Cheese whey wastewater treatment by combined Electrocoagulation-Electrooxidation

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Goat cheese whey wastewater

- Whey as a waste is characterized by high COD.
- It is a polluting by-product, which needs to be treated to protect the environment.
- In Europe, their direct discharges to surface waters are not permitted under the relevant European Directives 91/271/EEC and 97/771/EEC, respectively.
- Electrochemical processes such as electrocoagulation (EC) and electrooxidation (EO) have been reported to be the most effective for COD removal.

Electrocoagulation (EC)

- Mainly Fe and Al electrodes are used, which are immersed in wastewater.
- Its effectiveness is due to the formation of insoluble metal hydroxides $\text{M(OH)}_3$ through redox reactions, which act as coagulants and are capable of destabilizing organic matter.

$$
\text{M} \rightarrow \text{M}^{n+} + \text{n}e^{-}
$$

$$
\text{nH}_2\text{O} + \text{n}e^{-} \rightarrow \text{nOH}^{-} + (\text{n}/2)\text{H}_2(\text{g})
$$

Electrochemical wastewater treatment

Electrooxidation (EO)

- The organic charge is destroyed due to the hydroxyl radicals ($\cdot$OH) formed on the anode surface by the oxidation of water.

$$
\text{M} + \text{H}_2\text{O} \rightarrow \text{M}(-\text{OH}) + \text{H}^{+} + \text{e}^{-}
$$

- The use of Boron-doped diamond (BDD) electrode, is able to completely and non-selectively mineralize organic pollutants (R) with high efficiency.

$$
\text{BDD}(-\text{OH}) + \text{R} \rightarrow \text{BDD} + \text{nCO}_2 + \text{nH}_2\text{O} + \text{H}^{+} + \text{e}^{-}
$$

Magnisali, E., Yan, Q., & Vayenas, D. V. (2022) https://doi.org/10.1002/JCTB.6880

Experimental layout of the EC process

Reactor
0.5 L

300 ml wastewater

Al-Al-Al
Active anode surface
20 cm²
Experimental layout of the EO process

- Reactor: 0.4 L
- 300 ml wastewater
- graphite-BDD-graphite
  Active anode surface
  20 cm$^2$
Optimization of EC and EO operating parameters

The main parameters that affect the efficiency of EC and EO treatment were studied:

1) Operating time (h)
2) Agitation rate (rpm)
3) pH
4) Current density (mA/cm²)

The purpose was to find the optimal operating conditions for the highest efficient removal of COD from cheese whey wastewater

\[
\% \text{ Removal} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100
\]
Operating time (h)

Electrocoagulation (EC)

Electrooxidation (EO)
Current density (mA/cm²)

Electrocoagulation (EC)

The current determines the release rate of
Al → Al³⁺ + 3e⁻

↑ mA/cm²  ➔  ↑ e⁻  ➔  Al(OH)₃

Electrooxidation (EO)

The current determines the formation of
BDD + H₂O → BDD(·OH) + H⁺ + e⁻

↑ mA/cm²  ➔  ↑(·OH)
Agitation rate (rpm)

Electrocoagulation (EC)

Electrooxidation (EO)

<table>
<thead>
<tr>
<th>Parameter (n=3)</th>
<th>% Reducing weight of Al-Al-Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agitation rate (rpm)</td>
<td>190 rpm</td>
</tr>
<tr>
<td>190 rpm</td>
<td>0.5 %</td>
</tr>
<tr>
<td>380 rpm</td>
<td>0.7 %</td>
</tr>
<tr>
<td>570 rpm</td>
<td>1.1 %</td>
</tr>
</tbody>
</table>
According to Yilmaz Nayir and Kara et al. (2017)

Electrocoagulation (EC)

According to Stergiopoulos et al. (2021)

Electrooxidation (EO)
Combined of EC/EO processes

Optimal operating conditions:

**EC**
- 40 mA/cm²
- 190 rpm
- without pH adjustment

**EO**
- 60 mA/cm²
- 380 rpm
- without pH adjustment
<table>
<thead>
<tr>
<th>Type of wastewater</th>
<th>Electrochemical system</th>
<th>Electrode anode/cathode</th>
<th>Current density (mA/cm²)</th>
<th>Time (min)</th>
<th>pH</th>
<th>COD removal (%) *</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cheese whey wastewater</td>
<td>EC</td>
<td>Fe/Fe</td>
<td>60</td>
<td>20</td>
<td>5</td>
<td>86.4</td>
<td>Tezcan Un et al. (2014)</td>
</tr>
<tr>
<td>Artificial dairy wastewater</td>
<td>EC</td>
<td>Al/Al</td>
<td>-</td>
<td>30</td>
<td>7.1</td>
<td>61.0</td>
<td>Tchamango et al. (2010)</td>
</tr>
<tr>
<td>Dairy wastewater</td>
<td>EC</td>
<td>Al/Al</td>
<td>-</td>
<td>30</td>
<td>7.1</td>
<td>61.0</td>
<td>Tchamango et al. (2010)</td>
</tr>
<tr>
<td>Dairy wastewater</td>
<td>EC</td>
<td>6xAl</td>
<td>31.5</td>
<td>60</td>
<td>7.2</td>
<td>98.8</td>
<td>Bazrafshan et al. (2013)</td>
</tr>
<tr>
<td>Cheese whey wastewater</td>
<td>EC/EO</td>
<td>Al/Fe</td>
<td>25</td>
<td>120</td>
<td>5</td>
<td>82</td>
<td>Yilmaz Nayir &amp; Kara et al. (2017)</td>
</tr>
<tr>
<td>Dairy wastewater</td>
<td>EC/EO</td>
<td>Al/Al</td>
<td>60</td>
<td>6</td>
<td>6.6</td>
<td>40</td>
<td>Chakchouk et al. (2017)</td>
</tr>
</tbody>
</table>

* The % removal efficiency of COD is calculated based on its initial concentration, so the comparative results also depend on the initial content of wastewater in COD.
HiSorb TD-GC/MS sample analysis

The developed HiSorb TD-GC/MS method was used to analyze the VOCs of cheese whey wastewater before and after the optimal electrochemical processes (EC, EO and EC/EO).

\[
\text{Semi-quantified} = \frac{A_c}{A_{IS}} \times C_{IS} \text{ (mg L}^{-1}\text{)}
\]

\[
\text{Compound category (\%)} = \frac{\sum_{\text{category}} \frac{A_c}{A_{IS}}}{\sum_{\text{total VOCs}} \frac{A_c}{A_{IS}}} \times 100
\]
VOCs of raw cheese whey wastewater (n=9)

<table>
<thead>
<tr>
<th>Categories of VOCs</th>
<th>Number of emitted VOCs</th>
<th>Structure</th>
<th>Σ mg L⁻¹ (±CL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehydes</td>
<td>14</td>
<td>R\longrightarrow O</td>
<td>1.379 (±0.955)</td>
</tr>
<tr>
<td>Acids</td>
<td>9</td>
<td>R\longrightarrow OH</td>
<td>1.003 (±0.522)</td>
</tr>
<tr>
<td>Ketones</td>
<td>7</td>
<td>O\longrightarrow R</td>
<td>0.067 (±0.036)</td>
</tr>
</tbody>
</table>
| Hydrocarbons       | 9                      | R\longrightarrow R \ 
\longrightarrow R | 0.137 (±0.102) |
| Others             | 2                      | R\longrightarrow OH \ 
\longrightarrow S \ 
\longrightarrow R | 0.002 (±0.001) |
| Total VOCs         | 41                     |            | 2.588 (±1.616) |

![Chart showing the distribution of different categories of VOCs](chart.png)

![Graph showing the abundance of VOC emissions](graph.png)

<table>
<thead>
<tr>
<th>No</th>
<th>VOCs</th>
<th>No</th>
<th>VOCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,3-Cyclopentadiene, 1-methyl</td>
<td>11</td>
<td>Acetone</td>
</tr>
<tr>
<td>2</td>
<td>Hexanal</td>
<td>12</td>
<td>1-Hexene</td>
</tr>
<tr>
<td>3</td>
<td>Heptanal</td>
<td>13</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>4</td>
<td>Octanal</td>
<td>14</td>
<td>Butanal</td>
</tr>
<tr>
<td>5</td>
<td>Hexanoic acid</td>
<td>15</td>
<td>1-Heptene</td>
</tr>
<tr>
<td>6</td>
<td>Nonanal</td>
<td>16</td>
<td>Heptane</td>
</tr>
<tr>
<td>7</td>
<td>Octanoic acid</td>
<td>17</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>8</td>
<td>Nonanoic acid</td>
<td>18</td>
<td>2-Pentanone</td>
</tr>
<tr>
<td>9</td>
<td>2-Undecenal</td>
<td>19</td>
<td>Pentanal</td>
</tr>
<tr>
<td>10</td>
<td>n-Decanoic acid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**VOCs of EC-treated (2 h) cheese whey wastewater (n=3)**

<table>
<thead>
<tr>
<th>Categories of VOCs</th>
<th>Optimized EC process</th>
<th>(\Sigma) mg L(^{-1}) (±CL)</th>
<th>(\text{Efficiency} (\downarrow \uparrow))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehydes</td>
<td></td>
<td>0.293 (±0.144)</td>
<td>↓ 78.8 %</td>
</tr>
<tr>
<td>Acids</td>
<td></td>
<td>0.183 (±0.115)</td>
<td>↓ 81.8 %</td>
</tr>
<tr>
<td>Ketones</td>
<td></td>
<td>0.062 (±0.036)</td>
<td>↓ 7.5 %</td>
</tr>
<tr>
<td>C-H</td>
<td></td>
<td>0.074 (±0.057)</td>
<td>↓ 46.0 %</td>
</tr>
<tr>
<td>Others</td>
<td>(^a)S/N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total VOCs</td>
<td></td>
<td>0.612 (±0.352)</td>
<td>↓ 76.4 %</td>
</tr>
</tbody>
</table>

\(^a\) Low signal to noise ratio (S/N ≤3)

\(^b\) % Efficiency (\(\downarrow\)) = \(\frac{C_{\text{RAW}} - C_{\text{EC-treated}}}{C_{\text{RAW}}} \times 100\)
VOCs of EO-treated (2 h) cheese whey wastewater (n=3)

<table>
<thead>
<tr>
<th>Categories of VOCs</th>
<th>Optimized EO process</th>
<th>Efficiency (↓ or ↑)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehydes</td>
<td>1.074 (±0.253)</td>
<td>↓ 22.1%</td>
</tr>
<tr>
<td>Acids</td>
<td>1.155 (±0.281)</td>
<td>↑ 13.2 %</td>
</tr>
<tr>
<td>Ketones</td>
<td>0.236 (±0.050)</td>
<td>↑ 71.6 %</td>
</tr>
<tr>
<td>C-H</td>
<td>0.010 (±0.003)</td>
<td>↓ 92.7 %</td>
</tr>
<tr>
<td>Alcohols</td>
<td>0.062 (±0.019)</td>
<td></td>
</tr>
<tr>
<td>Esters</td>
<td>0.042 (±0.007)</td>
<td></td>
</tr>
<tr>
<td>Nitriles</td>
<td>0.212 (±0.012)</td>
<td></td>
</tr>
<tr>
<td>Chlorinated</td>
<td>0.659 (±0.150)</td>
<td></td>
</tr>
<tr>
<td>Furans</td>
<td>0.021 (±0.005)</td>
<td></td>
</tr>
<tr>
<td>Total VOCs</td>
<td>3.471 (±0.816)</td>
<td>↑ 25.4 %</td>
</tr>
</tbody>
</table>
VOCs of EC/EO treated cheese whey wastewater (n=3)
Conclusions

1) Implementation and optimization of EC and EO operating parameters

- **EC**
  - Current density: 40 mA/cm²
  - Rotation speed: 190 rpm
  - pH: 6.6
  - Treatment time: 120 min
  - COD reduction: 40.5%

- **EO**
  - Current density: 60 mA/cm²
  - Rotation speed: 380 rpm
  - pH: 6.6
  - Treatment time: 120 min
  - COD reduction: 55.3%

- **EC/EO**
  - Current density: 40/60 mA/cm²
  - Rotation speed: 190/380 rpm
  - pH: 6.6
  - Treatment time: 60/30 min
  - COD reduction: 82.4%

2) EC showed good efficiency in reducing all metered parameters, including VOCs

3) EO failed to reduce TPCs, PO₄³⁻, NO₃⁻ and Cl⁻
4) The HiSorb TD-GC / MS method identified and semi-quantified (Total VOCs):

**Identification**

<table>
<thead>
<tr>
<th>Method</th>
<th>VOCs</th>
<th>Semi-quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>41</td>
<td>2.588 mg L⁻¹</td>
</tr>
<tr>
<td>EC</td>
<td>26</td>
<td>0.612 mg L⁻¹</td>
</tr>
<tr>
<td>EO</td>
<td>52</td>
<td>3.471 mg L⁻¹</td>
</tr>
<tr>
<td>EC/EO</td>
<td>55</td>
<td>2.425 mg L⁻¹</td>
</tr>
</tbody>
</table>

**In conclusion**

EC appeared to be a favorable process for the reduction of VOCs emitted, while conjugated EC/EO as more effective for the reduction of cheese whey wastewater COD.
Thank you!