Winery wastewater treatment by a combined process: long term aerated storage and Fenton’s reagent

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ABSTRACT

The degradation of the organic pollutants present in winery wastewater was carried out by the combination of two successive steps: an aerobic biological process followed by a chemical oxidation process using Fenton’s reagent. The main goal of this study was to evaluate the temporal characteristics of solids and chemical oxygen demand (COD) present in winery wastewater in a long term aerated storage bioreactor. The performance of different air dosage daily supplied to the biologic reactor, in laboratory and pilot scale, were examined. The long term hydraulic retention time, 11 weeks, contributed remarkably to the reduction of COD (about 90%) and the combination with the Fenton’s reagent led to a high overall COD reduction that reached 99.5% when the mass ratio ($R = \frac{H_2O_2}{COD}$) used was equal to 2.5, maintaining constant the molar ratio $H_2O_2/Fe^{2+} = 15$.

Key words | aeration time, aerobic biological treatment, Fenton’s reagent, laboratory and pilot scale, winery wastewater

INTRODUCTION

Wine production processes generate organic and inorganic pollution mostly associated with solid wastes and liquid effluents. The liquid effluents usually referred as “winery wastewater” are mainly originated from various unit operations such as washing of the presses used to crush the grapes, rinsing of fermentation vats, rakings, barrels, bottles and other equipments or surfaces (Pirra 2005; Mosteio et al. 2007).

Winery wastewaters contain large amounts of biodegradable organics in addition to relatively small concentrations of recalcitrant compounds: polyphenols, organic acids and sugars with typical COD values in the range from 3 to 30 g L$^{-1}$. The disposal of winery effluents in streams, creeks, rivers and on soils involves unacceptable environmental risks. Hence, a responsible management of these effluents requires that their potential environmental impacts be minimal and within an acceptable range (Petrucioi et al. 2000; Malandra et al. 2003; Beck et al. 2005; Lucas et al. 2009).

Several physical and chemical processes are available to winery wastewater treatment but its major action is a phase transfer of pollutants. Biological waste treatment methods have been recognized as a reasonable alternative way for a significant degradation of wastewater with high organic content, such as those coming from wineries in particular. However, the presence of recalcitrant compounds for the microorganisms frequently makes impossible the complete treatment of a winery wastewater. Combination of biological treatment followed by chemical processes may prove useful in this situation (Beltran de Heredia et al. 2005; Lucas et al. 2007). Biological treatment mineralizes the large biodegradable portion, effectively reducing the residual COD of the wastewater. A chemical polishing treatment (Fenton reagent) is then applied to degrade the persistent compounds. The primary biological step reduces the number and concentration of compounds that may compete for the chemical oxidant, thus increasing overall efficiency and lowering costs.
Advanced Oxidation Processes offer a highly reactive, non-specific oxidant, namely hydroxyl radical (HO\textsuperscript{-}), capable of destroying a wide range of organic pollutants in water and wastewater (Legrini et al. 1993; Nogueira et al. 2005a, b; Mosteo et al. 2007; Lucas et al. 2008). Fenton reagent is a mixture of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) solution and ferrous iron, which generates hydroxyl radicals according to a complex mechanism in an aqueous solution that could be summarised by the following reaction:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^\cdot \]  

The ferrous ion initiates and catalyses the decomposition of H\textsubscript{2}O\textsubscript{2}, resulting in the generation of HO\textsuperscript{-} (Chen & Pignatello 1997; Feng et al. 2003).

High-intensity aeration processes commonly require excessive energy input, leading to prohibitive operative cost. Therefore, it is important to seek a cost-effective treatment method. In this paper, the main objective is to evaluate the capacity of treating winery wastewater in a long term biological aerated storage, with different aeration schemes, combined with Fenton’s reagent. This chemical oxidation process, which uses low-priced reactants, was used as a secondary chemical treatment step for the oxidation of the recalcitrant organic compounds or metabolites that could not be oxidized biologically.

MATERIAL AND METHODS

Winery wastewater

The original winery wastewater used in this study resulted from the mixture of different effluents collected from a Portuguese winery (Adega Cooperativa de Vila Real) located in the Douro region (northeast of Portugal), representing the total annual production of the winery. Table 1 summarizes the average values obtained after two analyses for each parameter of the main physico-chemical characteristics of the winery wastewater.

**Chemicals**

The Fenton experiments were performed using ferrous iron sulfate (FeSO\textsubscript{4}·7H\textsubscript{2}O), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30% w/w), sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) and sodium hydroxide (NaOH) for pH adjustment all provided by Panreac. Other chemicals used in these experiments were of reagent grade and used as received. Ultra pure distilled-deionised water obtained from a Milli-Q (Millipore Co.) system.

**Analytical determinations**

The COD, TSS, VSS, Nt, P and K were determined according to Standard Methods (APHA 1992). COD analysis was done in a COD reactor from HACH Co., and a HACH DR2010 spectrophotometer was used for colorimetric measurement. Biological oxygen demand (BOD\textsubscript{5}) was evaluated by the respirometric method. In Fenton reagent experiments before the COD analysis, the samples were conditioned removing the H\textsubscript{2}O\textsubscript{2} excess by addition of NaOH. Hydrogen peroxide concentration was controlled during and after the treatments using Merck Peroxide Test (0 to 25 mg H\textsubscript{2}O\textsubscript{2}/L and 0 to 100 mg H\textsubscript{2}O\textsubscript{2}/L). pH evolution was determined by means of a pH-meter (CRISON 507). Total polyphenols were evaluated by Folin-Ciocalteau method.

**Aerobic biodegradation**

The aerobic biodegradation experiments of winery wastewater were conducted in completely mixed biological batch reactors consisting of a 4 L cylindrical Pyrex glass (laboratory scale) and 60 L (pilot scale). These vessels, at environmental temperature, were provided with covers containing inlets for bubbling the gas feed and stirring, and outlets for sampling and venting. The activated sludge...
used as inoculum of the aerated storage was directly obtained from aerobic stage of a full-scale urban wastewater treatment plant located nearby Vila Real (Portugal) and applied with a two days acclimatization period. The initial Volatile Suspended Solids (VSS) content of the sludge was 5 g L$^{-1}$.

The air flow was fed to the reacting medium through a bubble gas sparger at a constant flow rate of 125 L h$^{-1}$ at room conditions and with four different aeration periods 2.4 h/day, 4 h/day, 8 h/day and 12 h/day. In this process, the bioreactors were initially loaded with the above mentioned inoculum and the reaction medium was completed with a load of winery wastewater containing an initial substrate concentration around 20 g COD/L, and then the bioreactor was aerated and stirred during an hydraulic retention time (HRT) of 11 weeks. During the experiment several samples were withdrawn at regular times to analyze the COD, TSS, VSS and pH of the reacting medium.

**Oxidation by Fenton’s reagent**

The winery wastewater from the biological treatment (supernatant after natural sedimentation) was further treated using Fenton’s reagent. The oxidation experiments were conducted in a 1 L stirred glass batch reactor. Typical experiments were carried out with 500 mL of the effluent biologically pre-treated to which a weighed amount of FeSO$_4$·7H$_2$O was added and dissolved under stirring. pH was adjusted to 3.5 by adding sulphuric acid solution. The Fenton oxidation began with the addition of hydrogen peroxide solution (30% w/w). Different concentrations of H$_2$O$_2$ and Fe$^{2+}$ were tested. Before the determination of final COD the total consumption of H$_2$O$_2$ was verified with Merckoquant strips.

**RESULTS AND DISCUSSIONS**

**Aerobic biodegradation**

**Lab scale**

Figure 1 shows the COD removal obtained with the biologic aerated storage during 11 weeks of experiment at different aeration periods. In Figure 1a are presented the COD evolution along time and in Figure 1b the final degradation rate achieved from the initial organic load (20 g O$_2$L$^{-1}$) with the aerobic treatment for the different aeration periods.

The COD conversion ($X_{COD}$) obtained in each experiment is defined as follows:

$$X_{COD} = \frac{COD_0 - COD_f}{COD_0} \times 100$$

where COD$_0$ and COD$_f$ are the initial and final concentrations of COD, respectively.

The COD decreases rapidly in the initial 2 weeks during the course of all experiments. The experiment performed with an air supply of 12 h/day achieves a high degradation level in a short reaction time, for example after 4 weeks reaches a COD removal of 87%, while the 8 h/day obtained 77%, the 4 h/day 76% and finally for 2.4 h/day 61%.

However, since the 9th week it is possible to verify that COD removal is almost similar for all the experiments. For example, increasing the HRT to 11 weeks the COD removal percentage improves to a similar level for all experiments and corresponding aeration periods. Therefore for 11 weeks...
reaction and aeration time of 12 h/day achieves a COD degradation of 88%, to 8 h/day was obtained 89%, for 4 h/day 96% and to 2.4 h/day 95%. Thus, even for small aeration period, high COD removal could be achieved with a long aeration time. As a final analysis it is possible highlight that a gradual reduction of the substrate occurs during the 11 weeks until it reaches a residual value of non-biodegradable organic matter (among 5 and 10%).

In addition to the experiments performed with different aeration periods, there were also performed experiments without any aeration: with winery wastewater plus inoculum (with sludge) and winery wastewater without inoculum (without sludge) to evaluate the influences of the aeration and of the inoculum sludge. The results reveal a lower degradation capacity throughout the experiment, though at the end they presented a similar depuration capacity. This means that in the experiment without any inoculum added, the natural microorganisms present in the winery wastewater showed the capacity to decompose the biodegradable organic matter. Another remark is that without aeration the degradation reached is very similar to the assays with aeration. However, this situation produces harmful bad odours as result of the anaerobic biodegradation. Therefore, experiments with aeration are always preferable even with small aeration times (e.g. 2.4 h/day) to reduce these odours production.

The volatile solids fraction generally represents the organic component of the TSS, which is more biodegradable than the rest of solids that are mainly associated with the coarse material in the slurry and effectively inert in a typical aerobic treatment process (Figure 2). In all the experiments biomass achieves values different than zero after the stage of decay. This can be explained due to the methodology adopted to measure the biomass (VSS) once death or inactivated cells are also accounted.

Figure 3 shows the pH evolution during the experiments performed at laboratory scale. The pH is a key factor on the microorganisms growth, once they can not support values higher than 10 and less than 4. The experiments started all at an acidic pH (among 4 and 6). However, along the experiments the pH changes to basic values achieving the higher value at 9.6. This fact happens due to the adaptation and type of microorganisms naturally occurring along time, which clearly prefer higher pH values.

Pilot scale

After the laboratory scale, experiments were done at pilot scale. This scale-up was performed to evaluate if the behaviour showed at the laboratory scale (4 L) would be similar to the observed in a 60 L pilot reactor. Figure 4 shows the COD removal results obtained in the pilot reactor. In general, these data reveal that, comparatively to lab scale data (Figure 1) the COD removal efficiency of the pilot scale is lower than the obtained at the laboratory scale.

Figure 4a presents the COD evolution along time in the pilot scale reactors and Figure 4b) the final degradation rate achieved from the initial organic load (20 g O2L−1) with the different aerobic treatments. It is shown that the experiment performed with an air supply period of 12 h/day follows the same behaviour verified in laboratory scale, achieving a high degradation level in a short reaction time. For example after 4 weeks it was reached a COD removal of 85%, whereas the 8 h/day obtain 76%, for 4 h/day 47% and finally to 2.4 h/day 45%. However, increasing the HRT to 11 weeks the COD removal rate improves for all aeration
periods. For 11 weeks of reaction a 12 h/day and aeration period achieves 96% COD removal, for 4 h/day 75% and to 2.4 h/day 64%.

Figure 5 shows the evolution of VSS in pilot scale experiments. A gradual decrease with some oscillations was observed throughout the 11 weeks experiment, being more significant for the experiment with an aerated period of 12 and 8 h/day. This fact can be justified by the natural evolution of the microorganisms along their life cycle. Once the biomass is already acclimatized in these experiments the exponential growth phase does not exist and the stationary phase occurs during a very short time. After which a decrease in the biomass value occurs due to lack of nutrients and cellular death (endogenous decayment).

Figure 6 shows the pH evolution followed during the experiments performed at pilot scale. As in laboratory scale, the experiments started at an acidic pH, however along the experiments the pH changes to basic values.

Oxidation by Fenton’s reagent

As described previously, winery wastewaters biodegraded by aerobic microorganisms were then treated with Fenton’s reagent, in a group of experiments where the initial concentration of hydrogen peroxide was modified, maintaining constant the molar ratio \( \frac{\text{H}_2\text{O}_2}{\text{Fe}^{2+}} = 15 \). Table 2 presents the characteristics of the winery wastewater after the biologic aerated treatment.

Chemical oxidation with Fenton’s process was analyzed in order to test further reduction in COD concentration to minimize the impact of winery wastewater discharge on natural water courses and/or municipal wastewater treatment plants.

In the experiments carried out with Fenton reagent, they have had as reference the mass ratio between the hydrogen peroxide and COD, \( R = \frac{\text{H}_2\text{O}_2}{\text{COD}} \). Hence, the value of R was changed from 0.25 to 2.5, remaining constant the initial pH (corrected after biologic treatment to 3.5), the initial temperature (30°C) and the molar ratio.

<table>
<thead>
<tr>
<th>pH</th>
<th>TSS (mg/L)</th>
<th>VSS (mg/L)</th>
<th>COD (mg O$_2$/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>3,600</td>
<td>2,800</td>
<td>1,560</td>
</tr>
</tbody>
</table>

Table 2 | Characterization of the winery wastewater after biologic pre-treatment
constant \((\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15)\) (Peres et al. 2004) evaluating mainly the final COD removal.

Table 3 shows the COD removal at different R values after 4 hours of experiment. From the data presented it is visible that COD removal increases from 17.4% to 93.2% when the R value \((\text{H}_2\text{O}_2/\text{COD})\) increases from 0.25 to 2.5, respectively.

As expected, the increase in \(\text{H}_2\text{O}_2\) concentration has a positive effect on the COD reduction. For the maximum R value studied \((R = 2.5)\), the COD removal reaches 93.2% after 4 hours. This demonstrates the ability of Fenton reagent to degrade a large part of recalcitrant organic matter present in winery wastewater. The reason for the increase in COD conversion with the increase of \(R\) is related to 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:

**Step 1:**

\[
\text{COD} + \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{species partially oxidized} \quad (3)
\]

**Step 2:**

\[
\text{species partially oxidized} + \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{inorganic salts} \quad (4)
\]

The extent of oxidation (and consequently the degree of COD removal) depends directly on the amount of \(\text{H}_2\text{O}_2\) used.

### CONCLUSIONS

The combined process of aerobic degradation followed by Fenton’s reagent oxidation was employed to treat winery wastewater, leading to good performances. The results indicate that aerobic biological treatment reaches a very high COD removal, corresponding to the biodegradable fraction taking Fenton reagent like a final polishing step. The main conclusions are: aerobic biological degradation rates reached between 76% and 96% COD removal in laboratory scale, and between 64% and 96% at pilot scale. It is preferable applying a biological process as a first treatment step of a winery wastewater rather than chemical oxidation, since the greater fraction of the original effluent is biodegradable.

Depending on the discharge objectives and urgency, different aeration periods can be applied. Therefore, for small wineries, long term aerated storage can be performed (e.g. ponds, old cement vats, etc.) followed by a Fenton reagent treatment as a final polish with relatively low investment and operation costs.

As a final remark, the results obtained starting with a typical winery effluent \((20 \text{ g COD/L})\) have demonstrated that this combined process (long term aeration plus Fenton reagent) can lead to COD removal efficiency higher than 99%, with final effluents that can be reused, rejected in the water streams or in the soil, according to Portuguese law.

### ACKNOWLEDGEMENTS

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### REFERENCES


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**Table 3** | COD conversion (%) obtained for different \(R = \text{H}_2\text{O}_2/\text{COD}\) values, after chemical oxidation of winery wastewater with Fenton reagent. Operational conditions: initial \(T = 30\, ^\circ\text{C}\), initial \(\text{pH} = 3.5\), molar ratio \(\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15\)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Mass ratio (R) ((\text{H}_2\text{O}_2/\text{COD}))</th>
<th>(\text{COD}_{\text{initial}}) (mg O2/L)</th>
<th>(\text{COD}_{\text{final}}) (mg O2/L)</th>
<th>(X_{\text{COD}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WW-1</td>
<td>0.25</td>
<td>1,560</td>
<td>1,289</td>
<td>17.4</td>
</tr>
<tr>
<td>WW-2</td>
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<td>1,072</td>
<td>31.3</td>
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<tr>
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<td>0.75</td>
<td>1,560</td>
<td>877</td>
<td>43.8</td>
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<tr>
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<td>84.7</td>
</tr>
<tr>
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<td>1,560</td>
<td>106</td>
<td>93.2</td>
</tr>
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