

## Integrated Fenton's reagent—coagulation/flocculation process for the treatment of cork processing wastewaters

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### Abstract

In the present work two methods were tested for the treatment of cork processing wastewaters. In a first phase, a coagulation/flocculation method was applied using  $\text{FeCl}_3$  as flocculating agent and  $\text{Ca}(\text{OH})_2$  as base-precipitant. One cycle of the treatment (1000 ppm of  $\text{FeCl}_3$ ) reduced chemical oxygen demand (COD), total polyphenols and aromatic compounds of the effluent by 45, 71 and 58%, respectively. Two cycles of treatment ( $2 \times 1000$  ppm of  $\text{FeCl}_3$ ) increase these reductions until values of 67, 92 and 85%, respectively.

In a second phase, an integrated Fenton-coagulation/flocculation process was applied (this second method only requires the addition of  $\text{H}_2\text{O}_2$ ). One cycle of the integrated process (1000 ppm of  $\text{FeCl}_3$  and 0.5 mol/l of  $\text{H}_2\text{O}_2$ ) reduced the COD, total polyphenols and aromatic compounds of the effluent by 74, 99 and 98%, respectively, which supposes a considerable improvement compared with the first method.

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**Keywords:** Cork processing wastewater; Depuration; Coagulation; Flocculation; Fenton's reagent

### 1. Introduction

The world production of cork is estimated to surpass 370 000 t per year, with the Mediterranean countries being the main producers (Spain and Portugal produce 270 000 t per year) [1].

The treatment of this cork requires great amounts of water, which in most cases are dumped into the environment untreated. In other cases, the commonest treatment is to retain them in evaporation ponds. This procedure, however, causes bad smells and the possibility of polluting surface and ground waters. The process therefore constitutes a major environmental problem due to the high organic load of this wastewater. Since the setting up of more stringent regulations concerning public waste disposal, there has been a growing interest in the development of new technologies and procedures for the purification of this water.

Amongst these procedures, biological methods, both aerobic [2] and anaerobic [3] degradation, have been recognized as being the most viable for wastewater depuration. Problems have arisen, however, in biological treatments due to

the high toxicity of these effluents, which partially inhibits microorganisms that are particularly sensitive to the presence of some organic compounds [4] especially to phenolic compounds [5].

Therefore other treatments have recently been investigated to deal with these pollutant wastewaters. Minhalma and de Pinho [6,7] studied the membrane technology (ultrafiltration) for the treatment of wastewater from cork processing industries aim at color removal or reduction of chemical oxygen demand as the result of organic matter retention. However, this treatment leads to severe problems of membrane fouling and drastic permeate flux decline. These authors concluded that the ultrafiltration performance of the cork processing wastewater is highly influenced by concentration polarization and adsorption of fouling compounds, for example phenolic/tannic compounds, to the membrane. An advantage of this treatment proposed by these authors is an integrated flocculation/flotation/ultrafiltration process [8].

Otherwise, advanced oxidation technologies (AOTs), which are based on the production of hydroxyl radicals (species with an extremely high oxidation potential,  $\bullet\text{OH}/\text{H}_2\text{O} = +2.73$  V) have been developed and proposed for a number of situations [9]. Some commonly used methods for  $\bullet\text{OH}$  production include Fenton's reagent

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[10], photolysis of  $\text{H}_2\text{O}_2$  [11] and radiolysis [12]. Recently, Guedes et al. [13] have used Fenton's oxidation for treatment of cork processing wastewaters. The process involves homogeneous reaction and is environmentally acceptable, is a mixture of hydrogen peroxide and iron salts ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) which produces hydroxyl radicals according to reaction (1):



The presence of  $\text{Fe}^{3+}$  also produces hydroperoxide radicals:



The chemical reactions of the hydroxyl radical in water are of four types: (a) hydroxyl radical addition to an unsaturated compound, aliphatic or aromatic, to form a free radical product; (b) hydrogen abstraction, where an organic free radical and water are formed; (c) electron transfer, where ions of a higher valence state are formed reducing hydroxyl radicals to hydroxide ions; and finally (d) radical interaction where the hydroxyl radical reacts with another hydroxyl radical to combine or to disproportionate to form a stable product. The global effects produced in the wastewaters are: organic pollutant destruction, toxicity reduction, biodegradability improvement, BOD, COD, odor and color removal.

On the other hand, due to the great amount of total solids present in this wastewater (see Table 1), a coagulation/flocculation treatment by  $\text{FeCl}_3$  and  $\text{Ca}(\text{OH})_2$  (considered the most effective of the bases commonly used) should reduce these solids, so reducing COD, BOD, color and odor. In the alkaline  $\text{Ca}(\text{OH})_2$  solution,  $\text{Fe}^{3+}$  can oxidize sulfides to insoluble products and also forms highly insoluble  $\text{Fe}(\text{OH})_3$  ( $K_{\text{sp}} = 10^{-36}$ ) in equilibrium with  $\text{FeO}(\text{OH})$ , to give a flocculent precipitate which facilitates the separation of suspended materials in effluent [14]. Also, this treatment can reduce the dissolved phenolic compounds by adsorption onto the ferric gel.

Therefore, in a first phase of the present work, a coagulation/flocculation method is applied for the depuration of the effluent. The second phase consists of an integrated Fenton-coagulation/flocculation process. The aim was to provide data on the removal of contaminant organic matter present in these effluents, to establish the influence of operating variables on the process and to compare the two studied methods.

Table 1  
Physico-chemical characteristics of cork processing wastewater

Parameter	Value
pH	5.02
BOD <sub>5</sub> (mg/l)	802
COD (mg/l)	4250
Biodegradability (BOD <sub>5</sub> /COD)	0.188
Total phenolic content (expressed as mg/l of caffeic acid)	994
Total solids (mg/l)	1720
Aromaticity (un.abs. at 254 nm in 1/25 diluted samples)	2.16

## 2. Experimental

The cork processing wastewater was obtained from the industrial plant "Corchos Mérida S.A." (San Vicente de Alcántara, Extremadura Community, Spain). Table 1 shows the main physicochemical characteristics.

In all cases, experiments were performed in a 250 ml stirred glass reactor with inlets for sampling and temperature measuring. The temperature was maintained constant to 35 °C in all cases. Effluent samples of 150 ml were treated as follows:

- a dose of  $\text{FeCl}_3$  was added at a concentration of 50–2000 ppm;
- pH was adjusted to 8.5 by addition of  $\text{Ca}(\text{OH})_2$ ;
- the sample was stirred for 10 min at 100 rpm;
- the supernatant was decanted over 1 day, a subsample was taken and its COD, total polyphenol and aromatic content was measured;
- in the case of subsequent treatment of the clarified effluent (two coagulation/flocculation steps) the remaining liquor was treated again by steps (a)–(d);
- in integrated Fenton-coagulation/flocculation experiments, a dose of  $\text{H}_2\text{O}_2$  (from 0.1 to 0.9 mol/l) was added between the steps (a) and (b). The Fenton's reaction time was 5 h in all cases. The remaining liquor was treated again by steps (b)–(d).

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. The result is a blue polymer in a basic medium [15]. The polyphenol content is expressed as mg/l of caffeic acid.

The aromatic content was determined by measuring the absorbance at 254 nm, 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 pathlength quartz cuvette.

## 3. Results and discussion

### 3.1. Coagulation/flocculation process

We performed coagulation/flocculation experiments using  $\text{FeCl}_3$  and adjusted the pH to 8.5 by adding  $\text{Ca}(\text{OH})_2$ . The study variables were: the dose of  $\text{FeCl}_3$  (from 50 to 2000 ppm), and the manner of adding the coagulant (in a single treatment or in two treatment cycles).

Let  $X_i$  be defined as the removal of a given indicator of water contamination (COD, total polyphenols, or aromatic compound content) that is achieved by a treatment:

$$X_i = \frac{C_0 - C_F}{C_0} \times 100 \quad (3)$$

Table 2  
Coagulation conditions and COD, total phenolic and aromatic removals obtained in each experiment

Experiment	FeCl <sub>3</sub> dose (mg/l)	COD <sub>F</sub> (mg/l)	X <sub>COD</sub> (%)	TP <sub>F</sub> <sup>a</sup> (mg/l)	X <sub>TP</sub> (%)	A <sub>F</sub> <sup>b</sup> (u.a.)	X <sub>A</sub> (%)	[Fe <sup>2+</sup> + Fe <sup>3+</sup> ] in the supernatant <sup>c</sup> (mg/l)
C-1	50	4140	2.6	890	10	2.25	-4.1	-
C-2	100	4115	3.2	890	10	2.23	-3.2	-
C-3	250	4050	4.7	863	11	2.27	-5.0	-
C-4	500	3030	29	495	50	1.41	35	-
C-5	1000	2345	45	284	71	0.90	58	-
C-6	1500	1707	60	135	86	0.46	79	-
C-7	2000	1635	62	106	89	0.36	83	123
C-8	250 (2×)	3423	19	747	25	2.27	-5.0	132
C-9	500 (2×)	2139	50	237	76	0.91	58	99
C-10	1000 (2×)	1407	67	82	92	0.33	85	15

<sup>a</sup> Total phenolic content expressed as mg/l of caffeic acid.

<sup>b</sup> Absorbance of the 1/25 diluted samples at 254 nm.

<sup>c</sup> Residual iron concentration expressed as mg/l of Fe.

where  $C_0$  and  $C_F$  are the initial and final concentrations, respectively, of parameter  $i$ .

In the present work we evaluated the removal of COD ( $X_{COD}$ ), total polyphenols ( $X_{TP}$ ), and aromatic compounds ( $X_A$ ). Table 2 gives the dose of coagulant used in each experiment, the final values of the three parameters ( $COD_F$ ,  $TP_F$  and  $A_F$ ) after the treatment, and the levels of removal attained ( $X_{COD}$ ,  $X_{TP}$  and  $X_A$ ). For some experiments, the table also gives the final concentrations of iron ( $Fe^{2+} + Fe^{3+}$ ) left in the supernatant after the treatment.

As can be seen in Fig. 1, with FeCl<sub>3</sub> doses in the range 0–250 ppm, the removals of these three indicators were practically nil. Further increasing the dose increased the elimination of COD, TP, and A, until for doses between 1500 and 2000 ppm there were no longer any substantial improvements. At the 1500 ppm dose, the removals,  $X_{COD}$ ,  $X_{TP}$  and  $X_A$  were 60, 86 and 79%, respectively.

The next variable studied was the manner of adding the coagulant, in particular, whether the coagulation/flocculation process was in one or two stages. Table 2 shows the comparison of the values of  $X_{COD}$ ,  $X_{TP}$  and  $X_A$ . One sees that, except for the lowest dose (500 versus 2× 250 ppm), the two-stage

coagulant addition improved the results of the single-stage procedure.

Lastly, we also analyzed the concentration of residual iron in the supernatant (in the form of  $Fe^{2+} + Fe^{3+}$ ). Table 2 shows the results for four procedures. One can draw two immediate conclusions: first, in the two-stage process, as the dose of FeCl<sub>3</sub> was increased the final concentration of residual Fe in the supernatant decreased, and second, adding the coagulant in two steps (2× 1000 ppm FeCl<sub>3</sub>) left a far lower concentration of iron in the supernatant than if it was added in a single step (2000 ppm FeCl<sub>3</sub>).

### 3.2. Integrated Fenton's reagent—coagulation/flocculation process

Operatively, the integrated Fenton's reagent—coagulation/flocculation process requires no more than a minimal extra effort with respect to the simple coagulation/flocculation process. The only difference is the addition of a certain amount of hydrogen peroxide after dissolving the FeCl<sub>3</sub>. After a wait of 5 h, and finally (as also in the simple coagulation/flocculation process) adjusts the pH to 8.5 by adding Ca(OH)<sub>2</sub>.

Table 3 lists the conditions under which the different experiments were carried out, and the values of COD, TP, and A, after the first Fenton's reaction stage (F), and finally after the second coagulation/flocculation stage (F + CF).

#### 3.2.1. Effect of the hydrogen peroxide concentration on the efficacy of the integrated process

Figs. 2–4 show the removals  $X_{COD}$ ,  $X_{TP}$  and  $X_A$ , respectively, for the experiments in which the initial hydrogen peroxide concentration was varied (0, 0.1, 0.5, and 0.9 mol/l), comparing the removals for each parameter in the first stage (Fenton's reaction, F) with those after the integrated treatment (Fenton's reagent treatment—coagulation/flocculation, F + CF). The dose of FeCl<sub>3</sub> in all the experiments was 500 ppm. The experiment with a hydrogen peroxide concentration of 0 mol/l corresponded to the simple

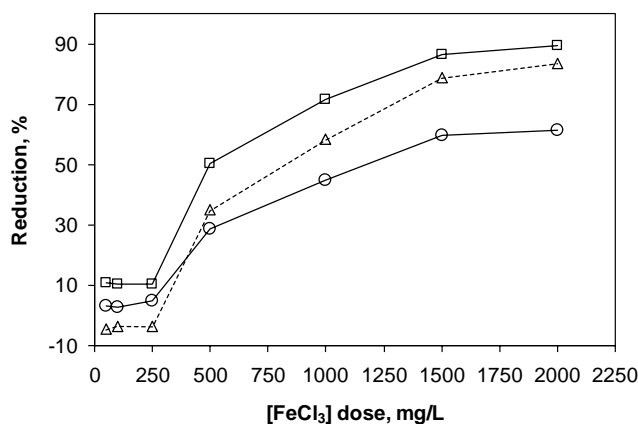


Fig. 1. Influence of the coagulant dose on the removal of organic matter: (□) phenolic compounds, (△) aromatic compounds, and (○) COD.

Table 3  
Results obtained in Fenton + coagulation integrated experiments

Experiment	FeCl <sub>3</sub> dose (mg/l)	H <sub>2</sub> O <sub>2</sub> dose (mol/l)	COD <sub>F</sub> (F) <sup>a</sup> (mg/l)	COD <sub>F</sub> (F + CF) <sup>b</sup> (mg/l)	TP <sub>F</sub> <sup>c</sup> (F) (mg/l)	TP <sub>F</sub> (F + CF) (mg/l)	A <sub>F</sub> <sup>d</sup> (F) (u.a.)	A <sub>F</sub> (F + CF) (u.a.)	[Fe <sup>2+</sup> + Fe <sup>3+</sup> ] final in the supernatant <sup>e</sup> (mg/l)	BOD <sub>5</sub> (F + CF) (mg/l)	Biodegradability, BOD <sub>5</sub> /COD (F + CF)
F + CF-1	500	0.1	2777	1253	629	58	1.88	0.27	17	568	0.45
F + CF-2	500	0.5	2124	1496	27	11	0.46	0.08	3	681	0.46
F + CF-3	500	0.9	1645	1640	30	11	0.45	0.08	3	833	0.50
F + CF-4	250	0.5	2094	1791	43	17	0.43	0.11	6	795	0.44
F + CF-5	1000	0.5	2466	1107	201	7	0.05	0.04	2	492	0.44

<sup>a</sup> Application of Fenton process.

<sup>b</sup> Application of the integrated process, Fenton + coagulation/flocculation.

<sup>c</sup> Total phenolic content expressed as mg/l of caffeic acid.

<sup>d</sup> Absorbance of the 1/25 diluted samples at 254 nm.

<sup>e</sup> Residual iron concentration expressed as mg/l of Fe.

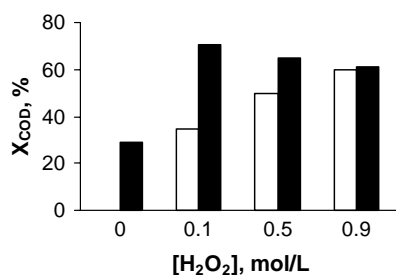


Fig. 2. Influence of the hydrogen peroxide dose on the removal of COD ( $\text{FeCl}_3 = 500$  ppm): (□) Fenton, (■) Fenton + coagulation/flocculation.

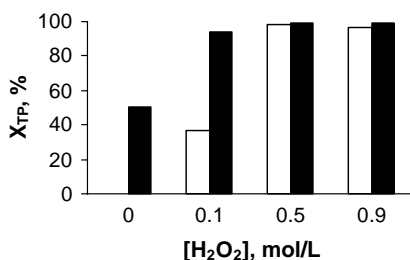


Fig. 3. Influence of the hydrogen peroxide dose on the removal of phenolic compounds ( $\text{FeCl}_3 = 500$  ppm): (□) Fenton, (■) Fenton + coagulation/flocculation.

coagulation/flocculation process (CF). One sees from the three figures that any of the additions of hydrogen peroxide led to a substantial improvement with respect to the simple coagulation/flocculation process.

It is worthy of note in Fig. 2 that, as was to be expected, greater doses of hydrogen peroxide led to greater removals of COD in the first Fenton's reaction stage ( $X_{\text{COD}(F)}$ ). The final COD removals of the integrated process ( $X_{\text{COD}(F+CF)}$ ), however, were smaller, so that the conclusion is that the best final results are obtained using a dose of 0.1 mol/l of hydrogen peroxide. The explanation seems to be that a greater intensity of the Fenton's oxidation leads to the large organic molecules (those which are easiest to coagulate/flocculate) fragmenting into smaller soluble molecules (more difficult to precipitate in the coagulation/flocculation process). This explanation is coherent with the results of other work with Fenton's reagent [16], in which increasing doses of hydrogen peroxide were observed to produce a greater decline in

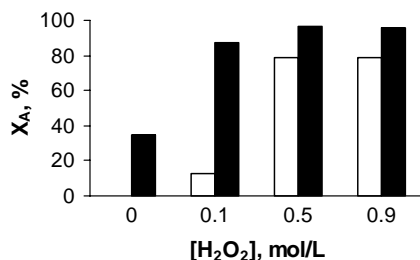


Fig. 4. Influence of the hydrogen peroxide dose on the removal of aromatic compounds ( $\text{FeCl}_3 = 500$  ppm): (□) Fenton, (■) Fenton + coagulation/flocculation.

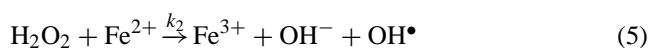
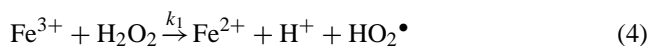
pH of the wastewater together with a greater increase in the volatile acidity of the water (a measure of the volatile organic acid content  $C_1$ – $C_4$ ).

Two observations need to be made concerning the removal of the phenolic compound content of the wastewater (Fig. 3): first, the substantial improvement provided by the integrated system (F + CF) with respect to the simple coagulation/flocculation ( $[\text{H}_2\text{O}_2]$  of 0 mol/l), and second, from  $[\text{H}_2\text{O}_2] > 0.5$  mol/l onwards most of these compounds have already been oxidized in the first Fenton's reaction stage. The final results of the integrated process (F + CF) using a hydrogen peroxide concentration of 0.1 mol/l are already very satisfactory, with removals greater than 94%.

Fig. 4 shows the removals of the aromatic compound content. As in the previous case, one observes that, on the one hand, the integrated system (F + CF) was a substantial improvement over the simple coagulation/flocculation and, on the other, that, although the removals observed in the first Fenton stage (F) depended on the initial added hydrogen peroxide dose, the end removals attained with the integrated system (F + CF) were very similar in the three cases (0.1, 0.5, and 0.9 mol/l), above 85%.

On the other hand, the values of biodegradability after a F + CF treatment were notably increased (from 0.19 to 0.50). This fact suggests that the final wastewater can be effectively treated by aerobic biological methods. As can be seen in Table 3, greater doses of hydrogen peroxide led to greater values of biodegradability.

Table 3 also shows the concentrations of residual iron ( $\text{Fe}^{2+} + \text{Fe}^{3+}$ ) left in the supernatant after the integrated treatment. One observes that the more intense was the Fenton's reagent treatment (greater hydrogen peroxide dose), the lower was the final iron concentration in the supernatant. This can be understood on the basis of the cycle of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  catalysis that occurs in Fenton's reaction. The following are the chemical equations involved in Fenton's reaction:



Although the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  catalytic cycle is a cycle with feedback, and without taking into account the possible oxidizing or reducing agents present in the wastewater, it seems to be observed that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio present in solution after the Fenton's reaction stage increases with increasing doses of added hydrogen peroxide. This would explain the fact that the coagulation/flocculation process (in which mainly  $\text{Fe}(\text{OH})_3$  is formed) leaves a lower concentration of iron in the supernatant in the experiments that used a greater dose of hydrogen peroxide.



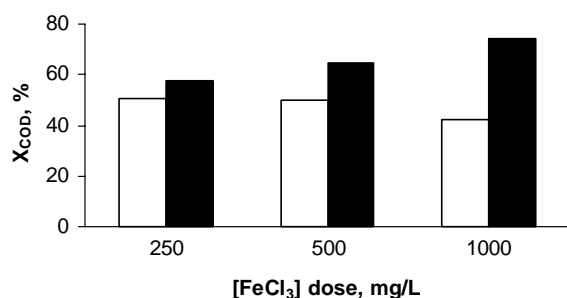


Fig. 5. Influence of the FeCl<sub>3</sub> dose on the removal of COD (H<sub>2</sub>O<sub>2</sub> = 0.5 mol/l): (□) Fenton, (■) Fenton + coagulation/flocculation.

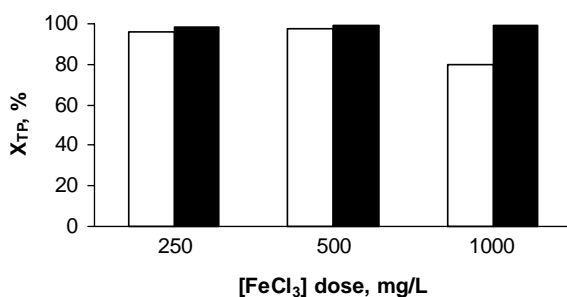


Fig. 6. Influence of the FeCl<sub>3</sub> dose on the removal of phenolic compounds (H<sub>2</sub>O<sub>2</sub> = 0.5 mol/l): (□) Fenton, (■) Fenton + coagulation/flocculation.

### 3.2.2. Effect of the FeCl<sub>3</sub> concentration on the integrated process

In the following block of experiments we studied the effect of the dose of FeCl<sub>3</sub> while maintaining the dose of hydrogen peroxide fixed at 0.5 mol/l. Figs. 5–7 show the removals obtained for the three parameters  $X_{\text{COD}}$ ,  $X_{\text{TP}}$  and  $X_{\text{A}}$ , respectively.

Two conclusions can be drawn from Fig. 5: first, there is a decline in the efficacy of the first phase of oxidation with Fenton's reagent as the dose of FeCl<sub>3</sub> is increased, and second, the following coagulation/flocculation phase is more efficient for the system with the greatest dose of FeCl<sub>3</sub> (1000 ppm). The reason for these findings could be that a greater added dose of FeCl<sub>3</sub> (for a given hydrogen peroxide concentration) accelerates the rate of decomposition of the hydrogen peroxide by reaction (4), generating hydroperox-

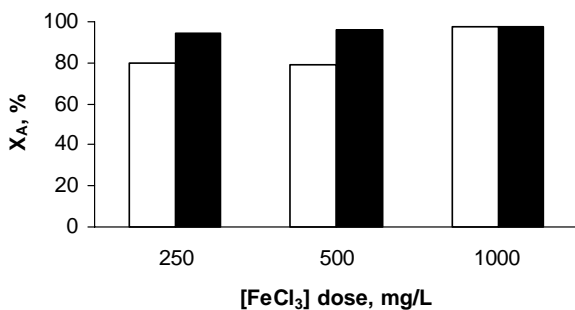


Fig. 7. Influence of the FeCl<sub>3</sub> dose on the removal of aromatic compounds (H<sub>2</sub>O<sub>2</sub> = 0.5 mol/l): (□) Fenton, (■) Fenton + coagulation/flocculation.

ide radicals. Lower doses of FeCl<sub>3</sub> favor the reaction of the ferrous ion formed in reaction (4) with the hydrogen peroxide according to reaction (1), generating  $\cdot\text{OH}$  radicals that are more reactive than the  $\text{HO}_2\cdot$  radicals. There have been studies [17] of optimal H<sub>2</sub>O<sub>2</sub>/Fe ratios to achieve the greatest efficacy of the Fenton's reagent system, although it seems that this ratio varies according to the chelating capacity of the wastewater.

A greater dose of FeCl<sub>3</sub> led to an increase in the efficacy of the second coagulation/flocculation stage. The best end results for the integrated process were obtained with the greatest coagulant dose (1000 ppm of FeCl<sub>3</sub>,  $X_{\text{COD}} = 74\%$ ).

With respect to the elimination of phenolic compounds (Fig. 6), the differences observed for the various coagulant doses used were minimal. The smallest FeCl<sub>3</sub> dose (250 ppm) already yielded final removals of these compounds that were greater than 98%. Increasing the dose to 1000 ppm increased the efficacy of the integrated process (F + CF) to values close to 100%. The phenolic content of the wastewater was reduced from 994 to 7 ppm (values expressed as ppm of caffeic acid).

Fig. 7 shows the removal of the parameter A (the measure of the concentration of aromatic compounds in solution). One sees that, whereas the first Fenton's reaction phase gives the best results for the greatest FeCl<sub>3</sub> dose (1000 ppm), the second coagulation/flocculation phase equalizes the end results for the different doses of coagulant used. In all the cases, the end removals for the integrated process were greater than 94%.

The residual concentrations of iron ( $\text{Fe}^{2+} + \text{Fe}^{3+}$ ) in the clear supernatant after the integrated treatment (F + CF) are shown in Table 3. One observes that the greater the FeCl<sub>3</sub> dose, the lower the residual iron concentration in the supernatant. This behavior seems to be inherent to the coagulation/flocculation process itself. The instantaneous formation of a greater quantity of Fe(OH)<sub>3</sub> nuclei removes the iron in solution more effectively by its being adsorbed and/or retained by the precipitate that is forming. A greater density of Fe(OH)<sub>3</sub> nuclei favors their union and hence more effective coagulation/flocculation.

## 4. Conclusions

One cycle of the simple coagulation/flocculation system, using 1000 ppm of FeCl<sub>3</sub>, efficiently removes suspended solids from cork processing wastewaters, reducing COD, total polyphenols and aromatic compounds by more than 45, 70 and 55%, respectively. Two cycles of the mentioned treatment ( $2 \times 1000$  ppm of FeCl<sub>3</sub>) increase these reductions until values of 67, 92 and 85%, respectively.

Experimental results indicated that the addition of hydrogen peroxide to the simple coagulation/flocculation system (resulting a Fenton-coagulation/flocculation integrated process) enhances the depuration process, reducing COD, total polyphenols and aromatic compounds by 74, 99 and 98%,

respectively. On the other hand, the values of biodegradability after a F + CF treatment were notably increased (from 0.19 to 0.50). This fact suggests that the final wastewater can be effectively treated by aerobic biological methods.

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