ doses (0.5-12.0 mg/L ozone) in bench-scale experiments (Antoniou et al, 2012). Concentrations of APIs were measured by SPE extraction using OASIS HLB cartridges followed by quantification using LC-MS-MS (Grabic et al, 2012).

Results. For each wastewater effluent a profile of sensitivity of each API to a range of ozone doses were generated as shown in Figure 1.

![Figure 1: Profiles of ozone dose dependency for the removal of pharmaceuticals in one of the 6 investigated wastewaters.](image)

In order to obtain a parameter to compare the sensitivity of APIs to ozone in each wastewater the specific dose of ozone required to achieve one decade of removal of each investigated API (DDO₃) was determined for each effluent by fitting a first order equation to the remaining concentration of API at each applied ozone dose (See example in Figure 2) (Hansen et al, 2010). Equation 1 describes the remaining API concentration in relation to its initial concentration after a specific O₃ dose is delivered (DO₃). The equation contains the O₃ dose required to remove 90% of the API as a constant (here...
noted as decadic dose of O₃ $DDO_3$. The fitted parameter is named the decadic dose of O₃, $DDO_3$.

$$\text{(Eq. 1)} \quad \log \left( \frac{C}{C_o} \right) = -\frac{DDO_3}{DO} \Rightarrow C = C_o \cdot 10^{-\frac{DO}{DDO_3}}$$

To fit the concentration curves of APIs that showed apparent lag of reactivity towards low O₃ doses (see figure 2B), a variation of Equation 1 was developed as shown in Equation 2.

$$\text{(Eq. 2)} \quad IF: DO_3 < LagO_3 \rightarrow C = C_o$$

$$IF: DO_3 > LagO_3 \rightarrow C = C_o \cdot 10^{-\frac{DO_3 - LagO_3}{DDO_3}}; \quad DDO_3 = D + LagO_3$$

Ozone dose requirements for APIs were found to vary significantly between wastewater effluents depending on their matrix characteristics.

**Figure 2:** Concentration profiles for selected APIs in six WWTP effluents, which follow first order decay with the delivered O₃ dose (DO₃) (A) or exhibiting an apparent lag-phase (B). The intersect of the black horizontal line with the 10% remaining API concentration indicates the corresponding $DDO_3$.

The specific ozone dose was normalized to the dissolved organic carbon (DOC) of each effluent as shown in Table 1. The $DDO_3$/DOC ratios were comparable for each API between the effluents. 15 of the 42 investigated APIs could be classified as easily degradable ($DDO_3$/DOC≤0.7), while 19 were moderately degradable (0.7<$DDO_3$/DOC≤1.4) and 8 were recalcitrant towards O₃-treatment (DDO₃/DOC >1.4).

**Table 1:** Ozone dose required for removal of the first decade of selected APIs in each wastewater and the dose relative to the DOC.

<table>
<thead>
<tr>
<th>API</th>
<th>Eff1</th>
<th>Eff2</th>
<th>Eff3</th>
<th>Eff4</th>
<th>Eff5</th>
<th>Eff6</th>
<th>DDO₃ (ppm O₃)</th>
<th>[DDO₃/DOC]</th>
<th>Ave</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbazepine</td>
<td>5.1</td>
<td>5.4</td>
<td>2.2</td>
<td>4.3</td>
<td>10.8</td>
<td>3.5</td>
<td>0.68</td>
<td>0.84</td>
<td>0.42</td>
</tr>
<tr>
<td>Naproxen</td>
<td>5.7</td>
<td>5.0</td>
<td>2.5</td>
<td>6.4</td>
<td>10</td>
<td>3.7</td>
<td>0.76</td>
<td>0.77</td>
<td>0.48</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>4.7</td>
<td>5.8</td>
<td>NA</td>
<td>3.5</td>
<td>10</td>
<td>NA</td>
<td>0.63</td>
<td>0.90</td>
<td>0.43</td>
</tr>
<tr>
<td>Citalopram</td>
<td>5.0</td>
<td>7.8</td>
<td>2.0</td>
<td>7.1</td>
<td>15</td>
<td>5.0</td>
<td>0.67</td>
<td>1.21</td>
<td>0.38</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>6.9</td>
<td>6.9</td>
<td>3.8</td>
<td>7.4</td>
<td>18.2</td>
<td>8.8</td>
<td>0.92</td>
<td>1.07</td>
<td>0.73</td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>6.6</td>
<td>6.8</td>
<td>3.1</td>
<td>7.7</td>
<td>20</td>
<td>11.3</td>
<td>0.88</td>
<td>1.05</td>
<td>0.60</td>
</tr>
<tr>
<td>Memantine</td>
<td>11.4</td>
<td>12.8</td>
<td>7.8</td>
<td>14.5</td>
<td>21.3</td>
<td>10.2</td>
<td>1.52</td>
<td>1.98</td>
<td>1.50</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>11.5</td>
<td>10.9</td>
<td>7.3</td>
<td>14.7</td>
<td>27</td>
<td>10.4</td>
<td>1.53</td>
<td>1.69</td>
<td>1.40</td>
</tr>
<tr>
<td>Beclomethasone</td>
<td>20</td>
<td>18</td>
<td>5.8</td>
<td>12</td>
<td>&gt;&gt;8.9</td>
<td>9.2</td>
<td>2.66</td>
<td>2.79</td>
<td>1.12</td>
</tr>
</tbody>
</table>

With this estimates of the required ozone dose required to remove any of the investigated APIs may be attained by multiplying the experimental average $DDO_3$/DOC obtained with the actual DOC of any effluent. The method predicts results which agrees with removal
rates and ozone doses found in literature (Hollender et al, 2009; Bahr et al, 2007; Huber et al, 2005).

In a follow up study with two effluents with high pH (around 8) and two effluents with low pH (around 6) some difference was found in the oxidation of pharmaceuticals by ozone between the two groups. This is explained by the longer lifetime of ozone in low pH as illustrated in figure 3. Then 1 mg/L H₂O₂ was added to the low pH effluents the ozone lifetime reduced similar to the ozone concentration profiles observed at high pH (figure 3, right) and the removal of pharmaceuticals was unchanged (not shown).

**Fig. 3.** Ozone consumption in WWTP effluent at pH 8 (A) without H₂O₂ and pH 6 (B) with and without H₂O₂ (H₂O₂/O₃ ratio = 0.10).

**REFERENCES**


