Application of ferrocene for the treatment of winery wastewater in a heterogeneous photo-Fenton process

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In the vintage, the grapes are collected.

In the grape reception, the grapes are selected and separated.

In white wines, the grapes are crushed and the must is fermented.

In red wines, the grapes are macerated and the must is fermented with the grapes.

After must fermentation and wine stabilization, the wine is filtrated.

Finally, the wine is bottled.
Winery wastewater main characteristics

Introduction

Objectives

Material and methods

Results and discussion

Conclusions

Mass balance applied to ACPB winery representing specific values, i.e., values per cubic meter of produced wine. Losses of water by evaporation were neglected [1].

**Introduction**

The document presents a flowchart illustrating the Photo-Fenton process. The key components include:

- **Ferrocene**
- **Fe$^{2+}$** (Ferrous iron)
- **Fe$^{3+}$** (Ferric iron)
- **H$_2$O$_2$** (Hydrogen peroxide)
- **HO•** (Hydroxyl radical)
- **UV-C lamp (254 nm)**
- **CO$_2$**
- **H$_2$O**
- **Species partially oxidized**

The process involves:

1. **Release of Fe$^{2+}$** from Ferrocene.
2. **Direct photolysis** of Fe$^{3+}$.
3. **Reabsorption of iron by ferrocene**.
4. **Degradation of organic carbon**.
5. **Species partially oxidized**.

The flowchart shows the regeneration of ferrous iron and the reactions involving UV-C lamp radiation as the radiation source.
Considering the low information regarding the treatment of winery wastewater by heterogeneous photo-Fenton, catalyzed by ferrocene, the aim of this work is:

1. To characterize ferrocene by FTIR and SEM
2. To optimize heterogeneous photo-Fenton
3. To study the kinetic rate and regeneration of ferrocene
Winery wastewater collection and storage

Winery wastewater characterization

Main chemical characteristics of winery wastewater (WW)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Portuguese Law Decree nº 236/98</th>
<th>WW</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.0-9.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Biochemical Oxygen Demand - BOD₅ (mg O₂/L)</td>
<td>40</td>
<td>550</td>
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<tr>
<td>Chemical Oxygen Demand - COD (mg O₂/L)</td>
<td>150</td>
<td>2145</td>
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<tr>
<td>Biodegradability – BOD₅/COD</td>
<td>0.26</td>
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</tr>
<tr>
<td>Total Organic Carbon – TOC (mg C/L)</td>
<td>400</td>
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<tr>
<td>Turbidity (NTU)</td>
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<td>296</td>
</tr>
<tr>
<td>Total suspended solids – TSS (mg/L)</td>
<td>60</td>
<td>750</td>
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<tr>
<td>Electrical conductivity (μS/cm)</td>
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<td>62.5</td>
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<tr>
<td>Total polyphenols (mg gallic acid/L)</td>
<td>0.5</td>
<td>22.6</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>2.0</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Winery wastewater used in this work

Storage in small containers

Conservation at -40°C
Equipment used in the heterogeneous photo-Fenton process

Ferrocene (Fc) + H₂O₂ → Power generator

UV-C Mercury lamp λ = 254 nm
Cylindrical photoreactor V = 500 mL
Stirrer
Characterization of Ferrocene

FTIR spectra of ferrocene.

- C–H stretching at 3093 cm\(^{-1}\)
- C=C stretching at 1631 cm\(^{-1}\)
- Fe peak at 476 cm\(^{-1}\)

Scanning Electron Microscopy (SEM) images of ferrocene (100 and 500x).

- The ferrocene catalyst in its initial form has an irregular shape
- The ferrocene has a lot of free space in between the particles
- The ferrocene has adsorption capacity
Heterogeneous photo-Fenton optimization

- The pH was varied from 3.0 to 7.0, and results showed that heterogeneous photo-Fenton process was highly dependent on pH (3.0 > 4.0 > 6.0 > 7.0) with 53.3, 42.1, 35.0 and 22.8% respectively.

- The $\text{H}_2\text{O}_2$ concentration was varied from 97 to 291 mM, and results showed a TOC removal of 48.5, 82.7 and 81.4%, respectively, for 97, 194 and 291 mM $\text{H}_2\text{O}_2$.

- The ferrocene catalyst concentration was varied (0.25 to 1.0 g/L) and results showed a TOC removal of 83.1, 82.7 and 54.2%, respectively, for 0.25, 0.50 and 1.0 g/L Fc.

- The durability of the Fc catalyst was examined by recovering the material and re-using it under the best operational conditions, as follows: [Fc] = 0.50 g/L, $[\text{H}_2\text{O}_2]$ = 194 mM, pH = 3.0, agitation = 350 rpm, $T = 298$ K, radiation UV-C, $t = 240$ min, for 3 consecutive cycles.

  - The results showed a TOC removal of 82.7, 76.2 and 63.9%, respectively for the 1st, 2nd and 3rd cycles, therefore, the FC catalyst can be reused.

Regeneration cycles from ferrocene catalyst along the 3 consecutive cycles of the heterogeneous photo-Fenton process ([Fc] = 0.50 g/L, $[\text{H}_2\text{O}_2]$ = 194 mM, pH = 3.0, agitation = 350 rpm, $T = 298$ K, radiation UV-C, $t = 240$ min).
Kinetic analysis

The Fermi’s non-linear kinetic model was used to determine the behavior of the ferrocene catalyst.

\[
\frac{\text{TOC}}{\text{TOC}_0} = \frac{1-x_{\text{TOC}}}{1+\exp[ k_{\text{TOC}}(t-t^{*}_{\text{TOC}})\text{TOC}]} + x_{\text{TOC}}
\]

- where \( k_{\text{TOC}} \) corresponds to the apparent reaction rate constant; \( t^{*}_{\text{TOC}} \) represents the transition time related to the TOC content curve’s inflection point, and \( x_{\text{TOC}} \) corresponds to the fraction of non-oxidizable compounds that are formed during the reaction;

- The results showed that a higher \( k_{\text{TOC}} \) was obtained under the operational conditions pH 3.0, Fc dosage 0.50 g/L, H\(_2\)O\(_2\) concentration 194 mM (addition in six steps) (\( k_{\text{TOC}} = 4.770 \times 10^{-2} \text{ min}^{-1} \); 82.7% TOC removal).
Based in the results, it is concluded

1. The ferrocene can be used as source of iron in heterogeneous catalysis in winery wastewater treatment

2. Under the optimal conditions, the heterogeneous photo-Fenton achieves a 82.7% TOC removal

3. Fermi’s kinetic model shows that under the best operational condition a $k_{TOC} = 4.770 \times 10^{-2}$ min$^{-1}$

4. Ferrocene can be reused for three consecutive cycles, with a TOC removal of 82.7, 76.2 and 63.9%, respectively, for the 1$^{st}$, 2$^{nd}$ and 3$^{rd}$ cycles
Acknowledgements

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Thank you for your attention