Treatment of olive mill wastewater by a combined process: Fenton's reagent and chemical coagulation

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Treatment of olive mill wastewater by a combined process: Fenton’s reagent and chemical coagulation

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Olive mill wastewater (OMW) was exposed to Fenton treatment and subjected to post Fenton coagulation/flocculation using lime. Several tests were performed for different $R = \frac{H_2O_2}{COD}$ ratios, from 0.25 to 3.0, promoting the gradual addition of $H_2O_2$ and $Fe^{2+}$, with the original condition of a pH = 3.5 and maintaining a constant relationship $H_2O_2/Fe^{2+} = 15$. A maximum reduction of COD of 96.8% was obtained using Fenton reagent with $R = 3.0$. In a second phase, the effluent which was neutralized with Ca(OH)$_2$ reached a higher reduction of COD, achieving a final degradation value of 99.3%. Overall, the results show evidence of the potential value of applying the combined process tested.

Keywords: Olive mill wastewater, Fenton reagent, chemical oxidation, lime treatment, chemical coagulation-flocculation.

Introduction

The disposal of olive mill wastewater (OMW) is a problematic issue in the countries located in the edge of the Mediterranean, including Portugal, due to their high organic load (e.g., Chemical Oxygen Demand (COD) of 50 to 120 g O$_2$/L), and their phytotoxicity and antimicrobial characteristics. More stringent environmental legislation and the lack of an efficient and economical process of OMW treatment has forced many olive mills to close, with significant socio-economical and cultural implications. As a result, in the last few years, there has been a great effort to develop new solutions for the treatment of OMW.[1] There are many methods proposed for OMW treatment,[2,3] the simplest solution consists of man made evaporation pools. An alternative and economical solution is controlled land application of OMW. The Italian and Portuguese law already allows annual spreading of up to 50 and 80 m$^3$ ha$^{-1}$ for OMW generated by press or continuous centrifugation method, respectively.

Alternatively biological treatments using aerobic or anaerobic micro-organisms have been suggested by different authors,[2,4] though high organic load, especially phenolic compounds, make OMW recalcitrant to aerobic biological degradation and inhibits the efficiency of anaerobic digestion.

Physico-chemical processes have also been applied to the OMW treatment including flocculation,[5] coagulation, filtration, integrated centrifugation-ultrafiltration, electrochemical oxidation,[6] electrocoagulation, sedimentation,[7,8] and combined physicochemical processes.[9] The reduction of the OMW pollution parameters can be increased when biological treatments are combined with chemical or physical processes.[10,11] Advanced Oxidation Processes (AOPs) are known for their capability to mineralise a wide range of organic compounds. AOP’s applied to OMW include ozonation, combination of ultrafiltration and UV/H$_2$O$_2$,[12] combination of UV/H$_2$O$_2$ and lime,[13] electro-Fenton oxidation, conductive diamond electro-oxidation,[14] wet air oxidation,[15] catalytic wet air oxidation,[16] supercritical water oxidation,[17] UV/TiO$_2$,[18] solar photocatalysis with TiO$_2$ and solar photo-Fenton.[19]

Fenton oxidation of OMW is not well studied[2,20] Rivas et al.[21] report Fenton’s treatment of OMW diluted with a synthetic urban wastewater (dilution factor of 10). Gomce et al.[22] applied Fenton’s oxidation to OMW after acid cracking and cationic polyelectrolyte treatment. The Fenton reagent is a homogeneous catalytic oxidation process involving the reaction of hydrogen peroxide with ferrous ions. This reaction generates hydroxyl radicals that have a high potential for oxidation:[23]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^+ \quad (1)$$
The excellent performance of the Fenton reagent occurs in acidic environment in the pH range 3–4. In addition to the main reaction, various additional competitive reactions are also possible involving Fe$^{2+}$, Fe$^{3+}$, H$_2$O$_2$, superoxide and the hydroxyl radical:\cite{23,25}

\begin{align}
\text{Fe}^{2+} + \text{HO} \rightarrow \text{Fe}^{3+} + \text{OH}^- & \quad (2) \\
\text{H}_2\text{O}_2 + \text{HO} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- & \quad (3) \\
\text{Fe}^{2+} + \text{HO}_2^- \rightarrow \text{Fe}^{3+} + \text{HO}_2^- & \quad (4) \\
\text{Fe}^{3+} + \text{HO}_2^- \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ & \quad (5)
\end{align}

In the presence of organic substrates (RH) the highly reactive hydroxyl radical, a species with a relatively short life span (rate constants in the range $10^7–10^{10}$ M$^{-1}$s$^{-1}$) undergoes oxidation generating a new radical:\cite{23}

\[ \text{RH} + \text{HO} \rightarrow \text{R} \cdot + \text{H}_2\text{O} \] (6)

This paper reports the effect of chemical coagulation using ferric ions (Fe$^{3+}$) generated as product of the Fenton reaction. Due to the high content of solids present in OMW, a coagulation/flocculation treatment by Ca(OH)$_2$ (lime) should reduce these solids, thus reducing COD, Biochemical Oxygen Demand (BOD), colour and odour.\cite{13,26,27}

**Materials and methods**

**Olive mill wastewater**

The OMW used in this study was obtained from the Agricultural Cooperative of Vila Flôr, which is an olive oil processing plant located in the Northeast of Portugal, operating in a discontinuous process. Wastewater samples with a dark red-brown colour were taken from the tanks of the processing plant located in the Northeast of Portugal, operating in a discontinuous process. Wastewater samples with a dark red-brown colour were taken from the tanks of classical mills where the liquid phase is placed. Samples collected in December were stored at 4°C during the transport to the laboratory and immediately analyzed.

The detailed description of the OMW is presented in Table 1. Before performing Fenton oxidation tests, the OMW was filtered, diluted 10 times with distilled water and stored at $-20^\circ$C, to reduce the COD to 5.34 g L$^{-1}$. For each experiment a new frozen sample was used in order to minimise discrepancies between experiments.

**Table 1.** Physicochemical characterization of the studied OMW.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.3</td>
</tr>
<tr>
<td>BOD</td>
<td>10.2 g L$^{-1}$</td>
</tr>
<tr>
<td>COD</td>
<td>60.5 g L$^{-1}$</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>6.8 g L$^{-1}$</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.56 g L$^{-1}$</td>
</tr>
<tr>
<td>Biodegradability (BOD$_5$/COD)</td>
<td>0.17</td>
</tr>
</tbody>
</table>

**Chemical oxidation**

The chemical oxidation experiments of OMW were undertaken in a stirred jacketed glass batch reactor (Fig. 1), temperature controlled through a Julabo F25-MP thermostatic bath. The reactor (1.0 L of capacity) was equipped with an ORP platinum electrode (Radiometer P101) in conjunction with a reference calomel electrode (Radiometer REF401) connected to an Ion Meter (Ion83 of Radiometer); an oxygen sensor StirrOx G connected to an oxygen meter (Oxi538 of WTW) and Mechanical stirring provided continuous mixing of the reaction.

The pH adjustment was carried out with diluted sulphuric acid (H$_2$SO$_4$) and sodium hydroxide (NaOH) solutions. Typical experiments were carried out with 500 mL of OMW to which a weighed amount of FeSO$_4$·7H$_2$O was added and dissolved under stirring. The Fenton oxidation began with the addition of hydrogen peroxide solution (30% w/w), which was added regularly in small amounts. Samples were withdrawn from the reactor at pre-determined times and reaction stopped by adding excess Na$_2$SO$_3$, which instantaneously consumes the remaining hydrogen peroxide.

In a second phase, the total consumption of H$_2$O$_2$ by Fenton’s reaction (verified with Merckoquant strips), an appropriate amount of Ca(OH)$_2$ (lime) was added to the reactor in order to adjust the pH of the medium to an alkaline value (pH = 8.5). Coagulation-flocculation was performed after 2 minutes of rapid mixing (120 rpm) and 30 minutes of slow mixing (40 rpm) before being left to stand for 4 hours. After 4 hours settling the supernatant was withdrawn for COD analysis.

**Reagents**

Research grade reagents used during experiments: H$_2$O$_2$ (30% w/w), Ca(OH)$_2$, Na$_2$SO$_3$, NaOH and H$_2$SO$_4$ from Merck and FeSO$_4$·7H$_2$O from Panreac, were used without further purification.

**Analytical methods**

The COD analyses were performed by the dichromate closed reflux Colorimetric Method using a Hach DR2010 Model spectrophotometer in accordance with Standard Methods (for a COD range 0–1500 mg/L). Hydrogen peroxide concentration was determined iodometrically. Biological oxygen demand (BOD$_5$) was evaluated by the respirometric method. In this case, 300 mL glass bottles containing known amounts of inocula were used. Other wastewater parameters presented in Table 1, were analysed according to standard methods.

Total Organic Carbon (TOC) was measured using a DC-190 Dohrmann carbon analyzer. TOC was calculated as the difference between the total carbon (TC) and inorganic carbon (IC) in the liquid sample. The UV-Visible scanning
spectrum 200–800 nm of OMW was determined using a Jasco V-530 UV/VIS (Tokyo, Japan) double-beam spectrophotometer. All of the oxidation experiments were performed in at least duplicate, and the observed standard deviation was always less than 5% of the reported value.

Results and discussion

Treatment with Fenton’s Reagent

Chemical oxidation with Fenton’s process was analyzed in order to further reduce COD thereby minimizing the impact of OMW discharge on natural water courses and municipal wastewater treatment plants. In the experiments carried out with OMW the Fenton reagent had as reference the mass ratio between the hydrogen peroxide and COD, \( R = \frac{\text{H}_2\text{O}_2}{\text{COD}} \). The value of \( R \) was changed from 0.25 to 3.0, with constant initial pH (3.5), initial temperature (30°C) and the molar ratio constant (\( \frac{\text{H}_2\text{O}_2}{\text{Fe}^{2+}} = 15 \))[28].

Table 2 shows the removal of COD at different values of \( R \) after 4 hours experimentation. From the data presented it is evident that COD removal increases from 25.0% to 96.8% when the value of \( R (\text{H}_2\text{O}_2/\text{COD}) \) increases from 0.25 to 3.0, respectively.

As expected, increasing the concentration of \( \text{H}_2\text{O}_2 \) (and proportionally in \( \text{Fe}^{2+} \)) has a positive effect on the reduction of COD. For the maximum \( R \) value studied (\( R = 3.0 \)), the reduction of COD reaches about 96.8% after 4 hours. This demonstrates the ability of Fenton reagent to degrade a large part of oxidizable organic matter present in OMW. The increase in COD conversion with the increase of \( R \) results from the generation of a greater amount of hydroxyl radicals and therefore, a greater extent of oxidation reactions.

One way to generally express the reaction of the Fenton system (\( \text{H}_2\text{O}_2 + \text{Fe}^{2+} \)) to the reduction of COD can be summarized as follows:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( \text{Mass ratio} \ (R) ) ( (\text{H}_2\text{O}_2/\text{COD}) )</th>
<th>( \text{COD}_{\text{initial}} ) ( (g \ \text{O}_2/L) )</th>
<th>( \text{COD}_{\text{final}} ) ( (\text{After Fenton reagent}) ) ( (g \ \text{O}_2/L) )</th>
<th>( X_{\text{COD}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMW-1</td>
<td>0.25</td>
<td>5.34</td>
<td>4.01</td>
<td>24.9</td>
</tr>
<tr>
<td>OMW-2</td>
<td>0.5</td>
<td>5.34</td>
<td>3.40</td>
<td>36.3</td>
</tr>
<tr>
<td>OMW-3</td>
<td>1.0</td>
<td>5.34</td>
<td>2.26</td>
<td>57.7</td>
</tr>
<tr>
<td>OMW-4</td>
<td>1.5</td>
<td>5.34</td>
<td>1.58</td>
<td>70.4</td>
</tr>
<tr>
<td>OMW-5</td>
<td>2.0</td>
<td>5.34</td>
<td>0.56</td>
<td>89.5</td>
</tr>
<tr>
<td>OMW-6</td>
<td>2.5</td>
<td>5.34</td>
<td>0.32</td>
<td>94.0</td>
</tr>
<tr>
<td>OMW-7</td>
<td>3.0</td>
<td>5.34</td>
<td>0.17</td>
<td>96.8</td>
</tr>
</tbody>
</table>

Operational conditions: initial \( T = 30^\circ \text{C} \), initial pH = 3.5, molar ratio \( \text{H}_2\text{O}_2/\text{Fe}^{2+} = 15 \).
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Fig. 2. Evolution of COD and TOC during the oxidation of OMW by Fenton system (Experience OMW-3). Conditions: mass ratio $\text{H}_2\text{O}_2/\text{COD} = 1.0$, temperature $= 30^\circ\text{C}$, initial pH $= 3.5$, molar ratio $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15$.

Step 1:
$$\text{COD} + \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{partially oxidized species} \quad (7)$$

Step 2:
$$\text{partially oxidized species} + \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{inorganic salts} \quad (8)$$

The extent of oxidation (and consequently the degree of COD reduction) depends directly on the amount of H$_2$O$_2$ used. In many cases, however, it is not necessary to achieve the complete mineralization of organic compounds. The partial oxidation to intermediary compounds minimizes the consumption of chemicals and often results in substantial reductions of COD and toxicity. The COD conversion ($X_{\text{COD}}$) obtained in each experiment is defined as follows:

$$X_{\text{COD}} = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \cdot 100 \quad (9)$$

where $\text{COD}_0$ and $\text{COD}_f$ are the initial and final concentrations of COD, respectively. A better assessment of the Fenton reagent performance can be achieved by analyzing the kinetic oxidation. Figure 2 shows COD (42%) + TOC (26%) reduction as a function of time for sample OMW-3.

Initially significant reduction is observed followed by stabilisation. The reduction in TOC is naturally lower than COD. Nevertheless a mineralization level exceeding 26% was observed, which shows that a significant part of the initial organic load is oxidised to carbon dioxide and water.

Additional treatment with calcium hydroxide

The second phase of this work consists of an integrated Fenton-coagulation/flocculation process with calcium hydroxide. The optimal pH performance for the Fenton reagent lies in the range from 3.0 to 4.0. Nonetheless the chemical coagulation is more effective at basic pH, particularly in the range of pH $= 8.0$–10.0.$^{[29]}$ Therefore at the end of the chemical oxidation it becomes necessary adjust the pH of the effluent through the addition of a base. In this study, Ca(OH)$_2$ (lime) was used after Fenton reagent in order to investigate the effect lime has on OMW treatment.

The maximum reduction of COD was achieved through the Fenton reagent process, with an R = 3.0, with 96.8%. In a second phase, the pH of the effluent was increased to 8.0 with Ca(OH)$_2$ and a further reduction of COD was obtained, reaching a final value of 99.3%. An important feature of this complementary treatment concerns the presence of Fe$^{2+}$ and Fe$^{3+}$ ions (resulting from the Fenton system) to achieve an additional reduction of COD, as shown in Table 3.

It can be assumed that the Fenton system has a dual function: on one hand the hydroxyl radical HO$_{\cdot}$, generated in-situ promotes chemical oxidation. On the other hand, the presence of Fe$^{2+}$/Fe$^{3+}$ ions (and, in this case, Ca$^{2+}$) makes the mixture of reaction undergo chemical coagulation.$^{[29]}$ It can be stated that a synergistic relation occurs between the advanced oxidation processes and the coagulation/chemical precipitation.

During the coagulation/chemical precipitation there will be an additional reduction of COD which can be explained by the precipitation of the original compounds or of the partially oxidized by-products. In the alkaline Ca(OH)$_2$ solution, Fe$^{3+}$ forms highly insoluble Fe(OH)$_3$ ($K_{sp} = 10^{-36}$) in equilibrium with Fe(OH)$_2$, to give a flocculent precipitate which facilitates the separation of suspended materials in effluent.$^{[30]}$ This way, the chemical coagulation will also reduce the concentration of dissolved iron in the wastewater after the Fenton oxidation process.$^{[31]}$ The factors leading to this precipitation are:

(i) The formation of Fe(OH)$_3$ and hydroxy-ferric complexes, among Fe$^{3+}$ ions from the reaction of Fenton and hydroxide ions, which are able to capture organic
molecules, and are reflected in mud-colour.\cite{31} For example:

\[
[\text{Fe}(\text{H}_2\text{O})_6]^3+ + \text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+ \tag{10}
\]

\[
[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+ + \text{H}_3\text{O}^+ \tag{11}
\]

There will be a successive replacement of water molecules by hydroxyl groups, leading initially to monomeric ions. For concentrations of Fe$^{3+}$ and/or high-OH the formation of dimer or other higher polynuclear complexes by elimination of the water between the hydroxyl groups may occur,\cite{32, 33} which will definitely contribute to the chemical coagulation of the Fenton reagent process. For example:

\[
2[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{3+} \rightleftharpoons [\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2]^4+ + 2\text{H}_2\text{O} \tag{12}
\]

\[
[\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2]^4+ + \text{H}_2\text{O} \rightleftharpoons [\text{Fe}_2(\text{H}_2\text{O})_7(\text{OH})_3]^3+ + \text{H}_3\text{O}^+ \tag{13}
\]

\[
[\text{Fe}_2(\text{H}_2\text{O})_7(\text{OH})_3]^3+ + [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} \rightleftharpoons [\text{Fe}_3(\text{H}_2\text{O})_{10}(\text{OH})_4]^{5+} + 2\text{H}_2\text{O} \tag{14}
\]

(ii) The formation of very insoluble iron-soluble organic compounds (oxidized by Fenton reagent), which will become visible in the form of small flakes:\cite{33}

\[
\text{Fe}^{3+}_{\text{aq}} + \text{H}_2\text{O} + \text{organic compounds}_{\text{aq}} \rightarrow [\text{Fe(OH)}_x - \text{organic compound}]_{\text{s}} \tag{15}
\]

(iii) A greater susceptibility of the organic components of OMW to suffer adsorption in the coagulants, due to its partial oxidation resulting in more polar substances. In other words, the organic compounds most likely to suffer co-precipitation with the ferric ions are those which contain the carboxylate or carboxylic groups (-COO, COOH), such as carboxylic acids (which will be privileged products resulting from the oxidation with the Fenton reagent).

However the further reduction of COD by chemical coagulation has itself the disadvantage of the generation of sludge and its consequent physical removal. This way, a final step of solids separation becomes necessary.

The effect of the H$_2$O$_2$/COD mass ratio or the increased concentration in H$_2$O$_2$ (and therefore also of Fe$^{2+}$, because the molar ratio H$_2$O$_2$/Fe$^{2+}$ remains constant and equal to 15) in the removal of the COD and in the increase of the percentage of sludge obtained is shown in Figure 3.

\[\text{Fig. 3. The effect of weight ratio } R = \text{H}_2\text{O}_2/\text{COD} \text{ the decrease of COD in OMW and the percentage of sludge obtained at the end (Operational conditions: temperature } = 30^\circ\text{C, pH initial } = 3.5 \text{ and molar ratio } \text{H}_2\text{O}_2/\text{Fe}^{2+} = 15:1).\]

Biodegradability

In addition to COD, BOD$_5$ tests were performed for selected samples, to research the effect of integrated Fenton’s reagent and lime treatment on biodegradability. The OMW studied shows a low BOD$_5$/COD ratio which, in this case, is equal to 0.17. The biodegradability of OMW, defined as the BOD$_5$/COD ratio, can be expressed in terms of the R value (H$_2$O$_2$/COD ratio) as shown in Figure 4.

For all the initial concentrations of H$_2$O$_2$ tested (that is for the different values of R) as the concentration of H$_2$O$_2$ and Fe$^{2+}$ was increased, the ratio BOD$_5$/COD also increased. Beginning on BOD$_5$/COD = 0.17 for original OMW until BOD$_5$/COD = 0.68 for R = 2.5. For example using a value of R = 1.0 a more acceptable value for secondary biological treatment: BOD$_5$/COD = 0.42 has been achieved. These results suggest a possible strategy involving the use of Fenton reagent as a pre-treatment step before an anaerobic or aerobic biological treatment.

\[\text{Fig. 4. The effect of weight ratio } R = \text{H}_2\text{O}_2/\text{COD} \text{ on the } \text{BOD}_5/\text{COD} \text{ ratio to treat OMW with the Fenton system: initial pH } = 3.5; \text{ molar ratio } \text{H}_2\text{O}_2/\text{Fe}^{2+} = 15.\]
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Colour removal

Although the overall UV/Vis spectrum absorption of OMW is the result of overlapping absorbance of different and numerous cromophor compounds corresponding to relatively complex structures (as polyphenolic compounds derived from lignin), the UV/Vis spectrum may be useful for comparison between different dosages of treatment with the Fenton reagent (Fig. 5).

The application of the combined Fenton reagent and chemical coagulation to treat OMW shows that the higher the mass ratio \( R = \frac{H_2O_2}{COD} \) values are used, greater removals of COD are obtained. This COD removal represents, in visual terms, a gradual decrease in the original dark-brown colour of OMW. At the end of the combined treatment it is possible to observe excellent colour removal: for example, to \( R = 2.5 \), the effluent did not show significant absorbance in the visible region, indicating that colour removal was practically complete (for the studied conditions). However, the spectrum in the UV region shows that the OMW was not completely mineralized.

The UV/Vis absorption spectra of samples of OMW before and after oxidation with the Fenton system and coagulation with lime were recorded. In Figure 5, the overall absorption of OMW decrease with the increasing wavelength is clear. While observing, a clear maximum or minimum characteristic is not evident, it is possible to consider in the OMW the two bands at 281 nm and 376 nm which after the combined treatment are diminished considerably.

In general it is possible to verify that an overall reduction of the absorbance of OMW from 200 to 800 nm follows the value of mass ratio \( R \). As the colour of the effluent is mainly due to the aromatic compounds (and aliphatic) of high molecular weight, the discoloration can serve as an indicator of the extent of degradation of such compounds by Fenton reagent and lime treatment as well as the successful destruction of the bulk organic matter.

Monitoring the Fenton system

In order to monitor in real time and also to record the data generated by the Fenton system an application using the software Labtech Notebook, coupled with an acquiring data system Advantech-PCL 818L, with an A/D converter 12-bit, connected to a PC was developed. Three parameters were continuously monitored over the period of reaction: oxidation-reduction potential (ORP), dissolved oxygen and pH.

Figure 6 shows the evolution of ORP in a typical experiment in which the ratio of weight \( R = \frac{H_2O_2}{COD} \) used was \( R = 2.5 \) and \( Fe^{2+} \) and \( H_2O_2 \) were added in successive doses (the first 3 marked with arrows). It appears that after the addition of \( H_2O_2 \) there is a sudden increase of the ORP due to the presence of species with a high oxidation potential such as the hydroxyl radicals (\( HO_\cdot \)) in the reaction media. The ORP then tends to suffer a decline while the more oxidative species decrease in the media, which indicates they have reacted with molecules present in OMW.

The results and analysis of the overall behaviour of this parameter in all experiments suggest, for maximum efficiency the value of oxidation-reduction potential should be maintained between +400 mV and +800 mV.

In treatment of OMW by the Fenton reagent it is essential the gradual addition of \( H_2O_2 \) in small portions (for example, 10% of the total amount) occurs instead of an initial single dose which through the experiment enables us to obtain a more effective process and avoiding any side reactions. These also moderate the increase in temperature that tends to occur as the reaction takes place. A common observation during the Fenton oxidation of OMW is the violent chemical reaction and foaming. With an excessive addition of hydrogen peroxide a quick increase in temperature and
the formation of foam in large amounts can be observed which can transform into situations of runaway. Dissolved oxygen, also shown in Figure 6 initially remains virtually unchanged; but later, as a response to the addition of H$_2$O$_2$, a gradual increase in the oxygen content was verified. This is probably due to reaction (5) that tends, in a final part, to decrease. The increase of dissolved oxygen tends to be higher probably due to reaction (5) that tends, in a final part, to de-agradual increase in the oxygen content was verified. This is

Fenton system. This decrease can be explained through the formation of dicarboxylic acids as degradation products of the phenolic compounds present in OMW. In practical terms, it will be necessary to avoid an exaggerated drop (for example, at pH lower than 1.5) to ensure the efficiency of the Fenton system.

It is possible to consider that the joint monitoring of these 3 parameters can be useful to follow the Fenton system. A more detailed study may establish correlation between these variables with a clear potential for practical assistance in monitoring the Fenton system. The online system and the acquisition of data that the software provides will also allow, if desired, a control and supervision of the process in real time.

Conclusion

On the basis of the above results, the following general conclusions can be drawn:

(i) Fenton reagent when combined with the process of chemical coagulation has an enormous potential to treat OMW: Fenton reagent is technologically simple and lime is a relatively cheap, raw material.

(ii) Fenton reagent considerably reduces the COD contained in the OMW, reaching a COD reduction of 96.8% for a mass ratio R=H$_2$O$_2$/COD of 3.0, with a pH=3.5 and maintaining a constant relationship H$_2$O$_2$/Fe$^{2+}$ =15.

(iii) Coagulation/flocculation with lime may easily be used as post-treatment in combination with the Fenton process to maximize the COD removal until 99.3%, for R=H$_2$O$_2$/COD = 3.0.

(iv) In a practical perspective the monitoring of three parameters (ORP, dissolved oxygen and pH) can be very useful in monitoring the Fenton system in real time.

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