

## Kinetic study and hydrogen peroxide consumption of phenolic compounds oxidation by Fenton's reagent

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**Abstract**—Synthetic solutions of phenol, o-, m- and p-cresol were oxidised by using Fenton's reagent. The application of substoichiometric dosage of H<sub>2</sub>O<sub>2</sub> led to the formation of intermediate compounds, continuing later the oxidation to complete oxidation. An important objective was to analyze the effect of hydrogen peroxide dosage applied and the reaction pH together with the iron oxidation state on the degradation level. A kinetic model was derived from a reaction mechanism postulated which was used to analyze the results of the experiments. Another aim was to analyze the hydrogen peroxide consumption. Noteworthy results include an increase in oxidant consumption to intensify phenol removal. Furthermore, oxidant consumption was analyzed through the ratio H<sub>2</sub>O<sub>2</sub> to phenol removed and the average specific rate of removal (ASRR). By analyzing these two parameters it has been possible to ascertain the most favorable strategy for an efficient application of H<sub>2</sub>O<sub>2</sub>.

Key words: Fenton, Phenol, Cresols, Hydrogen Peroxide

### INTRODUCTION

Phenols in water sources cause several problems: even at very low concentrations, about 5 ppb, they cause an unpleasant taste and odor after chlorination due to the formation of chlorophenols. These compounds are very toxic at concentrations higher than 2 mg/L and also have a high oxygen demand (2.4 mg/mg phenol), giving rise to a considerable decrease in oxygen concentration and problems for aquatic life. Several treatment methods are possible, including some that attempt to recover the phenol for reuse, incineration, sorption [1], biologic treatment [2] and chemical oxidation [3]. The method selected will depend essentially on pollutant concentration and other strategic and financial aspects.

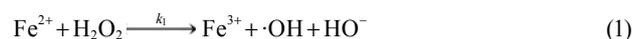
Chemical oxidation processes for phenol removal should be preferentially applied in some circumstances: a) instead of incineration for reasons of process economy or when the biological treatment is technically not possible; b) to amend the toxicity of streams prior to biological treatment; and c) as final treatment to fit the waste characteristics to disposal limitations. H<sub>2</sub>O<sub>2</sub> in the presence of a small amount of Fe<sup>2+</sup> salts (Fenton's reagent) is an efficient oxidant agent for non-biodegradable organic wastewaters in many cases [4]. Concretely, a wide range of concentrations of phenolic wastewater are able to be oxidized with this reagent. Oxidation takes place at pH within 3-5 interval and molar ratios (D, mol H<sub>2</sub>O<sub>2</sub>/mol phenol) of between 1 and 4. Iron salts have the advantage of not interfering in any subsequent biological treatment [5].

This paper studies the use of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> salts as a chemical oxidation reagent to destroy phenolic pollutants. H<sub>2</sub>O<sub>2</sub> in the presence of Fe<sup>2+</sup> or Fe<sup>3+</sup> ions generates hydroxyl radicals (·OH), plus other less significant radical species, as shown in reaction scheme proposed. This oxidizing system is generally known as Fenton's

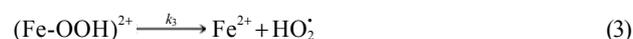
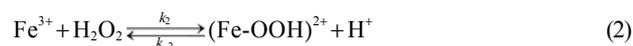
reagent, and its usage is a very interesting option for effluent treatment that has occupied the attention of many research studies found in the literature. As a rule Fe<sup>2+</sup> is used [6], but Fe<sup>3+</sup> can be also used in some circumstances [7]. These compounds are not expensive and do not create environmental problems. Explaining the differences observed between the usage of Fe<sup>2+</sup> or Fe<sup>3+</sup> on the oxidation consumption is the most important objective of this work because of its transcendence in the efficiency and process economy.

### 1. System Chemistry

Both di- and trivalent iron cations react with hydrogen peroxide, but the reaction of Fe<sup>2+</sup> with hydrogen peroxide according to Eq. (1) produces hydroxyl radicals, a highly reacting specie capable of oxidizing organics in wastewater [8-14].

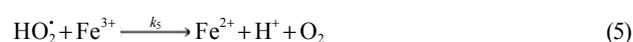


However, the reaction of Fe<sup>3+</sup> with hydrogen peroxide gives rise to hydroperoxide radicals and Fe<sup>2+</sup> according to the next reaction scheme [7]:



If [Fe<sup>2+</sup>] is very low with respect to [Fe<sup>3+</sup>] because reactions (2) and (3) are much slower than reaction (1) the overall phenol oxidation kinetic is slower.

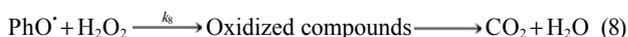
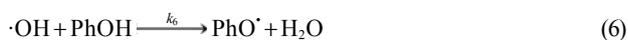
On the other hand, hydroxyl radicals can react with the oxidant lost [15], and the hydroperoxide radicals can react again with ferric species to regenerate Fe<sup>2+</sup> [7], but these reactions are much less significant than those mentioned above.



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Hydroxyl radicals react rapidly [9,10,14] with phenol following reactions (6-8) in water by removing an atom of hydrogen from the aromatic ring and forming a new radical which reacts with hydrogen peroxide [16].



Hydroquinone (o-dihydroxybenzene) and pyrocatechol (o-dihydroxybenzene) are compounds immediately oxidized from phenol which are later oxidized on an oxidation pathway leading to quinones, dicarboxylic acids and on to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [15].

## METHODOLOGY

### 1. Chemical Compounds

Synthetic phenol and cresol solutions were prepared by dissolving pure compounds (Panreac PRS 90%) in distilled water and preserving them in amber-colored bottles. Ferrous ion solutions were prepared from ferrous sulphate heptahydrated (Panreac PRS) and hydrogen peroxide was used as the oxidant (Panreac PRS, 30% v/v), diluted in distilled water.

### 2. Experimental Procedure

Synthetic phenol and cresol solution (250 mL) with an initial concentration of  $10^{-3}$  M were added to a batch reactor with the specific catalyst concentration to be studied in each case. The mixture was homogenized by magnetic stirring. The reaction started after a predetermined dose of oxidant was added to the reactor.

The experiment was carried out at atmospheric pressure and room temperature. pH was controlled by adding 0.1 M HCl to the initial dissolution. In this experimental study, all kinetic assays were carried out at an initial pH of 3 [16]. A very small change in pH over the course of the reaction was observed ( $\pm 0.05$ ).

Then the initial conditions were determined by taking 2 ml samples at different intervals of time.

### 3. Analytical Methods

Phenolic compounds were measured by means of high performance liquid chromatography (HPLC) using a Nucleosil 120 column with an ODS C18 filling, 5 mm diameter, by Teknokroma. To choose the appropriate wavelength, attention was paid to the absorption spectra of phenol and cresols obtained in a Perkin Elmer Lambda 10 spectrophotometer. All the compounds, colorless, were measured within the UV spectrophotometric band at 272 nm. The composition of the eluent was 30/70 (v/v) acetonitrile/water by using a 1.5  $\text{cm}^3/\text{min}$  volumetric flux. Under these conditions, the retention times were 7.6, 12.8, 12.8 and 14.2 min, respectively, for phenol m-, p- and o-cresol. Moreover, pH and temperature were measured with a pH-Tmeter by Crison, mod. pH-Rocon 18.

For measuring hydrogen peroxide concentrations in this work, one method of measurement was visible spectroscopy [19]. A Perkin Elmer Lambda 10 spectrophotometer was used. This method is based on measuring the yellow color which develops in the sample on adding titanium sulphate to the solution that contains  $\text{H}_2\text{O}_2$ . This method avoids possible interferences due to the presence of organic compounds [20-22].

## RESULTS AND DISCUSSION

Oxidation of phenol in diluted water solutions was studied without a catalyst, using only  $\text{H}_2\text{O}_2$  as an oxidizing agent. The reaction was performed under different experimental conditions, but no appreciable oxidation of phenol was found. For instance, when the oxidation of a  $10^{-3}$  M solution of phenol was carried out at pH 3 and D 8 mol  $\text{H}_2\text{O}_2/\text{mol}$  phenol, no appreciable oxidation was obtained even after 2 h.

These results show that phenol oxidation in diluted water solutions requires the presence of more active oxidizing species such as hydroxyl radicals [23]. Indeed, these can be generated from  $\text{H}_2\text{O}_2$  under the presence of chemical agents as a metallic cation [24] or other agents such as UV radiation with the appropriate wavelength [25,26]. It is even possible to generate these radicals by combining the two agents [27,28]. In this work, iron species were used as rad-

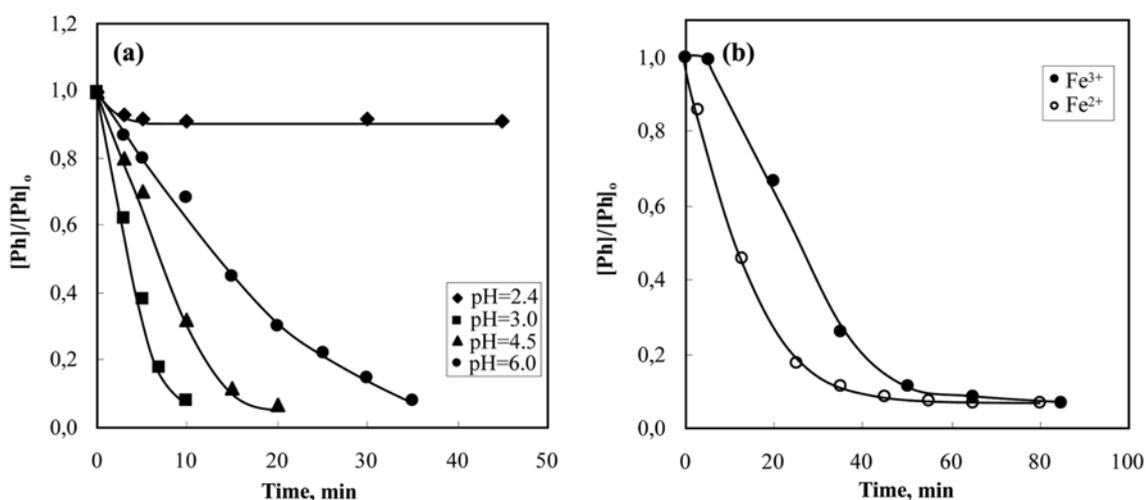


Fig. 1. (a) Removal efficiency of phenol for different initial pH (added  $[\text{Fe}^{2+}]$   $9 \cdot 10^{-5}$  M and D 8). (b) Phenol oxidation with  $[\text{Fe}^{2+}]$  and  $[\text{Fe}^{3+}]$  added of  $3.5 \cdot 10^{-5}$  M (pH 3 and D 4).

ical forming agents in an attempt to analyze the different behavior of the system with respect to the original iron oxidation state.

### 1. Reaction Conditions

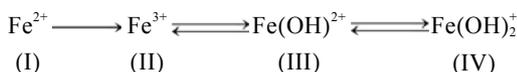
#### 1-1. Reaction pH

pH proved to be an important parameter which, to a large degree, determined the oxidation level achievable with  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  to. Some authors [22,29] express a preference for using a pH of around 3 for oxidation. This pH produces the best oxidation efficiency for the different conditions analyzed. The effect of pH seems to be justified because at higher pH levels the oxidizing species precipitate as ferric hydroxide, so that it is not possible to regenerate the active species ( $\text{Fe}^{2+}$ ). In any event, when  $\text{Fe}^{2+}$  is originally added, the first OH radicals formed are due to reaction (1), and theoretically oxidation would be possible using the corresponding stoichiometric amount of  $\text{Fe}^{2+}$  even at pH levels above 3.

To study this parameter,  $10^{-3}$  M phenol solutions were oxidized with  $9 \cdot 10^{-5}$  M of  $\text{Fe}^{2+}$  as catalyst to different initial pH levels (Fig. 1a).

Then, under especially active oxidizing conditions (high  $[\text{Fe}^{2+}]$ ), and with a high molar ratio, D, it was possible to obtain high oxidation efficiencies starting at pH levels of around 6. This can be explained by the formation during oxidation of acidic compounds that lower the pH close to 3. Consequently, although pH is high at the beginning of the experiment, it decreases rapidly and reaction finally takes place at a pH of around 3 most of the time. To confirm this fact, experiments were performed at neutral pH using buffered solutions and very low conversion levels were obtained. At pH levels lower than 3, as noted by various authors [24], inhibition of the radical forming activity of iron was observed, and consequently very low oxidation levels were obtained.

One possible explanation for the oxidation inhibition at pH lower than 3 is based on the main  $\text{Fe}^{3+}$  soluble species in equilibrium:



They are quantitatively distributed as a function of the solution pH. At pH 3 the majority species of  $\text{Fe}^{3+}$  is  $\text{Fe}(\text{OH})^{2+}$ . Thus, this  $\text{Fe}^{3+}$  species should be considered as an active catalyst [16]. At lower pH, the solution contains mainly nonhydrolyzed iron form, which would not be effective in the phenolic compounds degradation.

#### 1-2. Molar Ratio

According to the stoichiometry the molar ratio D needed for phenol to be completely oxidized by hydrogen peroxide is 14, as can be seen from reaction:



This globalizes the whole oxidation mechanism and derives from the sum of consecutive reactions that produce intermediate compounds such as those mentioned above. Reactions carried out under different molar ratios (D, mol  $\text{H}_2\text{O}_2$ /mol phenol) lead to different intermediate oxidized products, but in any case complete primary degradation of phenol would be possible at a much lower D than the stoichiometric level. A series of experiments was conducted using different values of D. It was observed that the conversion of phenol was only about 50% by using D 1; nevertheless, at D 3 conversion increased to around 95%, but only with D 4 was all the phenol eliminated. Using molar ratios within the 4-8 interval, the kinetics

were very similar, so there is no clear influence of  $\text{H}_2\text{O}_2$  on phenol elimination.

#### 1-3. Catalyst Species

As mentioned above, there are numerous references reporting oxidation either with  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ , but the kinetic curves have different profiles, since oxidation with  $\text{Fe}^{2+}$  is initially faster, while with  $\text{Fe}^{3+}$  catalyst a lag time is required to reach a reaction rate similar to  $\text{Fe}^{2+}$ . To confirm the oxidation mechanism proposed, phenol oxidation experiments were run using the same iron concentration ( $3.5 \cdot 10^{-5}$  M) but in the two aforementioned oxidation states, i.e., using ferrous sulfate and ferric sulfate. The experiments were conducted with an initial concentration of phenol of  $10^{-3}$  M, D 4 and pH 3. The results of phenol decomposition for both experiments are shown in Fig. 1b. These results are in accordance with the proposed mechanism, since when the catalyst was added as  $\text{Fe}^{2+}$  there was initially a rapid decrease in phenol concentration because hydrogen peroxide generates enough hydroxyl radicals from reaction  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Then, with a cyclic process of iron oxidation-regeneration a steady concentration of active iron for radical production was maintained; see Eqs. (1) to (3).

When  $\text{Fe}^{3+}$  was added initially, the generation of hydroxyl radicals depended on the appearance of  $\text{Fe}^{2+}$  from Eqs. (2) and (3). Because of this, an initial period with no oxidation appears while the  $\text{Fe}^{2+}$  species is being regenerated.

The degree of oxidation at the end of the reaction was very similar in both cases. Experimental data fit a first order reaction kinetic fairly well, with the pseudo first-order constants being  $0.060 \text{ min}^{-1}$  for  $\text{Fe}^{2+}$  and  $0.057 \text{ min}^{-1}$  for  $\text{Fe}^{3+}$ .

### 2. Kinetic Analysis of Phenol and Cresol Oxidation

In the first part of this study, the kinetics of phenol degradation were compared to those of cresols with the same conditions of pH, initial pollutant concentration, catalyst ( $\text{Fe}^{2+}$ ) and  $\text{H}_2\text{O}_2$  oxidant dose per phenol. Fig. 2 shows the oxidation kinetics of phenol and cresols, where more rapid kinetics can be observed for phenol than cresols, with the following refractory order: o-cresol > p-cresol > m-cresol > phenol [30].

Taking previous experimental results as a basis, a kinetic model based on the reaction mechanism explained above was applied to describe phenol or cresol degradation.

According to the mechanism mentioned above through reaction

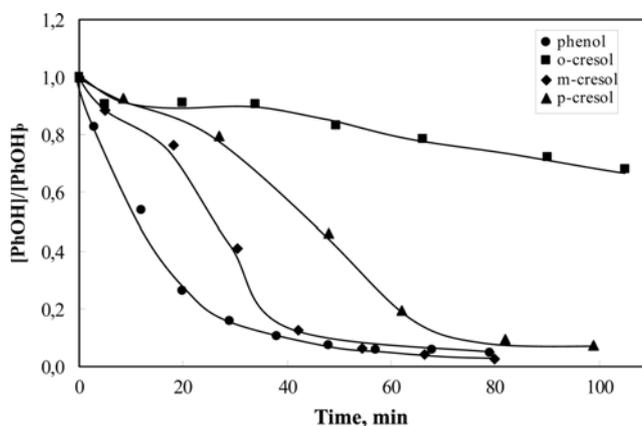


Fig. 2. Degradation efficiency of phenol and cresols (pH 3, added  $[\text{Fe}^{2+}] 3.5 \cdot 10^{-5}$  M and D 4).

(8), assuming a first order kinetic for both reactants, the following kinetics is considered:

$$-\frac{d[\text{PhOH}]}{dt} = k_8[\text{PhO}^*][\text{H}_2\text{O}_2] \quad (10)$$

To obtain the above reaction rate equation as a function of the reagent put into the system, the steady state condition is assumed for the radical species concentration [31,32], because of the high instability. The same assumption is applied to complex  $(\text{Fe}-\text{OOH})^{+2}$ , which in this sense is very similar to the radical species. Thus, from Eq. (2) and (3), the following equation is derived:

$$k_3[(\text{Fe}-\text{OOH})^{+2}] + k_{-3}[(\text{Fe}-\text{OOH})^{+2}][\text{H}^+] = k_2[\text{Fe}^{3+}][\text{H}_2\text{O}_2] \quad (11)$$

or

$$[(\text{Fe}-\text{OOH})^{+2}] = \frac{k_2[\text{Fe}^{3+}][\text{H}_2\text{O}_2]}{k_2[\text{H}^+] + k_3} \quad (12)$$

The kinetic constant corresponding to  $\text{Fe}^{2+}$  generation from complex  $(\text{Fe}-\text{OOH})^{+2}$  is very high and, on the contrary, values of proton concentration are low; this leads to [11]:

$$[(\text{Fe}-\text{OOH})^{+2}] = \frac{k_2[\text{Fe}^{3+}][\text{H}_2\text{O}_2]}{k_3} \quad (13)$$

The steady state hypothesis is also applied to species  $\text{Fe}^{2+}$ , since it reacts quickly with hydrogen peroxide, which is present in excess in the system.

$$k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] = k_3[(\text{Fe}-\text{OOH})^{+2}] + k_5[\text{HO}_2^*][\text{Fe}^{3+}] \quad (14)$$

The reaction of hydrogen peroxide with  $\text{Fe}^{2+}$  to yield  $\text{Fe}^{3+}$  is practically instantaneous in practice, because  $k_1$  is very high [33]. Thus, the reaction of  $\text{Fe}^{2+}$  regeneration from  $(\text{Fe}-\text{OOH})^{+2}$  is also very fast, and subsequently the term in which the constant  $k_3$  is included is numerically significant with respect to the others. All these assumptions explain why the term  $k_5[\text{HO}_2^*][\text{Fe}^{3+}]$  is negligible with respect to the other two, since on the one hand,  $k_1$  and  $k_3$  have high values [33], and on the other hand this term is the product of two species concentrations with very low values.

Inserting Eq. (13) above into the concentration of the ion complex of Eq. (14) and assuming that the term  $k_5[\text{HO}_2^*][\text{Fe}^{3+}]$  is negligible, the concentration of ferrous ions can be expressed according to the following equation:

$$[\text{Fe}^{2+}] = \frac{k_3[(\text{Fe}-\text{OOH})^{+2}]}{k_1[\text{H}_2\text{O}_2]} \approx \frac{k_2}{k_1}[\text{Fe}^{3+}] \quad (15)$$

Moreover, if the steady state hypothesis for hydroxyl radicals is applied, it yields:

$$k_4[\cdot\text{OH}][\text{H}_2\text{O}_2] + k_6[\cdot\text{OH}][\text{PhOH}] = k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] + k_7[\text{PhO}^*] \quad (16)$$

or

$$[\cdot\text{OH}] = \frac{k_1[\text{Fe}^{2+}][\text{H}_2\text{O}_2] + k_7[\text{PhO}^*]}{k_4[\text{H}_2\text{O}_2] + k_6[\text{PhOH}]} \quad (17)$$

Due to its high instability, the specie  $\text{PhO}^*$  reacts quickly and subsequently the concentration of that species is very low, so the corresponding additive term of Eq. (17) is negligible. On the other hand, it can be postulated that  $k_4[\text{H}_2\text{O}_2] \gg k_6[\text{PhOH}]$ , because the hydrogen

peroxide concentration in the system is greater than that of phenol and the value of  $k_4$  is also greater than  $k_6$ . Substituting the concentration of ferrous ion (Eq. (15)) in Eq. (17), the following equation is obtained for the concentration of hydroxyl radicals.

$$[\cdot\text{OH}] \approx \frac{k_2}{k_4}[\text{Fe}^{3+}] \quad (18)$$

Moreover, if the steady state hypothesis is considered for the radical  $\text{PhO}^*$ , it leads to:

$$k_7[\text{PhO}^*] + k_8[\text{PhO}^*][\text{H}_2\text{O}_2] = k_6[\cdot\text{OH}][\text{PhOH}] \quad (19)$$

or

$$[\text{PhO}^*] = \frac{k_6[\cdot\text{OH}][\text{PhOH}]}{k_7 + k_8[\text{H}_2\text{O}_2]} \quad (20)$$

Substituting the  $\text{PhO}^*$  concentration from Eq. (20) in the proposed general Eq. (10), the rate of phenol degradation is formulated as follows:

$$-\frac{d[\text{PhOH}]}{dt} = k_8 \frac{k_6[\cdot\text{OH}][\text{PhOH}]}{k_7 + k_8[\text{H}_2\text{O}_2]}[\text{H}_2\text{O}_2] \quad (21)$$

$$-\frac{d[\text{PhOH}]}{dt} \approx \frac{k_2 k_6 k_8}{k_4} [\text{Fe}^{3+}] \left( \frac{[\text{H}_2\text{O}_2]}{k_7 + k_8[\text{H}_2\text{O}_2]} \right) [\text{PhOH}] \quad (22)$$

It is important to remark that the active  $\text{Fe}^{3+}$  in the solution is not only that of this form but the sum of all soluble complex  $\text{Fe}^{3+}$  species. Nevertheless, as  $\text{Fe}^{2+}$  concentrations added in this experimentation would give rise to  $\text{Fe}^{3+}$  concentrations supported by its solubility,  $\text{Fe}^{3+}$  concentration actually coincides with the added  $\text{Fe}^{2+}$ . The rate of the oxidation reaction from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (Eq. (1)) is another important point in support of the above assertion.

Eq. (22) above can be considerably simplified under certain assumptions. At a high enough hydrogen peroxide concentration, it can be assumed that  $k_8[\text{H}_2\text{O}_2] \gg k_7$  and, consequently, kinetic Eq. (22) becomes:

$$-\frac{d[\text{PhOH}]}{dt} = \frac{k_2 k_6}{k_4} [\text{Fe}^{3+}][\text{PhOH}] \quad (23)$$

Finally, for a given  $\text{Fe}^{3+}$  amount catalyst Eq. (23) becomes:

**Table 1. Pseudo-first order constant for phenol removal and correlation coefficients**

$\text{Fe}^{2+}$ added (M) $\times 10^5$	D	$k_{app}$ ( $\text{min}^{-1}$ ) $\times 10^2$	$r^2$
2	1	0.82	0.87
2	3	2.51	0.96
2	4	2.27	0.97
2	8	2.82	0.98
3.5	1	2.23	0.92
3.5	2	5.31	0.96
3.5	4	6.36	0.99
3.5	6	6.00	0.98
3.5	8	5.35	0.99
3.5	9	6.04	0.99
9	4	20.73	0.97
9	8	21.80	0.94
18	8	44.02	0.99

$$-\frac{d[\text{PhOH}]}{dt} = k_{ap}[\text{PhOH}] \quad (24)$$

where  $k_{ap}$  is the apparent or experimental constant, obtained from fitting the kinetic results of phenol degradation to a first order kinetic from a certain iron concentration. Determination of  $k_{ap}$  values for several iron concentrations would enable the constant term  $k_2k_6/k_4$  to be estimated. Below, the values of  $k_{ap}$  are set out for different experiments. From this information a critical  $\text{H}_2\text{O}_2$ /phenol dose was obtained, so that above that concentration the degradation rate of the oxidant is independent of the oxidant dose applied. Values of first order experimental constants were obtained for different  $\text{Fe}^{3+}$  concentrations (or different  $\text{Fe}^{2+}$  added concentrations) and the corresponding critical  $\text{H}_2\text{O}_2$  concentration. In Table 1, together with the value of the kinetic constant, one can see the determination coefficient of experimental results to fit first order kinetics.

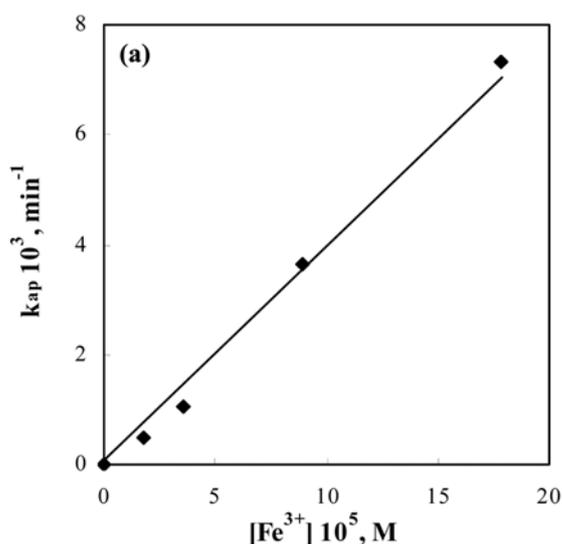
The experimental results obtained at low concentrations of oxidants showed a poor fit to first-order kinetics because in these conditions the kinetic constant depends on the oxidant concentration. Thus, the assumption for simplifying the kinetic equation is not valid. However, the dependence of the first order constant on oxidant concentration decreases to zero as deduced from Eq. (22).

According to the results presented in Table 1, it can be concluded that the first-order experimental constant is independent of the oxidant concentration for experiments carried out at a molar higher than 4. Under these conditions, the first order constants were represented in terms of  $\text{Fe}^{3+}$  concentration (or added  $\text{Fe}^{2+}$  concentration), and the relationship shown in Fig. 3a was obtained.

From the slope of the straight line, the value of the constant group  $k_2k_6/k_4$  in Eq. (23) was calculated. The determination coefficient ( $r^2$ ) obtained has been of 0.94. Thus, the kinetics of phenol elimination can be expressed as follows:

$$-\frac{d[\text{PhOH}]}{dt} = \left( 46.32 \frac{[\text{H}_2\text{O}_2]}{\frac{k_7}{k_8} + [\text{H}_2\text{O}_2]} \right) [\text{Fe}^{3+}][\text{PhOH}] \quad (25)$$

All the experiments conducted were grouped by the oxidant dose



added and the iron concentration used in order to calculate quotient  $k_7/k_8$ , and the degradation rate of phenol was analyzed according to Eq. (25).

The differential method was applied to calculate the phenol removal rate; thus, the values of experimental first-order constants ( $k'_{ap}$ ) were obtained for each oxidant dose taking finite time intervals. In Fig. 3b the values of constant  $k'_{ap}$  obtained for each time interval using  $3.5 \cdot 10^{-5}$  M  $\text{Fe}^{3+}$  concentration are plotted as a function of the corresponding hydrogen peroxide concentration.

The experimental data plotted in Fig. 3b were fitted to the following empirical equation as per Eq. (26):

$$k'_{ap} = \left( A \frac{[\text{H}_2\text{O}_2]}{B + [\text{H}_2\text{O}_2]} \right) \quad (26)$$

with a standard deviation of  $1.47 \cdot 10^{-4} \text{ min}^{-1}$ . Then, parameters A and B were obtained:

$$A = 46.32[\text{Fe}^{3+}] \quad (27)$$

$$B = \frac{k_7}{k_8} \quad (28)$$

Thus, for each  $\text{Fe}^{3+}$  concentration added to the reaction, a value of parameter B was obtained. This calculation was performed for different iron concentrations, leading to a value of  $B = 1.22 \cdot 10^{-3} \pm 0.01$ , with a correlation coefficient greater than 0.9. Consequently, from Eq. (24), the following equation was proposed to describe the phenol removal rate.

$$-\frac{d[\text{PhOH}]}{dt} = \left( 46.32 \frac{[\text{H}_2\text{O}_2]}{1.22 \cdot 10^{-3} + [\text{H}_2\text{O}_2]} \right) [\text{Fe}^{3+}][\text{PhOH}] \quad (29)$$

Phenol kinetics were plotted for different experiments together with the experimental results to see the correspondence between the two profiles. Since the hydrogen peroxide varies during the reaction, the theoretical profile of phenol was calculated, integrating Eq. (29) for finite time intervals between 5 and 8 min, by taking average values of hydrogen peroxide as constant in each interval.

The profiles of phenol degradation modelled according to Eq.

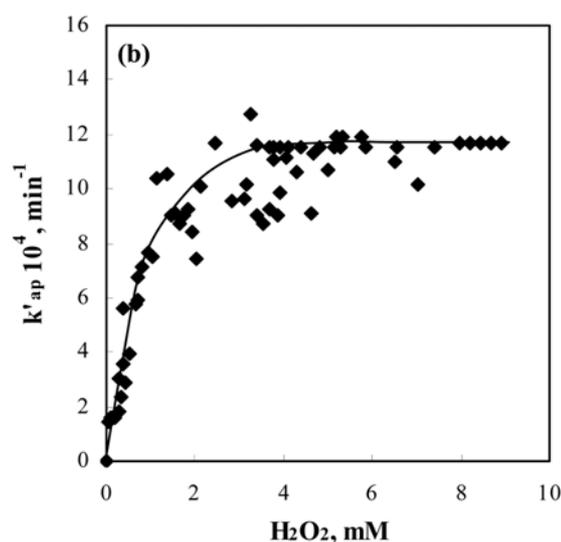


Fig. 3. (a)  $k_{ap}$  vs.  $[\text{Fe}^{3+}]$  to high molar ratios at pH 3. (b)  $k'_{ap}$  vs.  $[\text{H}_2\text{O}_2]$  at pH 3 and added  $[\text{Fe}^{2+}] 3.5 \cdot 10^{-5}$  M.

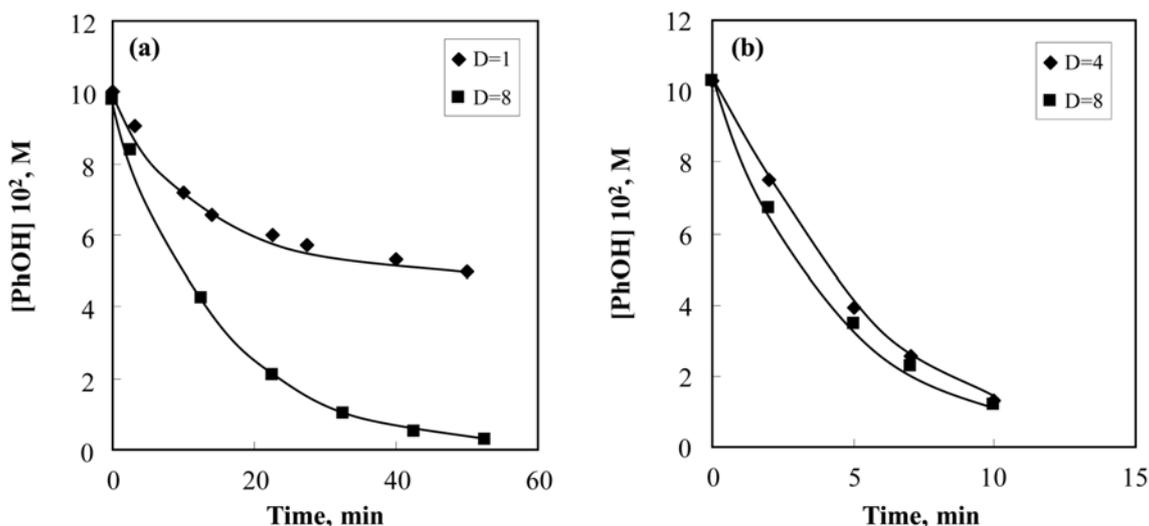


Fig. 4. Theoretical (—) and experimental (◆, ■) profiles of phenol degradation for different oxidant dose D. (a) added  $[\text{Fe}^{2+}] 3.5 \cdot 10^{-5} \text{ M}$ . (b) added  $[\text{Fe}^{2+}] 9 \cdot 10^{-5} \text{ M}$ .

(29), following the calculation procedure explained above, are shown simultaneously in Fig. 4. The experimental data are plotted simultaneously for the four oxidant to phenol doses analyzed, using  $3.5 \cdot 10^{-5}$  and  $9 \cdot 10^{-5} \text{ M Fe}^{3+}$  concentrations. The standard deviation obtained was between  $0.03 \cdot 10^{-2}$  and  $0.2 \cdot 10^{-2} \text{ M}$ . Then, a good fit can be deduced by comparing the two profiles. So, it can be concluded that the mechanistic model proposed according to Eq. (1) to (8) and the assumptions considered seem to be adequate for describing phenol degradation.

An analysis similar to that of phenol was performed for m-, p- and o-cresol. Consequently, the kinetic equation below was obtained for the different compounds.

$$-\frac{d[\text{mC}]}{dt} = \left( 41.81 \frac{[\text{H}_2\text{O}_2]}{1.61 \cdot 10^{-3} + [\text{H}_2\text{O}_2]} \right) [\text{Fe}^{3+}][\text{mC}] \quad (30)$$

$$-\frac{d[\text{pC}]}{dt} = \left( 32.12 \frac{[\text{H}_2\text{O}_2]}{2.13 \cdot 10^{-3} + [\text{H}_2\text{O}_2]} \right) [\text{Fe}^{3+}][\text{pC}] \quad (31)$$

$$-\frac{d[\text{oC}]}{dt} = \left( 19.39 \frac{[\text{H}_2\text{O}_2]}{2.83 \cdot 10^{-3} + [\text{H}_2\text{O}_2]} \right) [\text{Fe}^{3+}][\text{oC}] \quad (32)$$

As in the case of phenol, the experimental data on the degradation kinetics for the three cresols gave an acceptable fit to those obtained by integration of Eqs. (30) to (32). Reaction conditions were the same as in the cases shown in Fig. 4 for phenol.

### 3. Analysis of $\text{H}_2\text{O}_2$ Consumption in the Oxidation of Phenolic Compounds

In the second part of this study, hydrogen peroxide consumption in the degradation of different phenols was analyzed. Hydrogen peroxide is essential in radical generation. Hydroxyl and other radicals can react on the pollutant and intermediates or on the oxidant itself, which would cause a loss of efficiency. An analysis of its consumption is fundamental if the most adequate conditions are to be found and hydrogen peroxide is to be used efficiently [34]. In the analysis of oxidant consumption for phenol removal, two parameters that describe the efficiency of oxidant use were employed: ox-

dant composition itself or the mole of oxidant sent per mol of phenol removal (consumption) and the average specific rate of removal (ASRR). To calculate the first of these parameters a reaction time must be defined. In this study, oxidant consumption was determined for 50 and 90% phenol removal.

The second parameter analyzed to study oxidant consumption and complete the information from the first parameter was ASRR. It is defined as the average oxidation rate per mol of oxidant during the reaction period considered (mol PhOH/mol  $\text{H}_2\text{O}_2$  min), and it is a measure of oxidant efficiency, taking into account the time needed to achieve a certain level of phenol removal (95 and 50%). The results of both parameters are shown in Table 2 for the oxidant doses analyzed.

The most remarkable aspect of the data in Table 2 is the increase in hydrogen peroxide consumption to remove a greater amount of

Table 2. Consumption levels and ASRR values for 50 and 95% phenol removal

$\text{Fe}^{2+}$ added (M) $\times 10^5$	D	Consumption		ASRR $\times 10^3$	
		50%	95%	50%	95%
2	1	2.31		6.16	
	3	2.46		18.51	
	4	2.12	3.89	20.52	1.98
	8	2.26	3.52	14.73	2.58
3.5	1	2.13		9.39	
	2	2.27		36.71	
	4	3.65	4.09	48.00	3.76
	6	3.95	4.55	38.94	5.80
	8	4.13	4.88	24.22	4.10
9	9	3.97	5.11	25.20	4.35
	4	2.17	4.16	115.20	14.11
18	8	4.12	5.10	80.90	19.62
	8	3.76	6.34	177.30	26.31

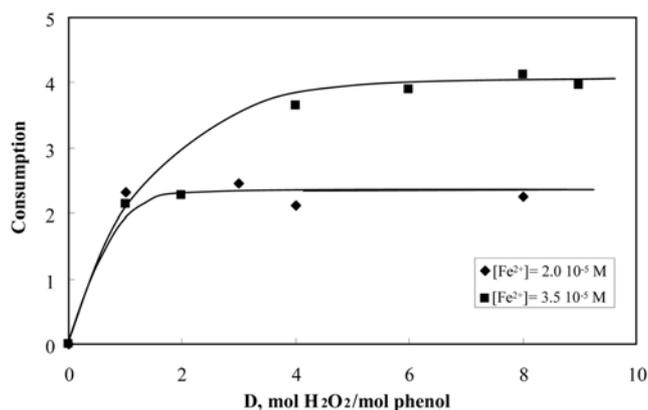


Fig. 5. Oxidant consumption vs. oxidant dosage to different added  $[Fe^{2+}]$  at 50% of phenol removal.

phenol. Moreover, consumption goes up as the initial oxidant per mol of phenol increases, tending to an asymptotic value as shown in Fig. 5. This behavior was found with all Fe concentrations, with the asymptotic values becoming greater as Fe concentration increased [35]. Nevertheless, to reach the asymptotic or limit value of consumption, a lower oxidant dose is required as the Fe concentration is decreased.

On analyzing the changes over time in ASRR with the oxidant

ratio applied, it can be concluded that a maximum of ASRR is observed for oxidant ratio 4, independently of the Fe added. This indicates that oxidant dose D 4 could be an appropriate value for the percentage of phenol removal analyzed. Moreover, ASRR increases with the catalyst concentration as shown in Fig. 6a, where data on the ASRR parameter in phenol removal are shown for  $2 \cdot 10^{-5}$ ,  $3.5 \cdot 10^{-5}$  and  $9 \cdot 10^{-5}$  M catalyst concentrations. The maximum observed at D 4 seems to be explained by the intensification of intermediate and hydrogen peroxide reactions at high oxidant doses.

In the  $Fe^{2+}$  concentration interval analyzed, ASRR increases with this concentration, as shown in Fig. 6b. In a way similar to the behavior of ASRR with the oxidant dose, it seems likely that there should be a maximum of ASRR for higher  $Fe^{2+}$  concentrations. This value would indicate the optimal concentration of  $Fe^{2+}$  taking into account not only the consumption of oxidant but also the time needed to achieve a certain phenol removal. The changes over time in ASRR over a wider  $Fe^{2+}$  interval were not observed due to a lack of experiments with higher catalyst concentrations. Technical difficulties in monitoring the reaction due to the speed at which it takes place did not allow such experimentation. Nevertheless, it does not seem probable that any significant advantage can be derived by using higher amounts of catalyst.

Experiments were also conducted for the oxidation of o-, m- and p-cresol, with a view to studying the oxidant consumption parameters defined above. Thus, it was possible to conduct a comparative

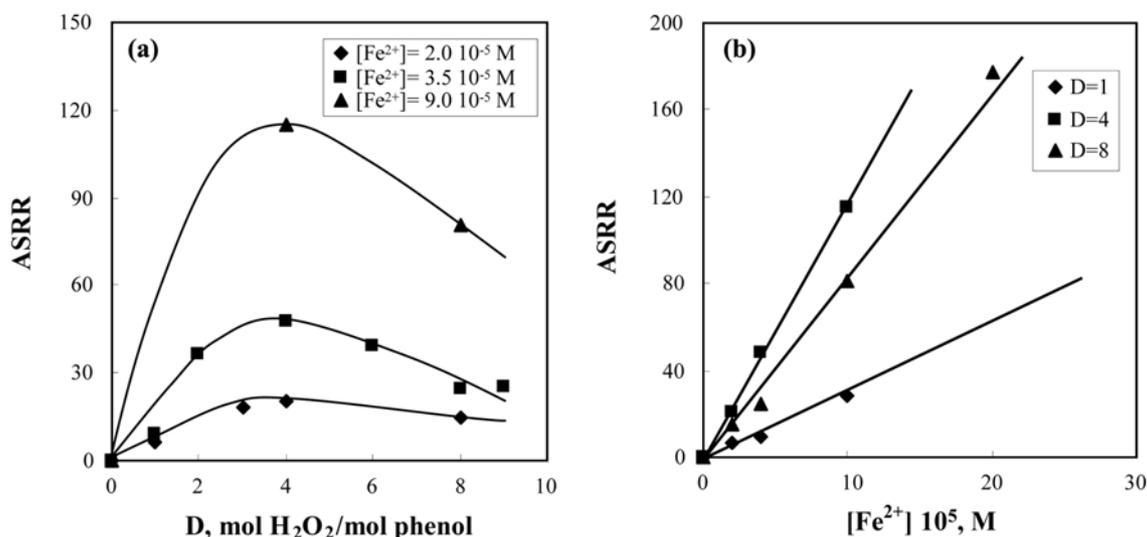


Fig. 6. To 50% of phenol removal: (a) ASRR vs. oxidant dosage to different added  $[Fe^{2+}]$ . (b) ASRR vs. added  $[Fe^{2+}]$  to different oxidant dosage.

Table 3. Consumption levels and ASRR values for different combination of conditions:  $Fe^{2+}$  added, dosage and percent of phenol removal.

Conditions			Phenol		m-Cresol		o-Cresol		p-Cresol	
$[Fe^{2+}] \times 10^5$	D	%PhOH <sub>rem</sub>	Cons.	ASRR $\times 10^3$	Cons.	ASRR $\times 10^3$	Cons.	ASRR $\times 10^3$	Cons.	ASRR $\times 10^3$
3.5	4	50	3.65	48.03	2.75	13.50	2.42	9.18	2.53	11.30
3.5	4	95	4.09	3.76	4.17	4.00	3.42	2.01	4.68	2.67
3.5	8	50	4.13	24.22	3.63	17.20	2.78	9.00	2.92	13.72
3.5	8	95	4.88	4.10	4.65	6.14	3.97	1.94	4.76	3.50
18	8	50	3.76	177.30	3.84	86.80	3.53	28.30	3.71	33.70
18	8	95	6.34	26.31	5.34	31.20	4.98	5.74	5.46	7.33

analysis of all phenolic compounds. The values of oxidant consumption and ASRR are shown in Table 3.

These values show, as a general trend, that either oxidant consumption or ASRR decreases in the following order: phenol>m-cresol>p-cresol>o-cresol. It is significant that this order is inverse to the observed resistance to oxidation mentioned above. From these results it seems that the slower the degradation kinetics of the phenolic analyzed are, the better the performance of the oxidant is. Moreover, it is important to remark that more efficient use of oxidant may be due to lower degradation or mineralization levels of intermediate compounds that appear during oxidation.

### CONCLUSIONS

Fenton's reagent has proven to be an effective method for the degradation of phenol and cresols if appropriate conditions of oxidation are selected. The oxidation reaction must be at pH 3, since poor degradation efficiencies with only slight variations are obtained below this value. This decrease is not so great when pH is increased due to the formation of carboxylic acids during the reaction which quickly decrease initial pH to values close to 3. Using molar ratios of hydrogen peroxide phenol to phenol of 4 (well below the stoichiometric value of 14) a phenol removal of more than 95% is achieved.

Oxidation of phenolics by the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system (Fenton's reagent) entails two clear steps. During the first step, the oxidation kinetic is very fast, corresponding to the generation of radicals associated with the transition from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . During the second step, the rate of radical generation and the subsequent oxidizing kinetics are slower because this stage is controlled by the reaction of  $\text{Fe}^{3+}$  with  $\text{H}_2\text{O}_2$ . When  $\text{Fe}^{3+}$  salts are used, a lag period (initiation) is observed, while the second step takes place in a way similar to that mentioned for Fenton's reagent based on  $\text{Fe}^{2+}$ .

A mechanism has been proposed for the removal of phenol and cresols that has enabled a kinetic model to be developed for these substrates, with a good fit to the experimental results.

The kinetics of cresol oxidation are slower than for phenol because these compounds are more refractory according to the sequence o-cresol>p-cresol>m-cresol>phenol. A reaction system has been proposed for the removal of phenol and cresols that has enabled a kinetic model to be developed for these compounds, with a good fit to the experimental results.

Hydrogen peroxide consumption increases with the oxidant dose applied, reaching an asymptotic maximum value dependent on the concentration of iron present in the system. For the average specific rate of removal (ASRR), a maximum was found by using an oxidant ratio around 4. This indicates an optimum in the hydrogen peroxide efficiency from the consumption point of view and the time required to produce a certain phenol removal. Above such optimum a massive oxidation of the intermediate compounds resulting from phenol oxidation is observed.

Either the oxidant consumption or the ASRR decreases in the same order as the resistance to oxidation of phenolics. Thus, according to the sequence mentioned above, consumption and ASRR should be considerably higher for o-cresol, which proved to be the most refractory to oxidation of the phenolics studied, than for phenol.

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### NOMENCLATURE

[OH $\cdot$ ] : hydroxyl radical concentration [mol/L]  
 [HO $_2\cdot$ ] : hydroperoxyl radical concentration [mol/L]  
 [PhOH] : phenol concentration [mol/L]  
 [PhO $\cdot$ ] : phenolic radical concentration [mol/L]  
 D : dosage of  $\text{H}_2\text{O}_2$ /phenolic compound [mol  $\text{H}_2\text{O}_2$ /mol phenolic compound]  
 $k_{op}$  : experimental first-order constant to high D [ $\text{min}^{-1}$ ]  
 $k_{lp}$  : experimental first-order constant to low D [ $\text{min}^{-1}$ ]  
 [mC] : m-cresol concentration [mol/L]  
 [pC] : p-cresol concentration [mol/L]  
 [oC] : o-cresol concentration [mol/L]  
 cons. : consumption of oxidant [mol  $\text{H}_2\text{O}_2$ /mol PhOH]  
 ASRR : average specific rate of removal [mol PhOH/mol  $\text{H}_2\text{O}_2$  min]

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