Physico-chemical treatment for the depuration of wine distillery wastewaters (vinasses)

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Abstract In the present work, an integrated Fenton-coagulation/flocculation process was applied for the depuration of wine distillery wastewaters, commonly known as “vinasses”. This study evaluates the Fenton process (H₂O₂/Fe²⁺), involving oxidation – in a first stage and coagulation/flocculation (using Ca(OH)₂ as base-precipitant) – in a second stage for the removal of chemical oxygen demand (COD). The experimental variables studied were the dosages of hydrogen peroxide and iron salts, the molar ratio [H₂O₂]₀ : [Fe²⁺]₀, the effluent dilution and the manner in which the reagents were added (splitting the reagent dose of hydrogen peroxide and ferrous salt into different fractions). The optimal operating conditions of the integrated process were: [H₂O₂]₀ = 0.5 mol/L using an optimal concentration ratio [H₂O₂]₀ : [Fe²⁺]₀ = 15 mol/mol. Under these conditions, the COD removal was 74%.

Keywords Coagulation; Fenton’s reagent; flocculation; oxidation; vinasses; wine distillery wastewaters

Introduction

“Vinasse” is the wastewater generated in the manufacture of ethyl alcohol by fermentation and subsequent distillation. Its special properties and high organic load make it highly polluting. All these vinasses have an acidic pH (3.5–4) and are characterized by their high chemical oxygen demand (COD in the range 10,000–50,000 mg/L). Frequently these effluents are eliminated through public sewers or disposed of into evaporation ponds, this procedure, however, causes bad odors and the possibility of the pollution of surface waters and underground aquifers. With the establishment of more stringent regulations concerning public waste disposal, there has been growing interest in the development of new technologies and procedures for the decontamination of this water.

In this situation, one can consider the use of various treatments including chemical procedures based on redox reactions (Benitez et al., 1999; Martin et al., 2003). One available treatment technology widely used in recent years is Fenton’s oxidation. This advanced chemical oxidation technology is based on the production of hydroxyl radicals, *OH, which have an extremely high oxidation potential (*OH/H₂O = +2.73 V). The Fenton oxidation process has been employed successfully to treat different industrial wastewaters (Lin and Peng, 1995; Lin and Lo, 1997). Fenton’s reagent, which involves homogeneous reaction and is environmentally acceptable, is a mixture of hydrogen peroxide and iron salts (Fe²⁺ or Fe³⁺) which produces hydroxyl radicals. The oxidation mechanism of an organic compound by Fenton’s reagent is very complex, and is thought to occur in the following stages (Beltran de Heredia et al., 2001):

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \underset{k_1}{\rightarrow} \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \\
\text{P} + \text{H}_2\text{O}_2 & \underset{k_2}{\rightarrow} \text{P}_{\text{ox}} \\
\text{P} + \text{OH}^* & \underset{k_3}{\rightarrow} \text{P}_{\text{ox}}
\end{align*}
\]
\[
\begin{align*}
H_2O_2 + OH^* & \xrightleftharpoons{k_i} HO_2^* + H_2O \\
OH^* + Fe^{2+} & \rightarrow Fe^{3+} + OH^- \\
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + H^+ + HO_2^* \\
Fe^{3+} + HO_2^* & \rightarrow O_2 + Fe^{2+} + H^+
\end{align*}
\]

On the other hand, in alkaline solution, Fe\(^{3+}\) forms highly insoluble Fe(OH)\(_3\) (Ksp = 10\(^{-36}\)) in equilibrium with FeO(OH) to give a flocculant precipitate which facilitates the separation of the suspended materials in the effluent (Garrote et al., 1995). Also, this treatment can reduce the dissolved phenolic compounds by adsorption onto the ferric gel.

In the present work, therefore, an integrated Fenton-coagulation/flocculation method was applied for the depuration of vinasses. This study evaluates the Fenton process (H\(_2\)O\(_2\)/Fe\(^{2+}\)), involving oxidation in a first stage, and coagulation/flocculation (using Ca(OH)\(_2\) as base-precipitant) in a second stage, for the removal of chemical oxygen demand (COD). The aim was to provide data on the removal of contaminant organic matter and to establish the influence of the operating variables on the process’s efficacy.

**Methods**

The main chemical characteristics of the residual vinasses were: pH = 3.76; COD = 15,000–16,500 mg/L; total phenolic compounds = 400–700 mg caffeic acid/L; total solids = 9.1 g/L; aromaticity = 11.7 u.a. (at 254 nm); turbidity = 115 NTU.

In all cases, experiments were performed in a 250 mL stirred glass reactor with inlets for sampling and temperature measuring. The temperature was maintained constant to 30°C in all cases. Effluent samples of 150 mL were treated as follows: a) a dose of FeSO\(_4\).7H\(_2\)O was added; b) a dose of H\(_2\)O\(_2\) was added (the Fenton reaction time was 3 h for all cases); c) a subsample was taken at 1 min and 3 hours and its COD was measured; d) in the remaining liquor, pH was adjusted to 8.5 by addition of Ca(OH)\(_2\); d) the sample was stirred for 10 min at 100 r.p.m.; e) the supernatant was decanted over one day, and its COD was measured.

**Results and discussion**

The oxidation-coagulation/flocculation of vinasses by Fenton’s reagent, using Ca(OH)\(_2\) as base-precipitant, was investigated in laboratory experiments. Operatively, the integrated Fenton’s reagent – coagulation/flocculation process requires no more than a minimal extra effort with respect to the simple coagulation/flocculation process. The only difference is the addition of a certain amount of hydrogen peroxide after dissolving the iron. After a wait of 3 hours, finally the pH is adjusted to 8.5 by adding Ca(OH)\(_2\).

**Effect of the initial hydrogen peroxide concentration on the efficacy of the process**

The reduction in the value of COD depended to a large degree on the initial reagent concentrations (of hydrogen peroxide and ferrous salt). Figure 1 shows the removals of COD for the experiments in which the initial hydrogen peroxide concentration was modified, maintaining constant the ferrous dose at 0.033 mol/L. This figure compares the removals of COD, in the first Fenton reaction (at two times, 1 min and 180 min) with those after the integrated treatment (Fenton’s reagent treatment + coagulation/flocculation). As was to be expected, greater doses of hydrogen peroxide led to greater removals of COD in the first Fenton’s reaction stage and therefore in the final COD removals of the integrated process. As can be seen, the later stage of coagulation–flocculation has only a moderate influence on the global process.
On the other hand, the economics of the process is reflected in the reaction’s mean stoichiometric coefficient. For the case of decontaminating wastewaters by means of Fenton’s reagent, the said mean stoichiometric coefficient can be expressed mathematically by Eq. (8):

\[
z = \frac{\text{COD removed (mg/L)}}{\text{H}_2\text{O}_2 \text{ consumed (mg/L)}}
\]  

(8)

As can be seen in Figure 2, the greater the hydrogen peroxide dose, the smaller the stoichiometric coefficient. This parameter ranged from 4.99 g COD/g H₂O₂ (for the experiment with a relationship \([\text{H}_2\text{O}_2]_o : [\text{Fe}^{2+}]_o = 0.1 \text{ mol/mol}\) to 0.23 g COD/g H₂O₂ (for a relationship \([\text{H}_2\text{O}_2]_o : [\text{Fe}^{2+}]_o = 50 \text{ mol/mol}\)).

![Figure 1](image1.png)  
**Figure 1** Influence of the molar ratio \([\text{H}_2\text{O}_2]_o : [\text{Fe}^{2+}]_o\) on the obtained COD removals

![Figure 2](image2.png)  
**Figure 2** Influence of the molar ratio \([\text{H}_2\text{O}_2]_o : [\text{Fe}^{2+}]_o\) on the Fenton reaction stoichiometric coefficient
Effect of the iron (II) concentration on the integrated process

In the following block of experiments we studied the effect of the iron (II) concentration while maintaining the dose of hydrogen peroxide fixed at 0.5 mol/L. Figure 3 shows the COD removal curves in the series of experiments in which the initial ferrous salt concentration was modified (from a relationship $[\text{H}_2\text{O}_2]_o: [\text{Fe}^{2+}]_o = 100$ mol/mol to 5 mol/mol). With an initial iron (II) concentration of only 0.005 mol/L the removal of COD was very strong (around 30%), showing this metal’s major catalytic role. There was a positive relationship between the dose and the COD removal: for any given time, the degree of removal increased with increasing ferrous dose. The difference was significant up to a ratio $[\text{H}_2\text{O}_2]_o: [\text{Fe}^{2+}]_o = 15$ mol/mol “optimal concentration ratio”. An additional rise in ferrous dose was not reflected in any further increase of COD removal. The authors have observed an optimal concentration ratio of 10 mol/mol in other wastewater studies (Beltran de Heredia and Dominguez, 2001a, b; Beltran de Heredia et al., 2004).

The above experimental results can be understood in the following form. When the ratio of concentrations $[\text{H}_2\text{O}_2]_o: [\text{Fe}^{2+}]_o$ is high (>15 mol/mol), the inhibiting character of hydrogen peroxide predominates (see Eq. (4)). When the ratio is too low (<15 mol/mol), however, the hydroxyl radical scavenging effect of ferrous salt predominates (see Eq. (5)).

The optimal concentration ratio will depend on the rate constants of both processes (Eqs. (4) and (5)) (Tang and Huang, 1997). Peres (2001) deduces a theoretical expression to calculate this optimal molar concentration ratio (see Eq. (9)).

$$\frac{[\text{H}_2\text{O}_2]}{[\text{Fe}^{2+}]_{\text{opt}}} = \frac{k_5}{k_4} = \frac{4.3 \times 10^8}{2.7 \times 10^7} = 15.9 \text{ mol/mol}$$

One observes that this ratio is independent of the nature of the substrate to be oxidized, and only depends on the values of the rate constants. There is a noteworthy agreement between the experimentally and theoretically obtained values of the said molar ratio. Table 1 shows the removals obtained for other parameters using the optimal molar ratio.
With respect to the stoichiometric coefficient, the greater ferrous dose, the smaller the stoichiometric coefficient. This parameter ranged from 0.72 g COD/g H₂O₂ (for the experiment with a relationship \([\text{H}_2\text{O}_2]_0 : [\text{Fe}^{2+}]_0 = 100 \text{ mol/mol}\)) to 0.53 g COD/g H₂O₂ (for a relationship \([\text{H}_2\text{O}_2]_0 : [\text{Fe}^{2+}]_0 = 5 \text{ mol/mol}\)).

Fenton-coagulation/flocculation experiments using the optimal molar ratio

The following block of experiments was carried out varying the initial reagent concentrations (of hydrogen peroxide and ferrous salt) but maintaining the molar ratio \([\text{H}_2\text{O}_2]_0 : [\text{Fe}^{2+}]_0 = 15 \text{ mol/mol}\). Table 2 lists the conditions of the different experiments were carried out and the results obtained after the first Fenton reaction stage (F).

In the Fenton oxidation, the efficiency in the use of hydrogen peroxide can be evaluated by the stoichiometric coefficient, \(z\). As can be seen in Table 2, the COD removal efficiency by Fenton oxidation was increased by increasing the reagent dosages (of hydrogen peroxide and ferrous salt), therefore, the stoichiometric coefficient, \(z\), decreases. The efficiency of hydrogen peroxide by increasing the dosage is gradually decreased due to two factors: first, the fraction of the organic substances, which cannot be oxidized, is increased, and second, when hydrogen peroxide concentration is high, its inhibiting character predominates. On the other hand, increasing doses of hydrogen peroxide were observed to produce a greater decline in pH of the wastewater together with a greater increase in the volatile acidity of the water (a measure of the volatile organic acid content \(\text{C}_1–\text{C}_4\)).

Table 3 lists the final results obtained after the second coagulation/flocculation stage. As can be seen the organic matter removed by coagulation/flocculation is moderate. The COD removal by coagulation with formation of the ferric hydroxo complexes is considerable at pH over 4. On the other hand, the organic matter removed, by adding \(\text{Ca(OH)}_2\), to give a flocculant precipitate of \(\text{Fe(OH)}_3\) \((K_{sp} = 10^{-36})\) facilitates the separation of suspended materials in effluent.

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**Table 1** Organic matter removal obtained using a hydrogen peroxide dose of 0.5 mol/L and an optimal ratio \([\text{H}_2\text{O}_2]_0 : [\text{Fe}^{2+}]_0 = 15 \text{ mol/mol}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial value</th>
<th>Value after Fenton's treatment</th>
<th>Final value after the integrated Fenton + coagulation/flocculation process</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>16,225</td>
<td>6,200</td>
<td>4,272</td>
</tr>
<tr>
<td>Polyphenols (expressed as mg/L of caffeic acid)</td>
<td>413</td>
<td>249</td>
<td>166</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>115</td>
<td>–</td>
<td>4.1</td>
</tr>
<tr>
<td>pH</td>
<td>3.76</td>
<td>1.38</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**Table 2** Results obtained after the first Fenton reaction stage for experiments carried out using the optimal molar ratio \([\text{H}_2\text{O}_2]_0 : [\text{Fe}^{2+}]_0 = 15 \text{ mol/mol}\)

<table>
<thead>
<tr>
<th>Expt.</th>
<th>(\text{H}_2\text{O}_2) dose mol/L</th>
<th>CODF mg/L</th>
<th>COD removal %</th>
<th>(z) g COD/g H₂O₂</th>
<th>pHF (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0033</td>
<td>13,728</td>
<td>15</td>
<td>21.5</td>
<td>3.72</td>
</tr>
<tr>
<td>2</td>
<td>0.033</td>
<td>13,584</td>
<td>16</td>
<td>2.29</td>
<td>3.61</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>9,840</td>
<td>39</td>
<td>0.56</td>
<td>2.68</td>
</tr>
<tr>
<td>4</td>
<td>0.66</td>
<td>8,040</td>
<td>50</td>
<td>0.36</td>
<td>2.19</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
<td>5,312</td>
<td>67</td>
<td>0.32</td>
<td>2.11</td>
</tr>
<tr>
<td>6</td>
<td>1.65</td>
<td>3,728</td>
<td>77</td>
<td>0.22</td>
<td>1.96</td>
</tr>
</tbody>
</table>

(a) pH after the first Fenton reaction stage
Influence of effluent dilution

We performed Fenton experiments (without coagulation/flocculation) with the same conditions ([H$_2$O$_2$]$_o$ = 0.5 mol/L and optimal molar ratio [H$_2$O$_2$]$_o$ : [Fe$^{2+}$]$_o$ = 15 mol/mol) but with different effluent dilution. The COD removal efficiency by Fenton oxidation at 3 hours was influenced by effluent dilution (see Figure 4).

COD removals of approx. 70% were noted for the 3/16 strength, 6/16 strength and 8/16 strength effluents, but the 11/16 strength and 14/16 strength effluents demonstrated removals of 62% and 55%, respectively. However, with respect to the stoichiometric coefficient, the greater dilution, the smaller the stoichiometric coefficient. This parameter ranged from 0.45 g COD/g H$_2$O$_2$ (for the 14/16 strength effluent) to 0.15 g COD/g H$_2$O$_2$ (for the 3/16 strength effluent).

On the other hand, as can be seen in Figure 4, the biodegradability of effluent (BOD$_5$/COD) was increased by increasing the dilution of effluent. This parameter ranged from 0.31 g/g (for the 14/16 strength effluent) to 0.70 g/g (for the 3/16 strength effluent).

Influence of the manner of adding the reagents

We performed trials with the same reagent dose ([H$_2$O$_2$]$_o$ = 0.5 mol/L and optimal molar concentration ratio [H$_2$O$_2$]$_o$ : [Fe$^{2+}$]$_o$ = 15 mol/mol), but splitting the reagent dose (of

<table>
<thead>
<tr>
<th>Expt.</th>
<th>H$_2$O$_2$ dose mol/L</th>
<th>Final COD mg/L</th>
<th>COD removal %</th>
<th>Turbidity removal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0033</td>
<td>13,740</td>
<td>15</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>2</td>
<td>0.033</td>
<td>13,610</td>
<td>16</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>8,928</td>
<td>48</td>
<td>95–100</td>
</tr>
<tr>
<td>4</td>
<td>0.66</td>
<td>5,528</td>
<td>66</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
<td>3,632</td>
<td>78</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>1.65</td>
<td>2,608</td>
<td>84</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4 Influence of effluent strength on the removal of COD by Fenton oxidation, stoichiometric coefficient $z$ and biodegradability ratio BOD/COD
hydrogen peroxide and ferrous salt) into two fractions (times: initial and 30 min), four fractions (times: initial, 15 min, 30 min and 45 min) and continuous addition (in 120 min). Figure 5 shows a comparison of the evolution of COD with reaction time in the equivalent experiments. As can be seen, the final COD removals were very similar, about 60%.

**Conclusions**

An integrated Fenton-coagulation/flocculation process using Ca(OH)₂ as base precipitant was employed in the present study to treat the wastewater of the wine distillery industry. The main findings include: A positive influence of the initial hydrogen peroxide concentration on the degree of COD removal. A positive influence of the initial ferrous concentration: the degree of COD removal increases with increasing ferrous dose. The difference was significant until the ratio \([\text{H}_2\text{O}_2]_o : [\text{Fe}^{2+}]_o = 15 \text{ mol/mol}\), the “optimal molar ratio”. An additional rise in ferrous dose was not reflected in any concomitant increase of COD removal.

In the Fenton experiments carried out using the optimal molar ratio \([\text{H}_2\text{O}_2]_o : [\text{Fe}^{2+}]_o = 15 \text{ mol/mol}\), the stoichiometric coefficient, \(z\), ranged from 21.5 g COD/g H₂O₂ (for the experiment with an hydrogen peroxide concentration of 0.0033 mol/L) to 0.22 g COD/g H₂O₂ (for the experiment with an hydrogen peroxide concentration of 1.65 mol/L).

The COD removal efficiency by Fenton oxidation at 3 hours was influenced by effluent dilution: COD removal of approximately 70% was noted for the 3/16 strength effluent, however, the 14/16 strength effluent demonstrated COD removal of 55%. With respect to the stoichiometric coefficient, the greater dilution, the smaller the stoichiometric coefficient. This parameter ranged from 0.45 g COD/g H₂O₂ (for the 14/16 strength effluent) to 0.15 g COD/g H₂O₂ (for the 3/16 strength effluent). On the other hand, the biodegradability of effluent (BOD₅/COD) was increased by increasing the dilution of effluent. This parameter ranged from 0.31 g/g (for the 14/16 strength effluent) to 0.70 g/g (for the 3/16 strength effluent).

With respect to the influence of the manner of adding the reagents, experiments carried out splitting the reagent dose (of hydrogen peroxide and ferrous salt) dose into two, four fractions or continuous addition (in 120 min) led to very similar final COD removals about 60%.
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