AOX removal from industrial wastewaters using Advanced Oxidation Processes: assessment of a combined chemical-biological oxidation

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Introduction and problem description

AOX = Adsorbable Halogenated Organic Compounds (Group parameter)
     = Hazardous / toxic organic pollutants
     = Source: mostly industrial production

→ Decreasing discharge limits (EU water framework directive 2000/60/EC)

AOX + AOP (O₃, H₂O₂/UV, O₃/UV Fe(II)/H₂O₂) → Degradation products
   (Parilli et al., Perez et al., Kusic et al.)

AOPs increase the biodegradability of waste water streams
   (Van Aken et al., Ballesteros et al., Guo et al.)

Presence of halogenated ions (Cl⁻, Br⁻,...) jeopardises the use of AOPs
   (Baycan et al., Sniegowski et al.)
Introduction and problem description

Industrial waste water: halogenated compounds (AOX) ↔ matrix compounds (COD)

\[
\text{AOX+oxidant} \xrightarrow{k_1} \text{degradation products}
\]

\[
\text{COD+oxidant} \xrightarrow{k_2} \text{degradation products}
\]

→ Selective AOX degradation is requested
→ Reaction order might change during experiments (especially with O₃)
→ Oxidant dose is a key parameter for removal efficiency

Potential of a combined chemical and biological oxidation for removal of AOX in industrial waste waters?

Sensitivity of AOX removal on operational parameters?
Methods and materials

100% Ozone : 16 g O₃/h
100% UV: 2000 W
100% H₂O₂: 2 mg H₂O₂ / mg COD

Pilot scale plant : Volume 50 L
Medium pressure Hg lamp, Philips
[Fe²⁺]/[H₂O₂] ratio of 1/100 ww
## Methods and materials

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chloride (mg/l)</strong></td>
<td>750</td>
<td>650</td>
<td>1500</td>
</tr>
<tr>
<td><strong>AOX (μg Cl/l) (discharge limit)</strong></td>
<td>1500 (400)</td>
<td>5000 (400)</td>
<td>10000 (1000)</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>7.8</td>
<td>7.9</td>
<td>8</td>
</tr>
</tbody>
</table>

- Biological oxidation (4h): Respirometry experiments using 500 ml waste water and 300 ml communal WWTP activated sludge (300 ml), periodically aerated.
- AOX measurements according WAC/IV/B/011 protocol, ThermoFischer Scientific 3000 systems TN/TS/TX (SphiNCX)
- Nanocolor® COD reactor and Nanocolor® 500 D colorimeter from Machery Nagel
Results waste water I

AOX removal after different AOPs

Reactant time (min)

AOX/AOX₀ %
AOX after respiration (4h) at different AOP reaction time

Results waste water I

AOX/AOX₀ %

0,00% 10,00% 20,00% 30,00% 40,00% 50,00% 60,00% 70,00% 80,00% 90,00% 100,00%

0 20 40 60

AOP reaction time (min)

- O3/UV pH9
- O3/UV pH7
- O3/UV50 pH7
- O350/UV pH7
- UV/H₂O₂ belucht pH7
- UV/H₂O₂ belucht pH9
- UV/H₂O₂ onbelucht pH7
- Fotofenton 25%
- Fotofenton 56%
- UV
• Biological oxidation of the original wastewater: ± 20%.
• Ozone based techniques: 50% removal after 60 minutes, more biodegradable than 
  \( \text{H}_2\text{O}_2 \) based techniques
• UV alone: 50% AOX, slightly biodegradable
Results: Selectivity coefficient

For H₂O₂-based experiments no selectivity parameter is reported. Varying H₂O₂ results in similar AOX and COD removal efficiencies.

<table>
<thead>
<tr>
<th>Technique</th>
<th>AOX₀</th>
<th>AOX₟</th>
<th>COD₀</th>
<th>COD₟</th>
<th>Overall selectivity S(AOX/COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃/UV pH 9</td>
<td>1647</td>
<td>804</td>
<td>206</td>
<td>184</td>
<td>4.9</td>
</tr>
<tr>
<td>O₃/UV pH 7</td>
<td>1700</td>
<td>894</td>
<td>184</td>
<td>102</td>
<td>1.1</td>
</tr>
<tr>
<td>O₃/UV(50%), pH 7</td>
<td>1517</td>
<td>847</td>
<td>177</td>
<td>94</td>
<td>0.9</td>
</tr>
<tr>
<td>O₃ (50%)/UV, pH 7</td>
<td>1660</td>
<td>631</td>
<td>170</td>
<td>93</td>
<td>1.4</td>
</tr>
</tbody>
</table>

- Ozone based AOP can selectively degrade AOX towards COD
- Selectivity: O₃(50%)/UV > O₃/UV > O₃/UV(50%)
  - lower ozone concentration with respect to UV intensity is recommended
- Increasing the pH to 9 enhances the selectivity for AOX removal
Results: Effect of UV intensity and H₂O₂ dose

<table>
<thead>
<tr>
<th>UV intensity (kW)</th>
<th>Oxidant + dose (g/h)</th>
<th>AOX₀ (µg Cl/I)</th>
<th>AOX (µg Cl/I) after AOP (60 min)</th>
<th>AOX (µg Cl/I) after biological oxidation (4 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>H₂O₂/6.79</td>
<td>4130</td>
<td>4401</td>
<td>3382</td>
</tr>
<tr>
<td>0.5</td>
<td>H₂O₂/6.79</td>
<td>4110</td>
<td>3835</td>
<td>2835</td>
</tr>
<tr>
<td>0.5</td>
<td>H₂O₂/3.4</td>
<td>4908</td>
<td>4106</td>
<td>3388</td>
</tr>
<tr>
<td>2.0</td>
<td>H₂O₂/6.79</td>
<td>5493</td>
<td>4572</td>
<td>3358</td>
</tr>
<tr>
<td>2.0</td>
<td>H₂O₂/4.53</td>
<td>4640</td>
<td>1707</td>
<td>1658</td>
</tr>
<tr>
<td>2.0</td>
<td>H₂O₂/2.5</td>
<td>5355</td>
<td>2506</td>
<td>1880</td>
</tr>
<tr>
<td>1.0</td>
<td>H₂O₂/6.79</td>
<td>5283</td>
<td>3357</td>
<td>2358</td>
</tr>
<tr>
<td>2.0</td>
<td>O₃/16</td>
<td>4438</td>
<td>4748</td>
<td>2205</td>
</tr>
</tbody>
</table>

- O₃/UV at pH 7 leads to an increase in (biodegradable) AOX
- H₂O₂-based techniques: high UV intensity and intermediate H₂O₂ dosage is requested.
- Variable effluent concentrations demand strict monitoring as the discharge limit is not reached within 60 minutes reaction time (+ biodegradation) due to high initial AOX level
Results: Sensitivity of operational parameters

AOX removal by UV/H₂O₂ at pH 7

- Reaction time and H₂O₂ dose should be balanced in order to avoid AOX formation.
- Optimal: H₂O₂ dosage of 3-4.5 g corresponding with a reaction time of 50-60 min.
Results: Sensitivity of operational parameters

AOX removal by UV/H₂O₂ at pH 7

• Best results: UV power between 1 - 2 kW
• Optimal combination of reaction time and UV intensity is crucial!
Conclusions

- AOX can be significantly reduced in industrial wastewater by a combined chemical-biological treatment. Monitoring is crucial with variable effluent composition.
- Oxidant concentration is a key parameter for selective degradation of AOX towards COD.
- For O₃/UV, lowering the ratio of O₃ dosage to UV intensity leads to a better selectivity for AOX.
- O₃-based AOPs remove less AOX than H₂O₂-based AOPs but increases the biological degradable fraction more.
- Reaction time, H₂O₂ dose and UV intensity needs to balanced for optimal AOX removal.
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