Wet air oxidation for industrial wastewater and sludge treatment: first results of a new research program in Quebec

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WET AIR OXIDATION FOR
INDUSTRIAL WASTEWATER AND SLUDGE TREATMENT:
FIRST RESULTS OF A NEW RESEARCH PROGRAM IN QUÉBEC


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Technology Transfer Center

Applied research on:

- Industrial waste valorization
- Clean processes
- Industrial symbiosis
WET AIR OXIDATION PROCESS (WAO)

- Subcritical water enriched with air or oxygen (≈150–350 °C, ≈3–20 MPa)
- Oxygen reacts with organic compounds → propagation of radicals: R•, OH•, HO2•, ROO• → Exothermic oxidation of organic compounds mostly into CO2, H2O, NH3, SO42-, PO43-
- Industrial opportunities for WAO: wastewater too toxic or too concentrated for biological processes, and too diluted for suitable incineration (> 80 % H2O)
- Better energy output than incineration (for sludge or wastewater)
- Cleaner gas emissions: no NOX, dioxins or furans
- Better efficiency and faster treatment than other advanced oxidation processes (AOPs) for highly concentrated waste (>10 g/L DCO)
- Economically-competitive and environmentally-friendly process industrialised in Europe, but still non-existent in the province of Québec.
WAO AT CTTÉI
APPLIED RESEARCH AND TECHNOLOGY TRANSFER
**MODE WASTEWATER**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene glycol</td>
<td>C₃H₈O₂</td>
<td>76 g/mol</td>
</tr>
<tr>
<td>Ethoxylated alcools</td>
<td>C₂₂H₄₆O₇</td>
<td>422 g/mol</td>
</tr>
<tr>
<td>Tripropylene glycol methyl ether</td>
<td>C₁₀H₂₂O₄</td>
<td>206 g/mol</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>C₆H₁₅NO₃</td>
<td>149 g/mol</td>
</tr>
<tr>
<td>Dodecylbenzene sulfonic acid</td>
<td>C₁₈H₂₉SO₃Na</td>
<td>348 g/mol</td>
</tr>
<tr>
<td>Polyoxyethylene monooleyl ether phosphate</td>
<td>C₂₈H₅₉O₁₀P</td>
<td>587 g/mol</td>
</tr>
</tbody>
</table>

- Industrial reality: heterogeneous mix of products.
- Modelling a precise oxidation mechanism becomes very difficult (numerous degradation by-products, interaction and recombination).
- Necessity of case-by-case lab studies and experimental design.
- A model wastewater was synthetised and studied:
  - Mix of 6 common chemicals used by our industrial partners (coolants, lubricants, solvants, surfactants)
  - COD: 10 – 60 g/L (range studied)
  - pH: 8
WAO OF MODEL WASTEWATER - EFFECT OF TEMPERATURE

Initial COD: 10 g/L
Oxydant: Air, 1,8 x required amount for complete oxidation
P = 160 bars (180 bars for essais at 320°C and 335°C)
Stirring 1000 rpm

H₃C

O

OH

°C

°C

°C

°C

°C
WAO OF MODEL WASTEWATER – EFFECT OF COPPER CATALYST

Initial COD: 10 g/L
Oxidant: Air, 1.8 x required amount for complete oxidation
P = 160 bars
Stirring 1000 rpm
AERATED LAGOON SLUDGES

- Sewage sludges are treated by WAO at industrial scale in Europe (ex.: Brussels, Aix-en-Provence, Trucazzanno, etc.)

- Aerated lagoons are common in Québec (require large surface areas). No study was found on WAO of lagoon sludge.

- In Sorel-Tracy, Québec: 20,000 tons of sludges to dispose. The cost of dewatering + landfilling would be prohibitive.
WAO - AERATED LAGOON SLUDGES

Initial diluted sludges: 5200 mg/L

COD of sludge samples (mg/L) vs. Reaction time (min) for different temperatures and pressures:
- 210°C - 100 bars
- 210°C - 175 bars
- 240°C - 100 bars
- 240°C - 175 bars
- 270°C - 100 bars
- 270°C - 175 bars
- 300°C - 100 bars
- 300°C - 175 bars

Note: The graph shows the decrease in COD over time under various conditions.
WAO - AERATED LAGOON SLUDGES

Example of Sorel-Tracy:
Before WAO: 20 000 tons of sludges
After: 1 400 tons of solid (> 99% inorganic) + biodegradable liquid

<table>
<thead>
<tr>
<th></th>
<th>Before WAO (sludge)</th>
<th>After WAO 300 °C (liquid phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>52 g/L</td>
<td>10 g/L</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>1,0 g/L</td>
<td>6,3 g/L</td>
</tr>
<tr>
<td>Biodegradability index (BOD$_5$/COD)</td>
<td>0,02</td>
<td>0,63</td>
</tr>
</tbody>
</table>
CONCLUSION AND FUTURE WORK

• Interesting opportunities for WAO and other green processes in Québec.

• Model wastewater: temperature has a major impact between 240 and 300 °C. Homogeneous copper catalyst shows good activity.

• Lagoon sludges can be treated effectively with ≈ 85% COD removal on liquid phase and > 99% on solids.

• Future work:
  – Economic analysis: CAPEX/OPEX of studied scenarios
  – New lab equipment to reach supercritical conditions (> 374 °C, 220 bars)
  – Study WAO for hospital wastewater and micropollutants

• Always seeking new industrial and academic partners!
QUESTIONS ?
COMMENTS ?