Photocatalytic Treatment of Winery Wastewater

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Experimental Studies Overview

Winery Wastewater

Grapes

Wine

Biological Oxidation Process

Solar Fenton Process

Final Effluent

Solar CPCs
Experimental Studies Layout

Bench scale
- Homogeneous Solar Fenton
- Heterogeneous Solar Fenton

Semi-pilot scale
- Pre-treated Winery Wastewater
- Raw Winery Wastewater

Pilot Scale Treatment Plant
- MBR
- Solar Fenton
Bench Scale Experiments

**Heterogeneous Solar Fenton**
- Catalyst: Fe$_2$O$_3$/SBA-15 (17% iron content)
- $[\text{Fe}_{\text{SBA-15}}] = 50$ - 200 mg/L; $[\text{H}_2\text{O}_2] = 50$ - 300 mg/L
- pH: 3; 8

**Homogeneous Solar Fenton**
- Catalyst: Fe$_2$SO$_4$.7H$_2$O
- $[\text{Fe}] = 5$ - 20 mg/L; $[\text{H}_2\text{O}_2] = 100$ - 300 mg/L
- pH: 3; 8

- Chemical Oxygen Demand (COD)
- Dissolved Organic Carbon (DOC)
- Dissolved Iron Content
- $\text{H}_2\text{O}_2$ consumption
- UV/Vis spectrophotometry
- Total Phenols
Heterogeneous Catalyst Fe$_2$O$_3$/SBA-15

- Easy retrieval from effluents
- Use in wide pH range
- Catalyst re-use

however...

- Low efficiency (mass transfer limitations)
- Light scattering effect
- Low stability (metal leaching)
Wastewater Characteristics
Sequential Batch Reactor

COD = 37.300 mg O2/L

IN

SBR

OUT

COD = 267 mg O2/L

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (20^\circ\text{C})</td>
<td>8.2 - 8.3</td>
</tr>
<tr>
<td>Total Solids (mg/L)</td>
<td>3672-3740</td>
</tr>
<tr>
<td>Total Volatile Solids (mg/L)</td>
<td>2430 - 2612</td>
</tr>
<tr>
<td>Suspended Solids (mg/L)</td>
<td>225 - 245</td>
</tr>
<tr>
<td>Suspended Volatile Solids (mg/L)</td>
<td>140 - 175</td>
</tr>
<tr>
<td>Total phenols (mg/L)</td>
<td>3.76 - 4.66</td>
</tr>
<tr>
<td>Total Nitrogen (mg/L)</td>
<td>6.72 - 6.82</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>264 - 270</td>
</tr>
<tr>
<td>BOD(_5) (mg/L)</td>
<td>111 - 113</td>
</tr>
<tr>
<td>Total Phosphorous (mg/L)</td>
<td>32 - 46.8</td>
</tr>
<tr>
<td>Fats and oils (mg/L)</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.18 - 0.20</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.17 - 0.19</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.05 - 0.07</td>
</tr>
<tr>
<td>Na(^+) (mg/L)</td>
<td>1.42 - 1.50</td>
</tr>
<tr>
<td>K(^+) (mg/L)</td>
<td>4.5 - 4.9</td>
</tr>
</tbody>
</table>
Heterogeneous Solar Fenton

Optimum $[\text{Fe}]$ and $[\text{H}_2\text{O}_2]$: 100 mg/L

Optimum pH: Similar efficiency in both acidic (i.e. 2.8) and inherent pH (i.e. 8)
Heterogeneous Solar Fenton

Solar Fenton

Dark Fenton

Solar + H2O2

Solar + Fe2O3/SBA-15

Photolysis

High

Low

Graph showing TOC/TOC₀ vs Time (min) with different treatments:
- Solar Fenton
- Dark Fenton at pH=2.8
- Solar + SBA-15
- Adsorption on SBA-15
- Solar + H2O2
- Photolysis
Heterogeneous vs. Homogeneous Solar Fenton

Optimal experimental conditions (150 W)
Homogeneous: 10 mg/L Fe, 100 mg/L H₂O₂, pH₀=2.8
Heterogeneous: 100 mg/L Fe₅BA-15, 100 mg/L H₂O₂, pH₀=2.8
Semi-pilot Scale Experiments

Operating Volume: 105-250 L

Irradiated Volume: 70 L

Irradiated Area: 6m²

Recirculation Rate: 0.8 – 4 L/min
### Wastewater Characteristics

#### Raw Winery Effluent (non-Vintage period)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>COD (mg O$_2$/L)</strong></td>
<td><strong>1200±150</strong></td>
</tr>
<tr>
<td><strong>BOD$_5$ (mg O$_2$/L)</strong></td>
<td>750</td>
</tr>
<tr>
<td><strong>DOC (mg C/L)</strong></td>
<td>435</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>5.5-6.5</td>
</tr>
<tr>
<td><strong>Cl$^-$</strong></td>
<td>0.02925</td>
</tr>
<tr>
<td><strong>Na$^+$ (mg/L)</strong></td>
<td>1.94</td>
</tr>
<tr>
<td><strong>SO$_4^{2-}$ (mg/L)</strong></td>
<td>0.82125</td>
</tr>
<tr>
<td><strong>K$^+$ (mg/L)</strong></td>
<td>50.14</td>
</tr>
<tr>
<td><strong>N-NO$_3^-$ (mg/L)</strong></td>
<td>0.00675</td>
</tr>
<tr>
<td><strong>Ca$^{2+}$ (mg/L)</strong></td>
<td>0.535</td>
</tr>
<tr>
<td><strong>P-PO$_4^{3-}$ (mg/L)</strong></td>
<td>0.2919</td>
</tr>
<tr>
<td><strong>Mg$^+$ (mg/L)</strong></td>
<td>0.63</td>
</tr>
<tr>
<td><strong>N-NH$_3$ (mg/L)</strong></td>
<td>2.1121</td>
</tr>
<tr>
<td><strong>CH$_3$COOH (mg/L)</strong></td>
<td>54.41</td>
</tr>
</tbody>
</table>

**non-Vintage period: February 2012**

- Stabilization
- Filtration
- Bottling
Experimental Design
(Optimization)

1. 11 preliminary bench-scale experiments
2. Measured response: CODi/CODo (%)
3. Irradiation time: 120 min
<table>
<thead>
<tr>
<th>Method</th>
<th>CODi/CODo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis/Solar+Fe</td>
<td>4-5%</td>
</tr>
<tr>
<td>Dark Fenton</td>
<td>10%</td>
</tr>
</tbody>
</table>
| Optimum [Fe^{2+}] & [H_{2}O_{2}] | Catalyst: 5 mg/L  
Oxidant in excess (100-500 mg/L) |
Effect of Iron Concentration

Semi-Pilot Study

- Solar Fenton 29 mg/L Fe, H2O2 in excess
- Solar Fenton 5 mg/L Fe, H2O2 in excess
- H2O2 consumed (mg/L)

CODi/CODo (%)

Consumed H2O2 (mg/L)

- 2000 mg/L H2O2 required
- 1270 mg/L H2O2 required
- 80 % removal

Consumed H2O2 (mg/L)

- t,30W (min)
Effect of Iron Concentration

Iron: 5 mg/L
- No separation step required
- No sludge formation
- Same mineralization efficiency, though lower rate
- Higher efficiency in H2O2 utilization

Iron: 29 mg/L
- Separation step required
- High sludge formation
- Higher mineralization rate
Semi-Pilot Study

Effect of H2O2

Consumed H2O2 (mg/L)

CODi/CODo (%)

Solar Fenton 5 mg/L Fe, H2O2 in excess
Solar Fenton 5 mg/L Fe, H2O2 limiting
H2O2 consumed (mg/L)
H2O2 consumed (mg/L)

49%
47%

500 mg/L H2O2
Semi-Pilot Study
Mineralization abatement

![Graph showing COD and DOC removal percentages over time.

| Optimum [Fe²⁺] & [H₂O₂] | Catalyst: 5 mg/L
| Oxidant in excess (100-500 mg/L) |
| % COD removal | 80 % (~6.5 hr solar irradiation 30 W) |
| % DOC removal | 80 % |

~1320 mg/L H₂O₂ consumed
Semi-Pilot Study

Toxicity Evaluation with Vibrio fischeri sp.

CODi/CODo

% Inhibition

<20%

Inhibition (%)

<table>
<thead>
<tr>
<th>t,30W (min)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Inhibition</td>
<td>60</td>
<td>50</td>
<td>40</td>
<td>30</td>
<td>20</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>
### What about Vintage Period?

Raw Winery Effluent (*Vintage period*)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg O&lt;sub&gt;2&lt;/sub&gt;/L)</td>
<td>7520</td>
</tr>
<tr>
<td>BOD&lt;sub&gt;5&lt;/sub&gt; (mg O&lt;sub&gt;2&lt;/sub&gt;/L)</td>
<td>6500</td>
</tr>
<tr>
<td>DOC (mg C/L)</td>
<td>435</td>
</tr>
<tr>
<td>pH</td>
<td>4.5-5.5</td>
</tr>
<tr>
<td>EC&lt;sub&gt;20&lt;/sub&gt;</td>
<td>36%</td>
</tr>
</tbody>
</table>

#### Vintage period: August 2012
- grapes crushing,
- tank & equipment cleaning
- grape juice fermentation

High biodegradable content (soluble sugars, alcohols,
Semi-Pilot Study

Vintage 2012

<table>
<thead>
<tr>
<th>Optimum [Fe$^{2+}$] &amp; [H$_2$O$_2$]</th>
<th>Catalyst: 5 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>% COD removal</td>
<td>13 %</td>
</tr>
</tbody>
</table>

Oxidant in excess (100-500 mg/L)

COD (mg/L)

Very Low Efficiency!

0 1000 2000 3000 4000 5000 6000 7000

0 30 60 90 120 150 180 210 240 270 300 330 360 390 420 450 480 510
t,30W (min)
Winery wastewater with higher organic strength (e.g. 7.5 g/L) that contains high biodegradable content (e.g. soluble sugars) proved resistant to chemical oxidation even after prolonged treatment.

The coupling of a biological step followed by solar Fenton process seems the most efficient option for highly biodegradable agro-industrial wastewaters.

However, Solar Fenton process has proved efficient in eliminating the organic content of not only biologically pre-treated effluents (e.g. 0.27 g/L COD), but also of raw winery wastewater with relatively high (e.g. 1.3 g/L) COD value; this is important since failures often occur in biological systems and, in such a case, the solar oxidation step could-under circumstances- act temporarily as an efficient pollution barrier and produce an effluent safe enough for discharge into the environment.
Thank you!

"So, how do you like it? I crushed the grapes myself!"