

# Application of Fenton oxidation to cosmetic wastewaters treatment

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## Abstract

The removal of organic matter (TOC and COD) from a cosmetic wastewater by Fenton oxidation treatment has been evaluated. The operating conditions (temperature as well as ferrous ion and hydrogen peroxide dosage) have been optimized. Working at an initial pH equal to 3.0, a  $\text{Fe}^{2+}$  concentration of 200 mg/L and a  $\text{H}_2\text{O}_2$  concentration to COD initial weight ratio corresponding to the theoretical stoichiometric value (2.12), a TOC conversion higher than 45% at 25 °C and 60% at 50 °C was achieved. Application of the Fenton oxidation process allows to reach the COD regional limit for industrial wastewaters discharges to the municipal sewer system. A simple kinetic analysis based on TOC was carried out. A second-order equation describes well the overall kinetics of the process within a wide TOC conversion range covering up to the 80–90% of the maximum achievable conversion.

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**Keywords:** Fenton's reagent; Oxidation; Cosmetic wastewater; Kinetics

## 1. Introduction

The cosmetic industry generates wastewaters characterized by high levels of COD, suspended solids, fats and oils, and detergents [1,2]. The reduction of the organic load of these effluents by conventional biological processes is not likely due to its low  $\text{BOD}_5/\text{COD}$  ratio and thus they are frequently treated by means of coagulation/flocculation with pressure-flotation to separate the resulting sludge [3,4]. This leads to an important reduction of COD. Nevertheless, the introduction of more stringent regulations concerning public waste disposal, makes necessary to develop new techniques for a more efficient cleaning of this type of wastewaters. A possible strategy can be the use of chemical oxidation as a previous treatment in order to reduce the toxicity and improve the biodegradability of the organic matter in these wastewaters [5].

In the last decades, advanced oxidation processes (AOPs) have been developed and proposed for a number of cases [6], particularly oxidation by Fenton's reagent [7], which has been efficiently used as a chemical oxidation process for wastewater treatment and pre-treatment. This oxidation method is based on

the use of a mixture of hydrogen peroxide and iron salts ( $\text{Fe}^{2+}$ ) which produces hydroxyl radicals ( $\text{OH}^\bullet$ ) at acidic pH in ambient conditions. The generally accepted mechanism of the Fenton process proposes that hydroxyl radicals are produced by reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  which is regenerated from the reaction of  $\text{Fe}^{3+}$  with  $\text{H}_2\text{O}_2$  or intermediate organic radicals [8,9].

One of the advantages of the Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide [10]. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. Furthermore, it commonly requires a relatively short reaction time compared with other AOPs [11]. Thus, Fenton's reagent is frequently used when a high reduction of COD is required [12].

The Fenton oxidation process has been employed successfully to treat different industrial wastewaters, including textile [13–16], paper pulp [17,18], pharmaceutical [12,19], dyes [20,21], cork processing [22–24], olive oil [25,26] and petroleum industry [27] wastewaters.

In this work, the Fenton process has been tested to remove the organic load (COD and TOC) of wastewaters from cosmetic manufacture characterized by a low biodegradability index ( $\text{BOD}_5/\text{COD}$ ). The wastewaters used in this work came from a Spanish cosmetic factory whose effluents were previously treated by means of coagulation–flocculation process in the own

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Table 1

Parameter values (average) from analyzes of a pre-treated cosmetic industry wastewater by coagulation/flocculation process and emission limit values

Analyzer parameter	Average value <sup>a</sup>	Limit value <sup>b</sup>
Oils and fats (mg/L)	25 ± 18	100
Conductivity (μS/cm)	1495 ± 580	5000
BOD <sub>5</sub> (mg/L)	1065 ± 660	1000
COD (mg/L)	2720 ± 870	1750
Biodegradability (BOD <sub>5</sub> /COD)	0.392	–
pH	7.0 ± 0.6	6.0–9.0
TSS (mg/L)	38 ± 54	1000

<sup>a</sup> Number of samples analyzed = 15.

<sup>b</sup> Emission limit value for industrial wastewater discharges into the municipal sewer system according to the 10/1993 Act passed by the Community of Madrid [28].

industrial plant. The treatment includes homogenization, filtration, coagulation, neutralization, flocculation and air-pressure flotation. A representative analysis of the wastewater as received in the lab is given in Table 1, together with the regionally allowable limits for industrial wastewaters discharges to the municipal sewer system [28]. As can be seen, the main problem of these wastewaters is that the COD is fairly higher than the limit, the difference corresponding essentially to non-biodegradable organic matter. Thus, an additional treatment is required capable to reduce the organic load up to the allowed limit for COD. Our objective was to analyze the influence of the operating variables (pH, temperature, iron and hydrogen peroxide doses) in order to establish the optimal working conditions for a potential application of the Fenton process to this type of wastewaters. Also, it has been studied the kinetic of the process from an overall approach based on the TOC reduction.

## 2. Materials and methods

Two samples of wastewater with significantly different values of COD (4730 and 2660 mg/L) were used in our experiments. The corresponding TOC values were 1215 and 785 mg/L, respectively. The BOD<sub>5</sub>/COD ratio was 0.133 and 0.169, respectively, indicative in both cases of a low biodegradability. The samples were stored at low temperature (4 °C) and in dark immediately after reception from the cosmetic factory.

The oxidation experiments were carried out in batch in 100 mL stoppered glass bottles placed in a thermostatised bath where they were shaken at an equivalent stirring velocity of 200 rpm. Each bottle was filled with 45 mL of wastewater. The doses of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> were adjusted by adding 2.5 mL of FeSO<sub>4</sub>·7H<sub>2</sub>O and 2.5 mL of H<sub>2</sub>O<sub>2</sub> aqueous solutions of the corresponding concentrations. Each bottle was left to react for a given time and then its content was immediately filtered using glass microfibre filters (Albet FV-C). The filtrate was analyzed for TOC, COD, and residual H<sub>2</sub>O<sub>2</sub> and Fe concentrations.

Total organic carbon (TOC) was determined using an OI Analytic Model 1010 TOC apparatus. Chemical oxygen demand (COD) was analyzed following the APHA standard method with potassium dichromate [29]. Previous to the COD determination it was necessary to remove the residual H<sub>2</sub>O<sub>2</sub> from the

sample by adding FeSO<sub>4</sub>·7H<sub>2</sub>O solution up to a final Fe<sup>2+</sup> concentration of 2000 mg/L and 6 N NaOH to freeze the reaction. Hydrogen peroxide concentration was measured spectrophotometrically (Shimadzu UV/vis, model UV-1603) at 410 nm as a Ti<sup>4+</sup> complex [30]. Dissolved iron concentration was determined colorimetrically at 478 nm as a complex with NH<sub>4</sub>SCN in acidic solution, using a Shimadzu UV/vis spectrophotometer, model UV-1603.

## 3. Results and discussion

The experimental study to analyze the influence of the operating variables has been accomplished, in principle, using the TOC as the representative parameter to follow the response of the system. This has the advantage of informing more directly on the degree of mineralization, namely, complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O, which undergoes the organic matter present in the wastewater. Nevertheless, as the local limits are fixed in terms of COD, we have also analyzed the relationship between the two parameters in a wide range of TOC conversion.

### 3.1. Influence of pH

Fig. 1 shows the conversion values referred to TOC as obtained at different pH values after 4 h of reaction at 25 °C. The dose of H<sub>2</sub>O<sub>2</sub> in these experiments was 9040 mg/L, which corresponds to the theoretical stoichiometric amount referred to initial COD (2.12 g H<sub>2</sub>O<sub>2</sub>/g COD) and the Fe<sup>2+</sup> initial concentration was 200 mg/L, which means a Fe<sup>2+</sup> to H<sub>2</sub>O<sub>2</sub> weight ratio of 2.2%. As can be seen, the highest TOC removal was obtained at a pH of 2.5–3. At lower and higher pH values a significant decrease in the efficiency of the process was observed. Kwon et al. [31] did not observe appreciable differences among the results obtained at pH values between 2.0 and 4.0 in *p*-chlorophenol oxidation by Fenton's reagent. San Sebastián et al. [12] and Beltrán de Heredia et al. [32] worked at an initial pH of 4.0 in the treatment of pharmaceutical and black-olive wastewaters by Fenton oxidation, while Rivas et al. [25] fixed the optimum range between

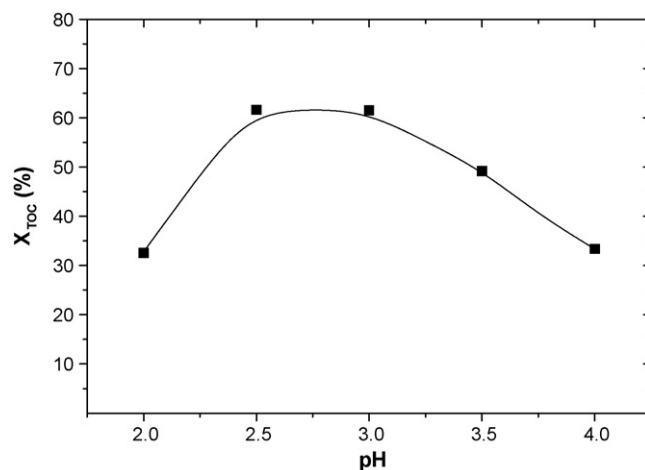


Fig. 1. Effect of initial pH value on the TOC removal (COD<sub>0</sub> = 4255 mg/L; TOC<sub>0</sub> = 1090 mg/L; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 9040 mg/L; [Fe<sup>2+</sup>]<sub>0</sub> = 200 mg/L; T = 25 °C).

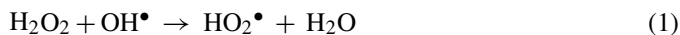
2.5 and 3.0 in the treatment of olive oil mill wastewaters by this process.

At low pH,  $\text{H}_2\text{O}_2$  is stabilized as  $\text{H}_3\text{O}_2^+$  [31] and moreover, the reaction between  $\text{OH}^\bullet$  and  $\text{H}^+$  becomes important [33] and the regeneration of  $\text{Fe}^{2+}$  by reaction of  $\text{Fe}^{3+}$  with  $\text{H}_2\text{O}_2$  is inhibited [9]. On the other hand, the decrease on the oxidation yield of the process at higher pH values is due to the precipitation of  $\text{Fe}^{3+}$  as  $\text{Fe}(\text{OH})_3$ , hindering the reaction between  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ , and therefore the regeneration of  $\text{Fe}^{2+}$ . Besides,  $\text{Fe}(\text{OH})_3$  catalyzes the decomposition of  $\text{H}_2\text{O}_2$  to  $\text{O}_2$  and  $\text{H}_2\text{O}$ , thus decreasing the production of  $\text{OH}^\bullet$  [19]. Moreover, at high pH values it is possible the formation of highly stable  $\text{Fe}(\text{II})$  complexes [34].

In the following, all the experiments are performed at an initial pH value of 3. The pH of the wastewater as received is about neutral and no buffering effects were observed so that it takes a very small acid consumption to bring the pH to 3.

### 3.2. $\text{H}_2\text{O}_2$ dose

Fig. 2 shows the evolution of TOC conversion versus reaction time at 25 °C with different  $\text{H}_2\text{O}_2$  to COD initial weight ratios, corresponding to 0.5, 1 and 2.5 times the theoretical stoichiometric value. The  $\text{Fe}^{2+}$  dose was 100 mg/L in all cases. A higher dose of  $\text{H}_2\text{O}_2$  means a higher production of hydroxyl radicals and this enhances the rate of mineralization (i.e., TOC conversion). Nevertheless, this effect is less significant as the  $\text{H}_2\text{O}_2$  dose increases because the higher the  $\text{H}_2\text{O}_2$  concentration the more favoured the occurrence of auto-scavenging reactions like:



According to the results of Fig. 2, using an amount of  $\text{H}_2\text{O}_2$  higher than the corresponding to the theoretical stoichiometric  $\text{H}_2\text{O}_2$  to COD ratio does not lead to any further improvement on the rate neither on the final efficiency of the process, in terms of TOC removal.

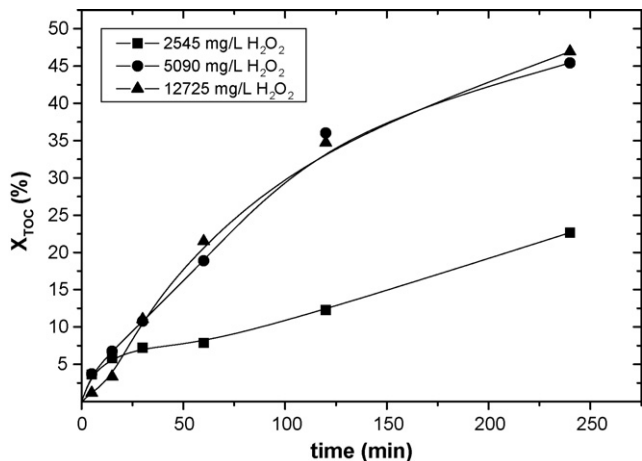


Fig. 2. Evolution of TOC conversion using different  $\text{H}_2\text{O}_2$  doses ( $\text{COD}_0 = 2395$  mg/L;  $\text{TOC}_0 = 705$  mg/L;  $[\text{Fe}^{2+}]_0 = 200$  mg/L;  $T = 25$  °C).

A main component of the cost in the Fenton process corresponds to the  $\text{H}_2\text{O}_2$  consumption and thus it is important to adjust it conveniently. On the other hand, the excess of  $\text{H}_2\text{O}_2$  remaining in solution after the treatment entails a toxicity which may be above the corresponding limit. In that respect, we have determined an  $\text{EC}_{50}$  value of 12 mg/L for  $\text{H}_2\text{O}_2$  using the Microtox Acute Toxicity Test with a preparation of the marine bacterium *Vibrio fischeri* following the ISO-11348-3. As the locally allowable limit of toxicity for industrial wastewaters discharges to the municipal sewer system is in our case 25 T.U., the  $\text{H}_2\text{O}_2$  residual concentration must not exceed from 300 mg/L and this without considering other contributions to the toxicity derived from the pollutant species remaining in the treated wastewaters. It is also true that  $\text{H}_2\text{O}_2$  undergoes further decomposition, in fact catalyzed by  $\text{Fe}^{3+}$  and the  $\text{Fe}(\text{OH})_3$  which precipitates upon neutralization, but a high excess of  $\text{H}_2\text{O}_2$  would require the necessary time for a sufficient removal previous to final disposal.

The discharge limits relative to the organic load of wastewaters are more commonly established in terms of COD rather than as TOC. Thus, at this point it is necessary to learn also on the evolution of COD. Fig. 3 shows the results obtained at 25 °C with an initial  $\text{H}_2\text{O}_2$  to COD ratio equal to the stoichiometric and a  $\text{Fe}^{2+}$  dose of 500 mg/L. The graph includes also the results for TOC thus providing a direct experimental relationship between the two parameters for these wastewaters within the whole range of TOC conversion values. The COD/TOC ratio has initially a value of 3.4 and decreases to reach a value of 2.4 after 1 h of reaction and 2.2 at the end of the experiment (4 h). This is consistent with the expected evolution of the organic matter remaining in the wastewater towards increasingly oxidised species. The frankly low value reached by the COD/TOC ratio suggests an important relative presence of low chain organic acids, including dicarboxylic acids. Due to the complex composition of these wastewaters a detailed screening of the chemical species and their evolution upon Fenton oxidation is not worthwhile but further work, now in course, is needed to learn more in this respect.

Except for the early stages of the process, the reduction of COD is comparable to that of TOC. In our case, the locally allowable limit for COD is 1750 mg/L which, according to the

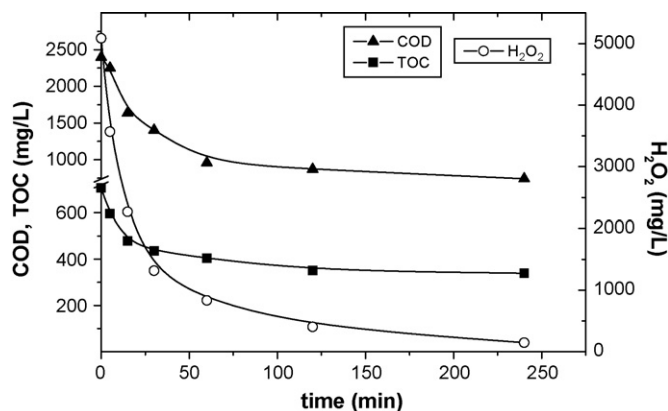


Fig. 3. Evolution of COD, TOC and  $\text{H}_2\text{O}_2$  concentration ( $\text{COD}_0 = 2395$  mg/L;  $\text{TOC}_0 = 705$  mg/L;  $[\text{H}_2\text{O}_2]_0 = 5090$  mg/L;  $[\text{Fe}^{2+}]_0 = 500$  mg/L;  $T = 25$  °C).

results of Fig. 3 would be confidently achievable in a relatively short reaction time of about 30 min using a  $\text{H}_2\text{O}_2$  dose equivalent to the stoichiometric  $\text{H}_2\text{O}_2$  to COD weight ratio and significant further removal of the organic load can be reached, if necessary or convenient, at higher reaction times.

Fig. 3 includes the evolution of the  $\text{H}_2\text{O}_2$  concentration which allows to calculate the consumption of reagent per unit COD removed. This consumption varies along the time of reaction and reaches a final value, at the end of the 4 h experiment, of 3.5 g  $\text{H}_2\text{O}_2$ /g COD removed, about 1.7 times the theoretical stoichiometric ratio. This value corresponds to a  $\text{H}_2\text{O}_2$  efficiency close to 60% which can be considered quite acceptable given the nature of these types of wastewaters.

### 3.3. $\text{Fe}^{2+}$ dose

Fig. 4 shows the TOC conversion values versus reaction time obtained at 25 °C using different  $\text{Fe}^{2+}$  doses and an initial amount of  $\text{H}_2\text{O}_2$  corresponding to the stoichiometric with respect to COD. The only difference between Fig. 4a and b is in the initial COD value of the wastewater. It can be observed a very important improvement on the rate and the efficiency of TOC removal when increasing the  $\text{Fe}^{2+}$  dose up to a limit, the value of which decreases as it increases the organic load of the starting wastewater and, correspondingly, the  $\text{H}_2\text{O}_2$  dose, since a con-

stant  $\text{H}_2\text{O}_2$  to COD ratio has been used. Thus, for an initial COD value of 2395 mg/L and a  $\text{H}_2\text{O}_2$  dose of 5090 mg/L (Fig. 4a) the beneficial effect of increasing the  $\text{Fe}^{2+}$  dose is still very important up to a value somewhere in the range of 200–500 mg/L, whereas at an initial COD and  $\text{H}_2\text{O}_2$  dose around 1.8 times higher (Fig. 4b) a dose of  $\text{Fe}^{2+}$  above 200 mg/L does not produce any further significant improvement.

For a given  $\text{H}_2\text{O}_2$  to COD ratio a higher COD means obviously a higher  $\text{H}_2\text{O}_2$  amount which entails a higher production of hydroxyl radicals for a given  $\text{Fe}^{2+}$  dose. Moreover, a higher concentration of organic matter favours the regeneration of  $\text{Fe}^{2+}$  from the reaction of  $\text{Fe}^{3+}$  and organic radicals:



Higher  $\text{Fe}^{2+}$  concentrations favour the occurrence of the scavenging reaction:



and thus, the effect of the  $\text{Fe}^{2+}$  dose on the enhancement of the oxidation process becomes progressively less significant. On the other hand, the use of a high  $\text{Fe}^{2+}$  concentration is not advisable in practice, not only because it entails a higher cost of reagent but also looking at the subsequent treatment needed to remove the residual iron concentration in the effluent. In this respect, the locally allowable limit of iron for industrial wastewater discharges into the municipal sewer system is in our case 10 mg/L, which means that a final treatment for iron removal will be always necessary after Fenton treatment. The higher the iron concentration the higher the amount of  $\text{Fe}(\text{OH})_3$  sludge and the corresponding conditioning and disposal costs.

The results obtained with this type of wastewaters allow concluding that a  $\text{Fe}^{2+}$  dose in the vicinity of 200 mg/L would be sufficient in most cases. At relatively low values of initial COD using this  $\text{Fe}^{2+}$  dose may require a higher reaction time to reach an acceptable level of COD removal, although it is also true that the lower the initial COD the lower the relative reduction needed to reach the allowable limit.

Taking a representative COD value around 2500 mg/L for these wastewaters and using the stoichiometric  $\text{H}_2\text{O}_2$  to COD ratio, a 200 mg/L  $\text{Fe}^{2+}$  dose means a  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  initial weight ratio close to 3.8%. The information reported in the literature on the application of the Fenton treatment provides a wide diversity of recommended  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  weight ratios. Eisenhower used a ratio higher than 50% working with phenol [35]. Tang and Huang [33] recommended a value around 15% for 2,4-dichlorophenol degradation, fairly coincided with the reported by San Sebastián et al. [12] and Beltrán de Heredia et al. [23] for pharmaceutical and cork processing wastewaters. For this last type of effluents Guedes et al. [22] recommended 20%. Pérez et al. [18] used a much lower value of 0.6% for paper pulp effluents.

According to our results, looking at the final reduction achieved for the organic load (here final TOC conversion) the attention should be paid to the  $\text{Fe}^{2+}$  dose (mg/L) rather than to the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio and in this respect a dose of 200 mg/L of  $\text{Fe}^{2+}$  would be enough for an efficient application of the Fenton treatment to the wastewaters used in this work.

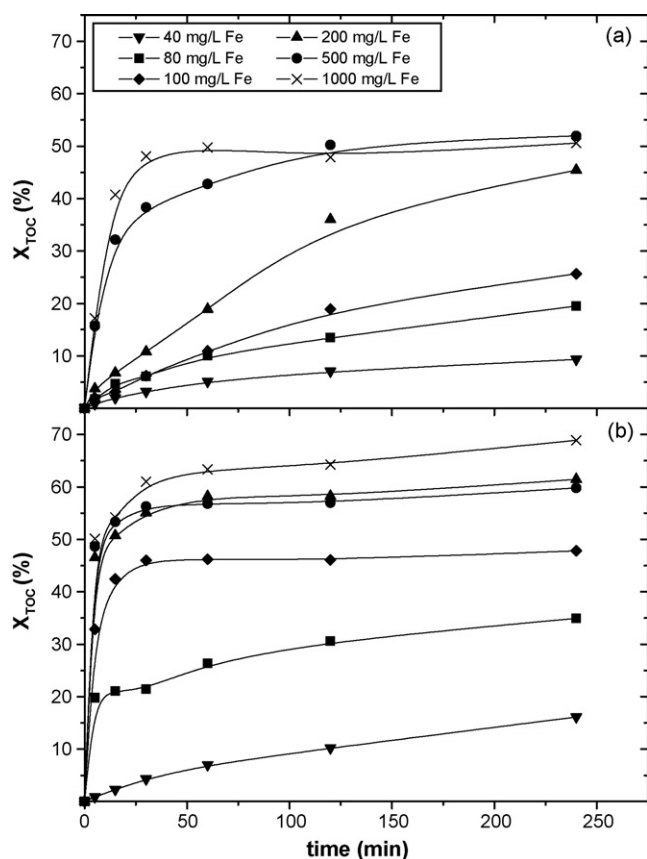


Fig. 4. Evolution of TOC conversion for different  $\text{Fe}^{2+}$  doses: (a)  $\text{COD}_0 = 2395$  mg/L;  $\text{TOC}_0 = 705$  mg/L;  $[\text{H}_2\text{O}_2]_0 = 5090$  mg/L;  $T = 25$  °C and (b)  $\text{COD}_0 = 4255$  mg/L;  $\text{TOC}_0 = 1090$  mg/L;  $[\text{H}_2\text{O}_2]_0 = 9040$  mg/L;  $T = 25$  °C.

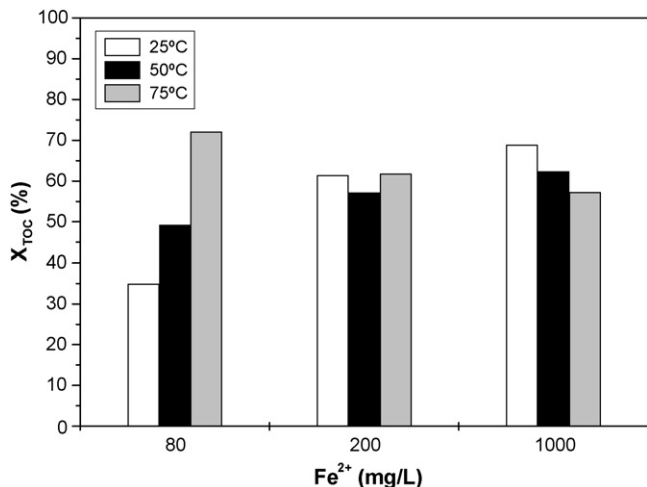


Fig. 5. Effect of temperature on TOC removal after 4 h of reaction for different Fe<sup>2+</sup> doses (COD<sub>0</sub> = 4255 mg/L; TOC<sub>0</sub> = 1090 mg/L; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 9040 mg/L).

### 3.4. Effect of temperature

The effect of temperature is shown in Fig. 5 at three different values of the Fe<sup>2+</sup> dose and a constant initial amount of H<sub>2</sub>O<sub>2</sub> corresponding to the stoichiometric H<sub>2</sub>O<sub>2</sub> to COD ratio. As can be seen, at a low Fe<sup>2+</sup> dose an increase of the temperature within the range investigated (25–75 °C) significantly improves the final TOC conversion. This effect diminishes and even disappears as the initial Fe<sup>2+</sup> amount increases and at very high Fe<sup>2+</sup> dose increasing the temperature becomes even detrimental for the efficiency of the process.

Increasing the temperature and the Fe<sup>2+</sup> dose both enhance the decomposition of H<sub>2</sub>O<sub>2</sub> giving rise to a very rapid generation of hydroxyl radicals and a high concentration of this species in the early stages of the process. This favors the occurrence of OH• consuming reactions other than those of oxidation of the organic matter. Moreover, an increase of temperature favours the decomposition of H<sub>2</sub>O<sub>2</sub> towards O<sub>2</sub> which has a very low oxidation capacity under the experimental conditions used in this work. Thus, a combination of high temperatures and Fe<sup>2+</sup> becomes detrimental for the efficiency of the Fenton process. At low Fe<sup>2+</sup> dose, H<sub>2</sub>O<sub>2</sub> decomposes more gradually giving rise to a more efficient availability of the hydroxyl radicals. This situation is enlightened in Fig. 6 which shows the time evolution curves of H<sub>2</sub>O<sub>2</sub> and TOC at 75 °C and a low (40 mg/L) and high (1000 mg/L) Fe<sup>2+</sup> dose.

### 3.5. Overall kinetics

The complex nature of these wastewaters strongly difficults to accomplish a kinetic analysis of Fenton oxidation based on the evolution of individual components. Furthermore, such an approach would be of scarce usefulness due to the variabilities in the chemical composition of these wastewaters. Instead, a more practical criterion has been adopted based on the evolution of TOC to establish the kinetics of the process from an overall sight.

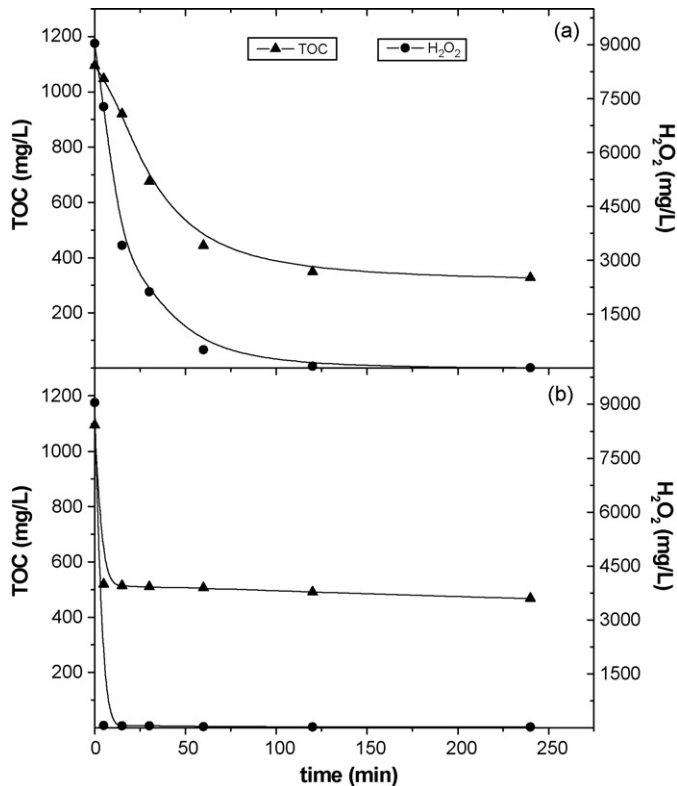


Fig. 6. Evolution of TOC and H<sub>2</sub>O<sub>2</sub> concentration at 75 °C using 40 mg/L (a) and 1000 mg/L (b) of Fe<sup>2+</sup> (COD<sub>0</sub> = 4255 mg/L; TOC<sub>0</sub> = 1090 mg/L; [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 9040 mg/L).

The kinetic analysis was carried out using the experimental TOC versus time values obtained from oxidation runs performed at an optimal Fe<sup>2+</sup> dose (200 mg/L) and an initial H<sub>2</sub>O<sub>2</sub> to COD ratio corresponding to the stoichiometric. Fig. 7a shows the time–evolution of TOC at different temperatures. As can be seen, most of the TOC reduction takes place within the first 60–120 min of reaction. The hydroxyl radicals are produced rapidly, leading to a fast decrease of TOC in the early stages of oxidation. A similar trend was observed by Szpyrkowicz et al. [20] for COD removal working with disperse dyes. In that work, the COD reduction was adequately described by a second-order reaction model during the first 20–30 min of reaction followed by smaller reaction rates.

The experimental results of Fig. 7a fit well to a pseudo-second order kinetic equation of the type:

$$-r_{\text{TOC}} = k[\text{TOC}]^2[\text{OH}\cdot] \cong k'[\text{TOC}]^2 \quad (6)$$

Fig. 7b shows the fitting of the experimental results to this equation. As can be seen it serves well to describe the rate of TOC removal within a wide range which covers up to the 80–90% of the maximum TOC reduction achieved, depending of the temperature. The values obtained for the apparent kinetic constants were  $6.64 \times 10^{-6}$ ,  $1.36 \times 10^{-5}$  and  $3.25 \times 10^{-5}$  L/mg min at 25, 35 and 50 °C, respectively. The Arrhenius plot is shown in Fig. 8. A value of 50.7 kJ/mol has been obtained for the apparent activation energy. This value is comparable to the one given by Guedes et al. [22] for cork processing wastewaters.

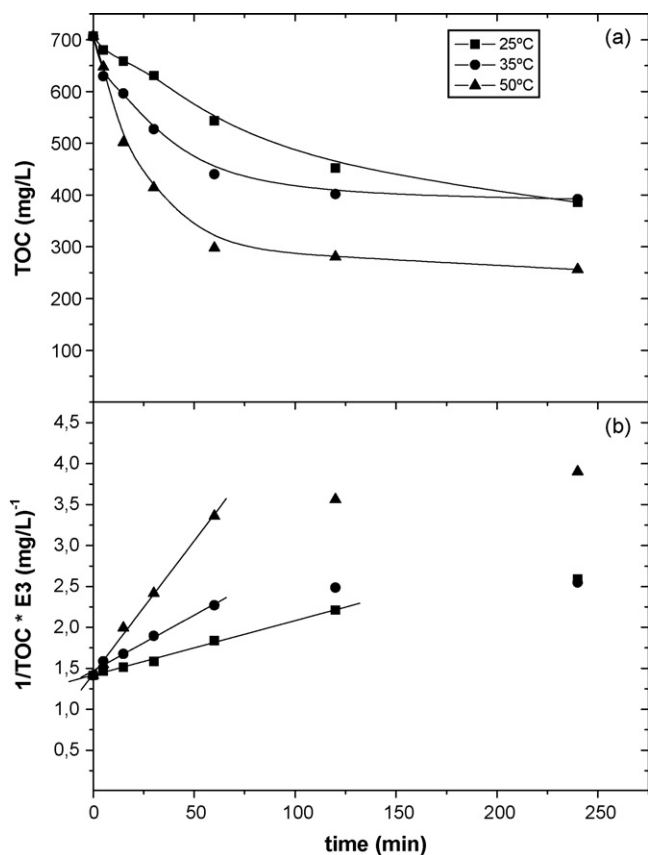


Fig. 7. Time-evolution of TOC (a) and fitting of the experimental data to a second-order kinetic equation (b) at different temperatures ( $\text{COD}_0 = 2395 \text{ mg/L}$ ;  $\text{TOC}_0 = 705 \text{ mg/L}$ ;  $[\text{Fe}^{2+}]_0 = 200 \text{ mg/L}$ ;  $[\text{H}_2\text{O}_2]_0 = 5090 \text{ mg/L}$ ).

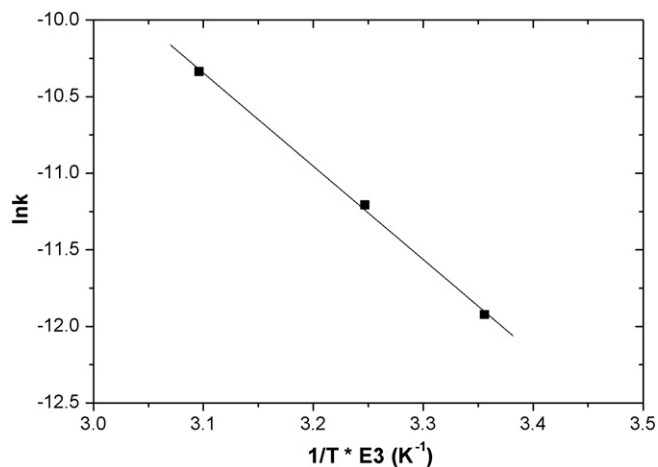


Fig. 8. Arrhenius plot of the apparent second-order kinetics constant.

#### 4. Conclusions

Fenton oxidation is a feasible treatment for cosmetic wastewaters as a complement for coagulation/flocculation allowing to achieve a significant decrease of TOC and COD. The best results were obtained using an initial pH in the interval 2.5–3, a  $\text{Fe}^{2+}$  dose of 200 mg/L and an initial  $\text{H}_2\text{O}_2/\text{COD}$  weight ratio corresponding to the theoretical stoichiometric value. The TOC con-

version increases with temperature, although this effect becomes less significant as the  $\text{Fe}^{2+}$  dose increases, and even the opposite trend takes place when high  $\text{Fe}^{2+}$  loadings are used. The overall kinetics of the process was adjusted to a second-order kinetic equation with respect of TOC. This simple equation describes well the rate of TOC reduction in a wide range covering up to 80–90% of the maximum achievable TOC conversion. A value of 50.7 kJ/mol was obtained for the apparent activation energy.

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