Degradation of wine distillery wastewaters by the combination of aerobic biological treatment with chemical oxidation by Fenton’s reagent

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Abstract The degradation of wine distillery wastewaters by aerobic biological treatment has been investigated in a batch reactor. The evolution of the chemical oxygen demand, biomass and total contents of polyphenolic and aromatic compounds was followed through each experiment. According to the Contois model, a kinetic expression for the substrate utilization rate is derived, and its biokinetic constant is evaluated. The final effluents of the aerobic biological experiments were oxidized by Fenton’s reagent. The evolution of chemical oxygen demand, hydrogen peroxide concentration and total contents of polyphenolic and aromatic compounds was followed through each experiment. A kinetic model to interpret the experimental data is proposed. The kinetic rate constant of the global reaction is determined.

Keywords Vinasses; aerobic biological treatment; Fenton’s reagent; oxidation; kinetic study

Introduction
Wine distilleries produce large volumes of wastewaters whose composition varies widely according to the raw material distilled: wine, lees, etc. In general, all of them have an acidic pH and a high organic substrate content with chemical oxygen demand in the range 15–40 g/L (Chapman, 2001). Usually these effluents are treated by aerobic (Benitez et al., 1999a) or anaerobic (Benitez et al., 1998) biological processes or disposed into stabilization ponds. This last solution represents a large-scale environmental problem, due to bad smells or pollution in underground waters (Shepherd et al., 2001). The biological treatments have several problems due to the toxicity of these effluents that lead to a partial inhibition of the biodegradation, because some microorganisms are particularly sensitive to the organics present, especially the polyphenolic compounds (Benitez et al., 2003). Therefore, other treatments, like some chemical oxidations have recently been investigated (Benitez et al., 1999b; Martin et al., 2003). Among these procedures, Fenton’s reagent (combination of ferrous salt and hydrogen peroxide) has been increasingly used because it has many properties desirable for wastewater treatments: a powerful oxidant that degrades many organic compounds, specifically aromatic compounds, soluble in water and low cost (Beltran de Heredia et al., 2001a).

In this paper, the degradation of wine distillery wastewaters by the combination of an aerobic biological process followed by the oxidation with Fenton’s reagent is studied. In both processes, the aim is to know the influence of operating variables on the evolution of organic matter (measured as COD, total polyphenolic and aromatic compounds) with reaction time. Likewise, a kinetic study is carried out in order to evaluate the kinetic rate constant of each model.
Methods

Wine distillery wastewater
The original wastewater were “vinasses” (WDW) collected from the industrial distillery “Vinicola del Oeste” located in Villafranca de los Barros (Badajoz, Extremadura community in southwestern Spain). This effluent was analyzed according to the procedures described in the literature (Beltran de Heredia et al., 2004b). The aromatic compounds were determined globally by measuring the absorbance of the samples at 254 nm (the maximum absorbance wavelength of these organic compounds) and are expressed as mg of phenol/L (Beltran de Heredia et al., 2004b). The total polyphenolic content was determined by the Folin–Ciocalteau method (Beltran de Heredia et al., 2004b). The mean values obtained for the main chemical characteristics are the following: pH = 3.8, COD = 18.5 g/L, total polyphenolic compounds = 0.63 g caffeic acid/L, volatile acidity = 0.98 g acetic acid/L, aromatic compounds = 4.3 g phenol/L, total solids = 13 g/L.

Aerobic biodegradation
The aerobic biodegradation experiments of WDW were conducted in a 1000 mL stirred glass batch reactor, which was submerged in a thermostatic bath with the necessary elements to maintain the temperature constant at 28 ± 0.5°C. The air flow was fed to the reacting medium through a bubble gas sparger at a constant flow rate of 125 L/h at room conditions. The pH was buffered at 7.0 and varied during the experiments by ± 0.4 units.

As WDW does not contain biomass capable of aerobic biodegradation, a pretreatment process was carried out in order to acclimatize an activated sludge taken from a municipal wastewater treatment plant to this vinasse. In this process, the bioreactor was initially loaded with the above mentioned inoculum and the reaction medium was completed with a load of diluted WDW containing an initial substrate concentration of 5 g COD/L, and then the bioreactor was aerated and stirred during 4 days. At the end of this treatment and after a settlement period, the biomass was separated by filtration from the supernatant liquid and charged again to the bioreactor. This procedure was repeated with successive additions of WDW loads to the biomass, each one containing increasing concentrations of substrate from 5–18 g COD/L. The biomass acclimatization was considered to be achieved when a similar removal of substrate was obtained after four experiments with the original WDW.

Once the acclimatization stage was finished, WDW degradation experiments were conducted. Thus, a 500 mL of this wastewater was introduced into the bioreactor which was inoculated with the previously acclimatized biomass in the amount required to obtain the desired initial concentration of biomass for the experiment. During an experiment (3–4 days), several samples were withdrawn at regular times to analyze the substrate and biomass concentrations and the total polyphenolic compounds content in the reacting medium.

Finally, the biologically pretreated wastewater was filter in order to separate the biomass and loaded into the oxidation reactor for the treatment with Fenton’s reagent.

Oxidation by Fenton’s reagent
The oxidation experiments were conducted in another 1000 mL stirred glass batch reactor with inlets for sampling, temperature and pH measurement. The temperature was maintained constant at 25 ± 0.5°C. The pH was adjusted to 3.5 by adding sulfuric acid or sodium hydroxide solutions. The reactor was filled with 500 mL of WDW pretreated by aerobic microorganisms. The initial concentration of ferrous salt (added as FeSO₄ 7 H₂O) was in the range 0.01 to 0.1 mol/L and that corresponding to hydrogen peroxide was between 0.1 mol/L and 0.65 mol/L.
During an experiment (180 minutes), several samples were withdrawn at regular times to analyze the organic matter (measured as chemical oxygen demand), the aromatic and total polyphenolic compounds content in the reacting medium. The remnant hydrogen peroxide concentration over the course of each experiment was measured using an iodometric method.

Results and discussion

Aerobic biodegradation

As has been described, WDW was firstly degraded by aerobic microorganisms, in a group of experiments where the initial biomass ranged from 0.50 to 2.80 g of VSS/L. During an experiment, the evolution of the concentration of the substrate, biomass and total polyphenolic compounds was followed. As an example, Figure 1 shows the evolution of those parameters during bioreaction time in an experiment, with similar trends being observed in the remaining runs.

Regarding the substrate evolution, this parameter decreases continuously with bioreaction time, as could be expected. The substrate removal is hardly affected by the initial biomass, and overall reductions in the range 75 to 94% are obtained. Regarding the biomass, as is seen in Figure 1, its evolution follows the typical growth-cycle phases for batch cultivation: after an acclimatization period (lag phase), the population of biomass is well adjusted to its new environment. Then, the microorganisms multiply rapidly and an important increase in the biomass concentration is observed (exponential growth phase), until a maximum size of population is reached (stationary phase). Finally, a decline in the biomass take place (death phase of microorganisms). Regarding the total polyphenolic compounds, its evolution also decreases continuously with bioreaction time (see Figure 1). The removal obtained for this parameter is in the range 54 to 79%.

From an industrial point of view, the most interesting period in the growth cycle of a batch cultivation is the exponential growth phase, when the population of biomass is perfectly acclimatized to the substrate. In this period, the rate of production of
biomass \((X)\) is well described by a first-order kinetic equation (Aiba et al., 1973):

\[
\frac{dX}{dt} = \mu X
\]

(1)

where \(\mu\) is the specific growth rate of biomass. Simultaneously to the production of biomass, the substrate \((S)\) is degraded, and its rate is also proportional to the biomass present, according to the expression:

\[
- \frac{dS}{dt} = qX
\]

(2)

where \(q\) is the specific substrate degradation rate.

The literature provides several expressions which relate the specific rates (\(\mu\) and \(q\)) to the substrate concentration (Aiba et al., 1973). Among them, the Contois model (Contois, 1959) is one of the most used, because it gives excellent fits to the experimental results. In the case of the specific degradation rate, this model proposes the following equation for \(q\) as a function of the substrate concentration:

\[
q = q_{\text{max}} \frac{S}{K_s X + S}
\]

(3)

where \(q_{\text{max}}\) represents the maximum rate of substrate utilization and \(K_s\) is the Contois saturation constant.

In order to obtain the specific kinetic parameters for this model, \(q_{\text{max}}\) and \(K_s\), Eq. (3) can be linearized in the form:

\[
\frac{1}{q} = \frac{1}{q_{\text{max}}} + \frac{K_s}{q_{\text{max}}} \frac{X}{S}
\]

(4)

According to this equation, a plot of \(1/q\) versus \(X/S\) must lead to a straight line for every experiment conducted, whose intercept and slope will be \(1/q_{\text{max}}\) and \(K_s/q_{\text{max}}\), respectively.

For this purpose, the specific rate \(q\) must be previously evaluated for each bioreaction time, by transforming its definition expression (Eq. (2)):

\[
q = - \frac{1}{X} \frac{dS}{dt}
\]

(5)

For this evaluation, the term \(-dS/dt\) is calculated by fitting the experimental data \((S, t)\) to a polynomic expression by least-square regression analysis, deriving this expression with respect to the time and dividing by the biomass concentration \((X)\) at any time. According to this procedure, Figure 2 shows this plot for an experiment taken as an example. It can be seen that, points lie satisfactorily around a straight line, which confirms that the selected Contois model is adequate to correlate the aerobic biodegradation of WDW.

After least-square regression analysis, the slope and intercept are determined, which provide values of 28.6 h for \(K_s/q_{\text{max}}\) and 0.49 g VSS h/g COD for \(1/q_{\text{max}}\). This small value for \(1/q_{\text{max}}\) suggests a very high value for \(q_{\text{max}}\) that cannot be calculated accurately. Therefore, the term \(1/q_{\text{max}}\) can be eliminated in Eqs (4) and (3) can be transformed into:

\[
q = \frac{q_{\text{max}} S}{K_s X}
\]

(6)

This is a particular situation of the Contois model, when \(K_s X \gg S\) and the substrate degradation rate follows a first-order kinetics:

\[
- \frac{dS}{dt} = 0.035 S
\]

(7)

Another kinetic parameter is related to the biomass evolution during the growth phase of a batch cultivation: the cellular yield coefficient \(Y_{X/S}\). This parameter is defined
as the ratio of biomass produced and substrate consumed, and can be expressed by the equation:

$$Y_{X/S} = -\frac{dX}{dS}$$  \hspace{1cm} (8)

This equation can be integrated to give:

$$(X - X_0) = Y_{X/S}(S_0 - S)$$  \hspace{1cm} (9)

According to Eq. (9), a plot of $(X - X_0)$ values versus $(S_0 - S)$ values in the experiments must lead to a straight line whose slope will be $Y_{X/S}$ and an intercept zero. Figure 3 shows...
this plot for an experiment taken as an example. It can be seen, points lie satisfactorily around a straight line which confirms the validity of Eq. (8). After least-square regression analysis, a slope of 0.27 g VSS/g COD is obtained. This value is very close to with others proposed in the literature for the aerobic biodegradation of different wastewaters (Beltran de Heredia et al., 2000a,b).

**Oxidation by Fenton's reagent**

As has been described previously, WDW biodegraded by aerobic microorganisms was treated by Fenton’s reagent, in a group of experiments where the initial concentration of ferrous salt and hydrogen peroxide was modified. During an experiment, the evolution of the concentration of organic matter (as COD), aromatic and total polyphenolic compounds, and hydrogen peroxide content was followed.

As an example, Figure 4 shows the evolution of reduction of those parameters measured versus reaction time for an experiment. A very important reduction of aromatic and total polyphenolic compounds can be seen in only 5 minutes. The maximum reduction of COD was achieved practically at 30 minutes, as well as the presence of hydrogen peroxide in the reacting medium. Similar trends were observed in the remaining runs.

COD removal was strongly affected by the initial hydrogen peroxide concentration, and overall reductions in the range 50 to 80% were obtained. Aromatic and total polyphenolic compounds removals were always very high, larger than 90% in both cases.

A kinetic study considering a simple, irreversible, second-order reaction with respect to COD and hydrogen peroxide has been carried out (Beltran de Heredia et al., 2001b):

$$\frac{\text{d}(\text{COD})}{\text{dt}} = k'(\text{COD})(\text{H}_2\text{O}_2)$$

(10)

where $k'$ is an apparent kinetic constant that includes the initial ferrous ion concentration:

$$k' = k(\text{Fe}^{2+})$$

(11)
By separating variables and integrating Eq. (10), it is deduced that:

\[
\ln \left( \frac{\text{COD}_0}{\text{COD}} \right) = k_0 Z_0 t - k_0 \int_0^t (\text{H}_2\text{O}_2) \, dt, \text{ mol min/L}
\]

In this equation, the integral term was calculated by fitting the experimental data \((\text{H}_2\text{O}_2, t)\) to a polynomial expression by least-square regression analysis, and the later integration from initial time to any reaction time gave the integral value for this reaction time (Beltran de Heredia et al., 2004a). Figure 5 shows a plot of Eq. (12) for an experiment taken as an example. As can be seen, points lie satisfactorily around a straight line with positive slope and an intercept practically zero, confirming the validity of Eq. (12). By least-square regression analysis, the slope of this line is deduced, being 0.61 L/mol.min and taking into account Eq. (11), the value of apparent kinetic constant \(k\) is 26.5 L\(^2\)/mol\(^2\).min.

**Conclusions**

A combined aerobic biodegradation/Fenton’s reagent oxidation process was employed in the present study to treat wastewaters from a wine distillery. The main conclusions are: first, aerobic biological degradation reduces the COD between 75 and 94%, and the total polyphenolic compounds in the range 54 to 79%. Secondly, the experimental data were correlated to the Contois model, determining the first-order kinetic constant 0.035 h\(^{-1}\). Thirdly, the cellular yield coefficient calculated from experimental results was 0.27 g VSS/g COD. Fourthly, Fenton’s reagent oxidation degraded the pretreated biologically wastewater with high efficiency. COD removal was in the range 50 to 80%. Aromatic and total polyphenolic compounds removals were always higher than 90%. Finally, experimental data from Fenton’s reagent process were adjusted to a complex reaction kinetic model (first order with respect COD, hydrogen peroxide and iron concentration), deducing the apparent kinetic constant 26.5 L\(^2\)/mol\(^2\).min.
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