

## Treatment of Cork Process Wastewater by a Successive Chemical–Physical Method

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In cork processing, the operation of boiling the raw cork generates large volumes of wastewater which are more often than not released directly into the environment untreated. Even when the wastewater is treated, this is usually by retention in evaporation ponds. This procedure, however, causes bad odors and may pollute surface water and groundwater. The present study evaluates a physicochemical method involving Fenton oxidation and coagulation/flocculation for the removal of chemical oxygen demand (COD), total polyphenols (TP), and aromatic compounds (A) from cork manufacturing process wastewater. The experimental variables studied were the dosages of iron salts (from 0.001 to 0.2 mol/L) and hydrogen peroxide (between 0.06 and 1 mol/L). The integrated Fenton-coagulation/flocculation process reduced the COD of the effluent by from 22% to 85%. The removal of total polyphenols ranged from 4% to 98%, and of aromatic compounds from 2% to 97%. A further two experiments were performed modifying the manner in which the reagents were added, splitting the reagent dose (of hydrogen peroxide and ferrous salt) into two and three fractions. Finally, an economic study was made of the chemical costs deriving from the application of this purification system. The cost of a treatment with an  $[H_2O_2]_0/COD_0$  ratio of 1.8 g/g (splitting the reagent dose into three fractions) that yields a COD removal of 73% was estimated to be 11.5 euros/m<sup>3</sup> of wastewater.

**KEYWORDS:** Cork processing wastewater; decontamination; coagulation; flocculation; Fenton's reagent

### INTRODUCTION

Cork oak stands are one of the most important forest types in Mediterranean countries (mainly Portugal and Spain). The main product of these stands is cork, a thick continuous layer of suberin-walled cells produced by the meristem cambium that forms the external envelope of the trunk and branches. Usually, the first cork layer is removed when the tree attains a circumference over bark of 70 cm at chest height (virgin cork) and then periodically at 9-year intervals (reproduction cork). Cork stripping is done manually using an axe. The stripper makes long vertical and horizontal slits in the cork and then carefully detaches large slabs of cork. The cork cambium is destroyed during the cork stripping process, but the sustainability of production is ensured because the species has the capacity to regenerate new cambium in the inner part of the bark, immediately below the cells that die as a consequence of the stripping. World cork production is about  $250\text{--}450 \times 10^3$  t per year, with Portugal being the leading producer (55% of the world's production and 33% of the area) (1). Cork and cork-product exports (mainly cork stoppers) represent 33% of the country's total exports of forestry products.

The raw cork slabs are submerged in near-boiling water (temperature of around 98 °C) for approximately 1 h in a vat

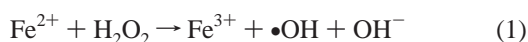
(called the "caldera") for disinfection (elimination of fungi, invertebrates, reptiles, etc.) and to improve the cork's mechanical properties (elasticity, texture, consistency, etc.). The water is not changed for 2–3 days, until approximately 20–30 vat-loads of cork have been cooked. The vat is then emptied and cleaned, to be refilled with clean water the following day.

These residual wastewaters are in most cases dumped into the environment untreated. In other cases, the commonest treatment is to retain them in evaporation ponds. This procedure, however, causes bad odors and the possibility of polluting surface water and groundwater. The high organic load of this wastewater means that the process represents a major environmental problem. 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. The complicated nature of cork wastewater ( $BOD_5/COD = 0.19$ ) makes biological treatment ineffective. There are a few investigations related to this wastewater. Minhalma and de Pinho (2, 3) found that polyphenolic compounds present in cork processing wastewater are responsible for membrane fouling and drastic flux decline in the ultrafiltration process. Flocculation and flotation pretreatments with chitosan and air, respectively, reduce the total polyphenol content up to 45% and 17%, respectively. After these pretreatments, the permeate fluxes in the ultrafiltration process increase up to 130% with respect to the raw wastewater (4).

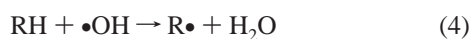
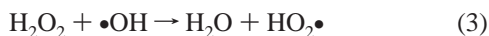
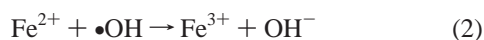
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Benitez et al. (5) studied the purification of cork processing wastewaters by ozone, aerobic biodegradation, and by their two sequential processes. The removal obtained in the ozonation process was between 12 and 54% for the COD. The activated sludge system yielded COD removals between 13 and 37%. The combined processes increased the substrate removal up to 65% (ozonation followed by aerobic biodegradation) or 77% (aerobic biodegradation followed by ozonation). One readily available treatment technology that has become widely used in recent years is Fenton's oxidation process (6–8), which has the dual function of oxidation and coagulation/flocculation (9, 10). However, the large amount of total solids present (about 1300 mg/L) make a second coagulation/flocculation step (by adding NaOH) necessary to diminish the quantity of these solids, and thus reduce COD, BOD, color, and odor.

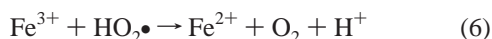
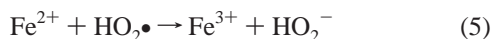
Recently, several papers have been published reviewing the chemistry and applications of Fenton's reagent (11–13). The Fenton's oxidation process generates hydroxyl radicals (14) according to:



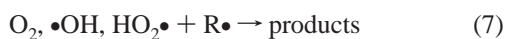
This hydroxyl radical can react both the ferrous ion, hydrogen peroxide, or organic matter:



Moreover, the hydroperoxyl radical reacts with ferrous and ferric ions:



The organic radical can react with oxygen or hydroxyl and hydroperoxyl radical to oxidation products:



A wide variety of Fenton's oxidation process applications have been reported to treat wastewaters. A lot of work has been carried out using this reaction system to degrade organics. Thus, oxidation of alcohols (15), organonitrogenated (16), organochlorinated (17), hydrocarbons (18), aromatics (19), phenols (8, 20–22), dyes (23), surfactants (24), pesticides (25–29), etc. have been studied. Examples include textile wastewaters (30, 31), pharmaceutical effluents (32), treatment of paper pulp manufacturing wastewaters (33), photographic developing effluents (34), brines of table olive (35, 36), olive oil mill wastewater (37), and cork cooking wastewater (38).

Usually, the Fenton oxidation process consists of four stages: (a) addition of a dose of ferrous salt; (b) pH adjustment to 3.5 (in this work by adding concentrated  $\text{H}_2\text{SO}_4$ ); (c) oxidation reaction (by adding  $\text{H}_2\text{O}_2$ ); and (d) coagulation-flocculation, using a base-precipitant (in this case by adding NaOH concentrated to pH 10). This last stage of coagulation/precipitation has a threefold function: (1) to halt or "freeze" the Fenton oxidation reaction, (2) to eliminate suspended or colloidal organic matter that had not been eliminated in the oxidation process, and (3) to break down the residual hydrogen peroxide because of its potential interference in the COD determination. The organic compounds are hence removed in two stages: oxidation and

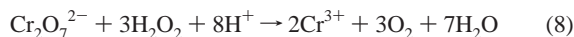
coagulation-flocculation. Lee et al. (39) observed that there is a major COD removal by coagulation with the formation of ferric hydroxocomplexes. Furthermore, the organic matter removed by adding NaOH to give a flocculant precipitate of  $\text{Fe}(\text{OH})_3$  ( $K_{\text{sp}} = 10^{-36}$ ) facilitates the separation of suspended materials in the effluent (40).

In the present work, therefore, an integrated Fenton-coagulation/flocculation method was applied for the decontamination of this effluent. The aim was to provide data on the removal of contaminant organic matter and to establish the influence of the operating variables (the dosages of iron salts and hydrogen peroxide) on the process's efficacy.

## MATERIALS AND METHODS

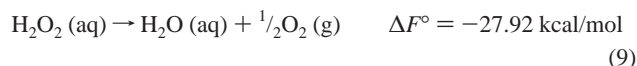
The cork processing wastewater used was provided by the industrial plant Corchos Mérida S.A. in Extremadura (Autonomous Community, Spain). This water had been used for 3 days with a total of 15 vat-loads. Its characteristics were pH 4.8–5.0, COD 3500–3900 mg/L,  $\text{BOD}_5$  650–750 mg/L, total solids (TS) 1140–1460 mg/L, total suspended solids (TSS) 50–90 mg/L, total dissolved solids (TDS) 1120–1340 mg/L, total mineral solids (TMS) 340–400 mg/L, total volatile solids (TVS) 850–1010 mg/L, total phenolic content (expressed as mg/L of caffeic acid) 480–580 mg/L, aromatic compounds (expressed as the absorbance of the 1/50 diluted samples at 254 nm) 0.96–1.17 AU,  $[\text{Cl}^-]$  453–520 mg/L,  $[\text{Ca}^{2+}]$  187–225 mg/L,  $[\text{Fe}^{3+}]$  10–40 mg/L and conductivity 1400–1640  $\mu\text{S}/\text{cm}$ .

In all cases, experiments were performed in a 2000-mL stirred glass reactor with inlets for sampling and temperature measurements. The temperature was maintained constant at  $30 \pm 1$  °C in all cases. The reactor was first filled with 500 mL of cork wastewater and the pH was adjusted with concentrated sulfuric acid to 3.5. The second step was the addition of ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) to the desired concentration. The third was the addition of hydrogen peroxide to initiate the Fenton oxidation reaction. Finally, the coagulation/flocculation step was carried out by adding NaOH to take the pH over 10. After being left to settle for 1 day, the supernatant was decanted and an aliquot was taken for COD, total polyphenol, and aromatic content assay. However, excess  $\text{H}_2\text{O}_2$  in the Fenton process can lead to problems in the COD assay (increasing the apparent COD) because of interference due to consumption of  $\text{K}_2\text{Cr}_2\text{O}_7$  (41) by the following reaction:



This possible interference of the hydrogen peroxide excess in the measurement of COD can be eliminated by modifying two factors: by increasing the temperature (a factor of 2.2 increase in  $\text{H}_2\text{O}_2$  decomposition rate for each 10 °C) and by increasing the pH (in particular to pH >6–8). For this reason, in all cases the pH was increased to over 10 in the last coagulation/flocculation step and the samples were heated to 80 °C (for 10 min).

The last coagulation/flocculation step therefore had a threefold function: (i) to eliminate suspended or colloidal organic matter; (ii) to halt the Fenton's reaction; and (iii) to break down the residual hydrogen peroxide and thus avoid its possible interference with the COD determination. The precipitate of  $\text{Fe}(\text{OH})_3$  catalyses the following decomposition reaction:



The total polyphenol concentrations were measured using Folin–Ciocalteu reagent (a mixture of phosphomolybdic and phosphotungstic acids) after prior extraction of the sample with ethyl acetate (42). The result is a blue polymer in a basic medium. The polyphenol content is expressed as mg/L of caffeic acid.

The aromatic content was determined by measuring the absorbance at 254 nm (43, 44), the wavelength at which the aromatic and unsaturated compounds present an absorption maximum. The determination was made in a Hitachi model U-2000 spectrophotometer, using a 1 cm optical path length quartz cuvette.

**Table 1.** Experimental Conditions and COD Removals Obtained at Two Reaction Times (1 and 150 min) for the Different Experiments Carried out

expt <sup>a</sup>	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> (mol/L)	[Fe <sup>2+</sup> ] <sub>0</sub> (mol/L)	X <sub>COD</sub> (1 min) (%)	X <sub>COD</sub> (150 min) (%)
FCF-1	0.2	0.02	42	64
FCF-2	0.6	0.02	46	75
FCF-3	0.2	0.002	28	46
FCF-4	0.2	0.2	59	60
FCF-5	0.06	0.02	18	22
FCF-6	1	0.02	52	85
FCF-7	0.2	0.001	27	40
FCF-8 <sup>b</sup>	0.2	0.02	37	71
FCF-9 <sup>c</sup>	0.2	0.02	10	73
CF-1	0	0.001	—	0
CF-2	0	0.002	—	0
CF-3	0	0.02	—	19
CF-4	0	0.2	—	61
H-1	0.2	0	—	10

<sup>a</sup> H, experiments using hydrogen peroxide alone; CF, coagulation/flocculation experiments; FCF, Fenton-coagulation/flocculation experiments. <sup>b</sup> Addition of reagents in two fractions (0 and 60 min). <sup>c</sup> Addition of reagents in three fractions (0, 30, and 60 min).

The remnant hydrogen peroxide concentration over the course of each experiment was measured after the Fenton oxidation and before the coagulation/flocculation stage (in a second aliquot and without the addition of NaOH) using the iodometric method (45).

## RESULTS AND DISCUSSION

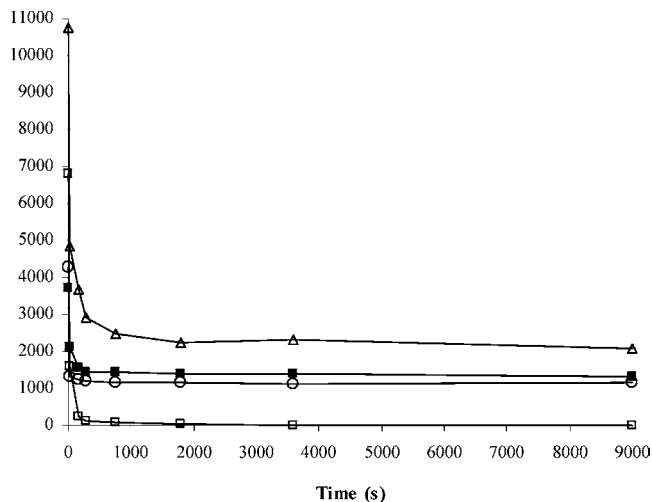
The oxidation-coagulation/flocculation of cork-processing wastewater by Fenton's reagent, using NaOH as base-precipitant, was investigated in laboratory experiments by modifying the initial reagent concentrations (of hydrogen peroxide and ferrous salt). Likewise, experiments with hydrogen peroxide (without the addition of iron salts) and coagulation/flocculation with iron salts and sodium hydroxide (without hydrogen peroxide) have been carried out. All the experiments were carried out at  $30 \pm 1$  °C. **Table 1** lists the values of the initial conditions of the operating variables in each experiment. Experiments FCF-8 and FCF-9 were performed modifying the manner in which the reagents were added.

As was indicated above, the evolution of the elimination of the organic matter was monitored in each Fenton-coagulation/flocculation experiment by measuring the chemical oxygen demand (COD), total polyphenol content (TP), and aromaticity (A).

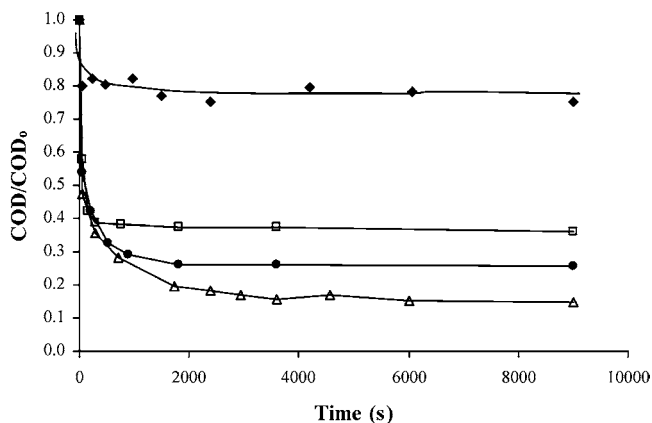
We also followed the residual hydrogen peroxide concentration over the course of each Fenton experiment (in a second aliquot taken after the Fenton oxidation and before the coagulation/flocculation stage).

**Figure 1** shows the curves of disappearance of the variables in a typical Fenton-coagulation/flocculation experiment (experiment FCF-2). One clearly observes a sharp fall in the concentrations of the four variables, which practically attain their final values in the experiment after 5–15 min. Similar levels of treatment were obtained in the other experiments, except for experiment FCF-5, which was performed with 0.06 mol/L of hydrogen peroxide in which the reduction of the variables was very small (COD 22%, TP 4%, and A 2% in 150 min) and only took place gradually over the course of the experiment.

**Removal of COD.** As can be seen in **Table 1**, the reduction in the value of this variable depended to a large degree on the initial reagent concentrations (of hydrogen peroxide and ferrous salt). **Figure 2** shows the COD removal curves in the series of



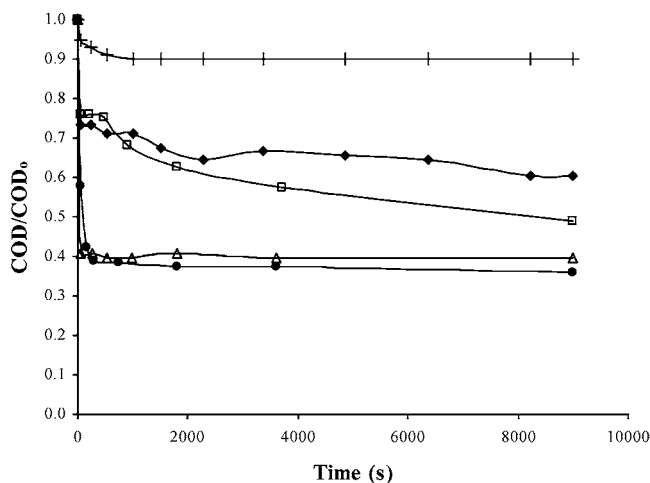
**Figure 1.** Curves of disappearance of the variables in a typical Fenton-coagulation/flocculation (experiment FCF-2): (■) COD (mg/L); (○) total polyphenols  $\times 10$  (mg/L of caffeic acid); ( $\Delta$ ) aromatics  $\times 10^4$  (absorbance at 254 nm of 1/50 diluted samples); ( $\square$ ) remnant H<sub>2</sub>O<sub>2</sub> concentration (mg/L).



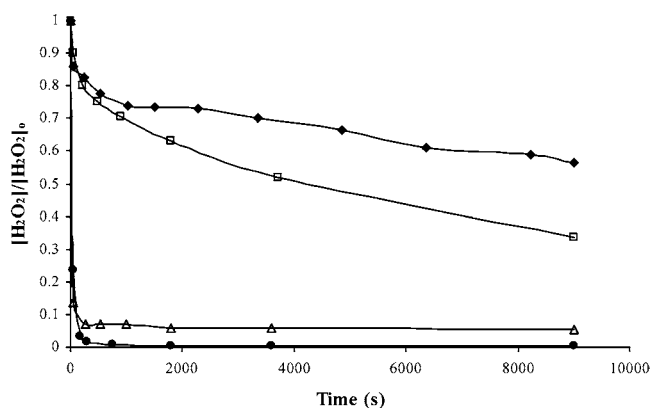
**Figure 2.** COD reduction curves in the series of experiments in which the initial hydrogen peroxide concentration was modified (initial Fe<sup>2+</sup> concentration was in all cases constant, at 0.02 mol/L): ( $\blacklozenge$ ) 0.06 mol/L (FCF-5); ( $\square$ ) 0.2 mol/L (FCF-1); ( $\bullet$ ) 0.6 mol/L (FCF-2); ( $\Delta$ ) 1 mol/L (FCF-6).

experiments in which the initial hydrogen peroxide concentration was modified (experiments FCF-5, FCF-1, FCF-2, and FCF-6). One can see the sharp initial fall in the COD in all the experiments, and the positive influence of the initial hydrogen peroxide concentration. The COD removal ranged from 22% for experiment FCF-5 to 85% for experiment FCF-6. The experiment without hydrogen peroxide (experiment CF-3) reduced COD to 19%. Therefore, the later stage of coagulation-flocculation has only a moderate influence on the global process when the initial concentration of hydrogen peroxide is more than 0.2 mol/L. In the experiment FCF-5, the stage of chemical oxidation has a very scarce influence on the global reduction of COD.

**Figure 3** shows the COD removal curves in the series of experiments in which the initial ferrous salt concentration was modified (experiments H-1, FCF-7, FCF-3, FCF-1, and FCF-4). The effect of hydrogen peroxide (without the addition of iron salts) on the cork wastewater oxidation is very reduced (alone 10%). Also, this slight oxidation can be due to the catalytic effect of the ferric ions present in wastewater. These ions have a catalytic activity to decompose hydrogen peroxide much lower



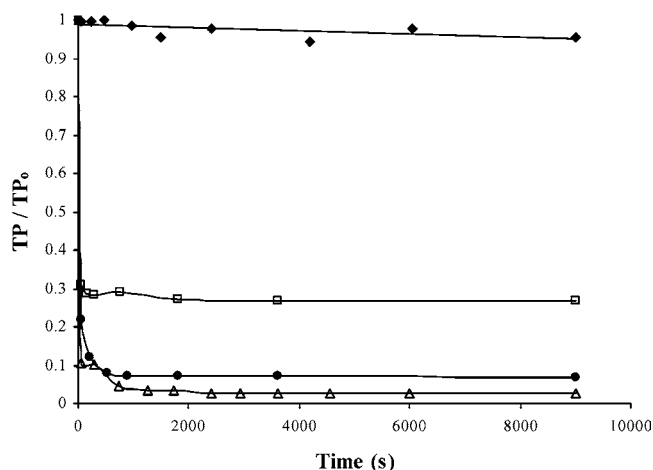
**Figure 3.** COD reduction curves in the series of experiments in which the initial ferrous salt concentration was modified (initial  $\text{H}_2\text{O}_2$  concentration was in all cases constant, at 0.2 mol/L): (+) 0 mol/L (H-1); (◆) 0.001 mol/L (FCF-7); (□) 0.002 mol/L (FCF-3); (●) 0.02 mol/L (FCF-1); (△) 0.2 mol/L (FCF-4).



**Figure 4.** Evolution of the  $\text{H}_2\text{O}_2$  concentration in those experiments in which the initial ferrous salt concentration was modified (initial  $\text{H}_2\text{O}_2$  concentration was in all cases constant, at 0.2 mol/L): (◆) 0.001 mol/L (FCF-7); (□) 0.002 mol/L (FCF-3); (●) 0.02 mol/L (FCF-1); (△) 0.2 mol/L (FCF-4).

that ferrous ions. With an initial  $\text{Fe}^{2+}$  concentration of only 0.001 mol/L, the removal of the organic matter was very strong (COD 40%, TP 90%, and A 62%, in 150 min), 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 ferrous dose of 0.02 mol/L (a ratio of  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 10$  mol/mol). An additional rise in ferrous dose (experiment FCF-4) was not reflected in any further increase of COD removal. The authors have observed this optimal concentration ratio in other studies (6, 7).

**Conversion of Hydrogen Peroxide.** As is shown in **Figure 1**, the evolution of the hydrogen peroxide concentration over the course of the experiment (measured in a second aliquot and before the coagulation/flocculation stage) was similar to the COD case, that is, a sharp initial decline followed by a slight reduction during the rest of the experiment which, however, was greater for the hydrogen peroxide than for the COD. By way of example, **Figure 4** shows the trend of the hydrogen peroxide concentration in those experiments in which the initial ferrous salt concentration was modified. One sees that, in the experiment with a ferrous salt concentration of 0.001 mol/L (experiment FCF-7), the hydrogen peroxide conversion was very



**Figure 5.** Total polyphenol reduction curves in the series of experiments in which the initial hydrogen peroxide concentration was modified (initial  $\text{Fe}^{2+}$  concentration was in all cases constant, at 0.02 mol/L): (◆) 0.06 mol/L (FCF-5); (□) 0.2 mol/L (FCF-1); (●) 0.6 mol/L (FCF-2); (△) 1 mol/L (FCF-6).

**Table 2.** Total Polyphenol and Aromatic Content Removals Obtained in Each Experiment at Two Reaction Times (1 and 150 min)

expt	$[\text{H}_2\text{O}_2]_0$ (mol/L)	$[\text{Fe}^{2+}]_0$ (mol/L)	$X_{\text{TP}}$ (1 min) (%)	$X_{\text{TP}}$ (150 min) (%)	$X_{\text{A}}$ (1 min) (%)	$X_{\text{A}}$ (150 min) (%)
FCF-1	0.2	0.02	69	74	55	81
FCF-2	0.6	0.02	78	93	58	90
FCF-3	0.2	0.002	74	90	41	73
FCF-4	0.2	0.2	77	78	74	77
FCF-5	0.06	0.02	1	4	1	2
FCF-6	1	0.02	90	98	65	97
FCF-7	0.2	0.001	79	90	41	62
FCF-8 <sup>a</sup>	0.2	0.02	23	83	2	83
FCF-9 <sup>b</sup>	0.2	0.02	3	86	1	86
H-1	0.2	0	—	77	—	20

<sup>a</sup> Addition of reagents in two fractions (0 and 60 min). <sup>b</sup> Addition of reagents in three fractions (0, 30, and 60 min).

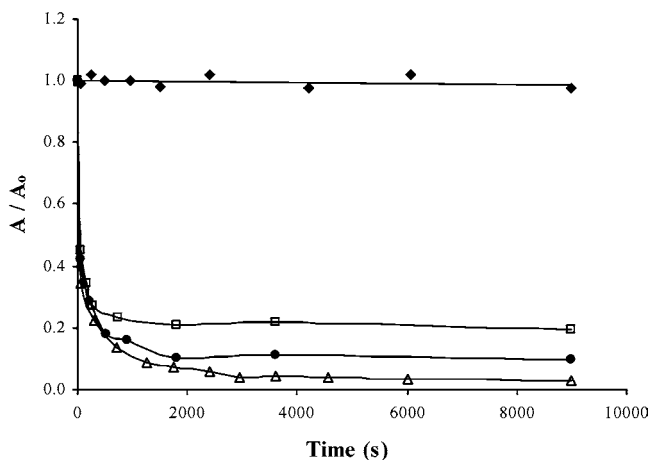
small (14% at 1 min and 43% in 150 min), whereas in the experiment with a catalyst dose of 0.02 mol/L (relationship  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 10$  mol/mol) it reached 77% at 1 min and 99.7% at 150 min. An additional rise in ferrous dose (experiment FCF-4) was not reflected in an increase of the  $\text{H}_2\text{O}_2$  decomposition rate (the decomposition rate actually declined).

The other operating variable modified (initial hydrogen peroxide concentration) had a negative influence on hydrogen peroxide conversion, as was to be expected (for experiments with the same initial ferrous salt concentration). These data are not shown in this paper.

**Removal of Polyphenols.** Due to the inhibitory character to biological processes, the removal of these compounds is an interesting aspect in the present work. Polyphenol removal was strongly positively affected by the initial hydrogen peroxide concentration. **Figure 5** shows the total polyphenol removal curves in the series of experiments in which the initial hydrogen peroxide concentration was modified (experiments FCF-5, FCF-1, FCF-2, and FCF-6). The removal values shown in **Table 2** varied between 4% (for experiment FCF-5) and 98% (for experiment FCF-6). The experiment carried out with hydrogen peroxide (without the addition of iron salts, experiment H-1) reached a high effectiveness in the elimination of polyphenols, 77%.

The effect of initial ferrous salt concentration was studied in the series of experiments FCF-7, FCF-3, FCF-1, and FCF-4.





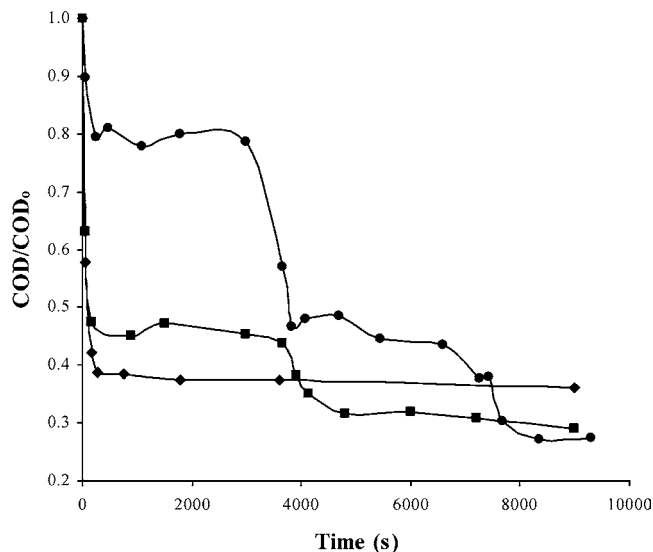
**Figure 6.** Aromatic compound reduction curves in the series of experiments in which the initial hydrogen peroxide concentration was modified (initial  $\text{Fe}^{2+}$  concentration was in all cases constant, at 0.02 mol/L): (◆) 0.06 mol/L (FCF-5); (□) 0.2 mol/L (FCF-1); (●) 0.6 mol/L (FCF-2); (△) 1 mol/L (FCF-6).

As one observes in **Table 2**, this operating variable generally had a mildly negative effect on TP removal. The experiment of the series that gave the smallest value of TP removal was, however, experiment FCF-1 (the experiment with a ratio  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 10$  mol/mol). However, as can be seen in **Figures 3** and **4**, the maximum COD degradation rate and hydrogen peroxide decomposition rate also corresponded to these conditions. Hydrogen peroxide thus seems to be an effective and selective oxidant of these compounds (with respect to the hydroxyl radical).

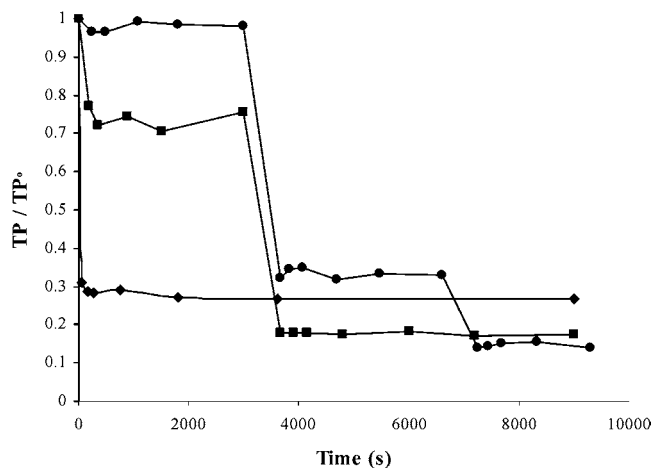
**Removal of Aromatic Substances.** The removal of aromatic compounds was between 2% (experiment FCF-5) and 97% (experiment FCF-6). As can be observed in **Table 2**, the reduction of the level of this contaminant depended to a large degree on the initial reagent (hydrogen peroxide and ferrous salt) concentrations. The experiment without the addition of iron salts (H-1) reduced aromatic substances only by 20%. **Figure 6** shows the aromatic compound removal curves in the series of experiments in which the initial hydrogen peroxide concentration was modified.

As is seen in **Table 2**, the initial ferrous salt concentration had a positive effect on the aromatic removal (experiments H-1, FCF-7, FCF-3, FCF-1, and FCF-4). Again, the experiment that gave the greatest oxidation of this compound type was experiment FCF-1 (with a ratio  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 10$  mol/mol).

**Influence of the Manner of Adding the Reagents.** It is well known that the division of the dose of reagents in several fractions conduct to a higher effectiveness of the process (26–29). We performed trials with the same conditions as experiment FCF-1, but splitting the reagent dose (of hydrogen peroxide and ferrous salt) into two fractions (times: initial and 60 min; experiment FCF-8) and three fractions (times: initial, 30 min, and 60 min; experiment FCF-9). **Figure 7** shows a comparison of the temporal evolution of COD in the FCF-1 experiment and the equivalent experiments with the addition fractioned (experiments FCF-8 and FCF-9). As can be seen, while the initial rate of COD elimination was greater in experiment FCF-1, the final reduction was greater for the fractioned experiments. Similar results were obtained for polyphenols (see **Figure 8**). For aromatic compounds, however, the differences between a single addition and fractioned additions were minimal. These results thus suggest that a greater total amount of organic matter could be removed if the reagent dose were split up into a number of fractions over time.



**Figure 7.** Comparison of the temporal evolution of COD in the FCF-1 experiment and the equivalent experiments with the addition fractioned: (◆) single addition (FCF-1); (■) two fractioned additions, 0 and 30 min (FCF-8); (●) three fractioned additions, 0, 30, and 60 min (FCF-9).



**Figure 8.** Comparison of the temporal evolution of total polyphenols in the FCF-1 experiment and the equivalent experiments with the addition fractioned: (◆) single addition (FCF-1); (■) two fractioned additions, 0 and 30 min (FCF-8); (●) three fractioned additions, 0, 30, and 60 min (FCF-9).

**Table 3.** Chemical Costs of the Integrated Fenton-Coagulation/Flocculation Process (FCF)

$\text{H}_2\text{O}_2/\text{COD}$ ratio (g/g)	$X_{\text{COD}}$ (%)	price per ton of COD removed (euros/ton)	price of treatment (euros/m <sup>3</sup> )
1.8	64	4830	11.5
5.4	75	12071	34.3
0.5	22	4164	3.4
9.7	85	19217	57.2
1.8 <sup>a</sup>	73	4234	11.5

<sup>a</sup> Addition of reagents in three fractions (0, 30, and 60 min).

**Economic Study.** We performed an economic study of the chemical costs of this batch-processing wastewater treatment. Due to the simplicity of the procedure, the chemical costs represent practically the whole of the total cost. The study did not take into account energy costs (which are minimal in this type of treatment) or the initial fixed capital costs. **Table 3** lists the costs in euros/m<sup>3</sup> of wastewater treated and per ton of COD removed. They vary between 3.4 and 57 euros/m<sup>3</sup>, depending

on the percentage of COD elimination ( $X_{\text{COD}}$ ) that is desired. Both of these parameters depend on the initial  $[\text{H}_2\text{O}_2]_0/\text{COD}_0$  ratio. It is noteworthy that the cost of treatment with a  $[\text{H}_2\text{O}_2]_0/\text{COD}_0$  ratio of 1.8 g/g (splitting the reagent dose into three fractions) yielding a COD removal of 73% is 11.5 euros/m<sup>3</sup> of wastewater.

## CONCLUSIONS

An integrated Fenton-coagulation/flocculation process was employed in the present study to treat the wastewater of the cork processing industry. The principal findings include the following:

1. A positive influence of the initial hydrogen peroxide concentration is seen in the range 0.06–1 mol/L. The COD removal ranged from 22% to 85%.

2. A positive influence of the initial ferrous concentration is demonstrated by the degree of COD removal increasing with increasing ferrous dose. The difference was significant until the ratio  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 10$  mol/mol. An additional rise in ferrous dose was not reflected in any concomitant increase of COD removal.

3. The  $\text{H}_2\text{O}_2$  decomposition rate increases with increasing catalyst dose until the ratio  $[\text{H}_2\text{O}_2]_0:[\text{Fe}^{2+}]_0 = 10$  mol/mol. A further rise in the ferrous dose was not reflected in an increase of the  $\text{H}_2\text{O}_2$  decomposition rate.

4. Splitting the addition of the Fenton reagent (hydrogen peroxide and ferrous salt) dose into three fractions (at 0, 30, and 60 min) led to an increased COD removal from 64% to 73%.

5. Taking into account the level of COD removal, the optimal operating conditions of the integrated process were  $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}] = 0.02$  mol/L and  $[\text{H}_2\text{O}_2] = 0.2$  mol/L (splitting the reagent dose into three fractions at 0, 30, and 60 min); 150 min of treatment time; an initial pH of around 3.5; and finally a coagulation/flocculation stage using NaOH as base-precipitant. Under these conditions, the COD removal was 73%, and the chemical costs were estimated at around 11.5 euro/m<sup>3</sup>.

## ABBREVIATIONS USED

COD, chemical oxygen demand; TP, total polyphenols; A, aromatic compounds; BOD, biological oxygen demand; CF, coagulation/flocculation experiment; FCF, Fenton-coagulation/flocculation experiment; H, experiment with hydrogen peroxide alone;  $X_{\text{COD}}$ , removal of chemical oxygen demand;  $X_{\text{TP}}$ , removal of polyphenols;  $X_{\text{A}}$ , removal of aromatic compounds.

## NOTE ADDED AFTER ASAP

Corrections to eqs 3 and 5–7 have been made June 24, 2004, after the original ASAP posting of June 18, 2004.

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