



# Mineralization lumping kinetic model for abatement of organic pollutants using Fenton's reagent

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## ARTICLE INFO

### Article history:

Available online 12 March 2010

### Keywords:

Fenton's reagent  
Mineralization  
Kinetic model  
Hydrogen peroxide

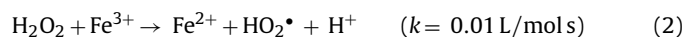
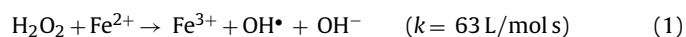
## ABSTRACT

A simplified pseudokinetic model to predict the mineralization evolution of organic pollutants by Fenton's reagent (FR) has been developed. The model has been validated by fitting phenol oxidation data by using FR in a batch way but could be applied to other wastewaters. The proposed model can be applied to the whole range of hydrogen peroxide dosage, values lower than those theoretically required for total mineralization or excess. To do this the model takes into account the change in the hydrogen peroxide concentration. Moreover, the model is able to explain and predict the asymptotic value obtained for mineralization of the initial TOC due to the complexation of the catalyst (iron cation) with chelating oxidation intermediates. Finally, the model can optimize the dosage of hydrogen peroxide in order to avoid the loss of this reagent.

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## 1. Introduction

Industrial wastewaters have become a problem of increased importance in recent decades [1]. Many industries generate wastewater containing organic compounds refractory to conventional biological oxidation [2]. The technology with the greatest potential to eliminate these pollutants is oxidation being one of the most powerful oxidants the hydroxyl radical (advanced oxidation processes, AOPs) [3]. Fenton's reagent is one of the most employed AOPs to eliminate non-biodegradable pollutants from wastewaters [4–7]. The most accepted mechanism is based on a complex scheme of radical reactions. [8]. Main reactions are summarized in Eqs. (1) and (2). The hydroxyl radicals are generated by oxidation of ferrous iron(II) to ferric iron(III), and the catalytic cycle is closed by reduction of iron(III) to iron(II) by the same hydrogen peroxide. As can be seen from kinetic constants in Eqs. (1) and (2) the controlling step is reaction (2). Despite these two main reactions, many other radicalic reactions can occur. Some of them are summarized in Table 1. The process may be applied to wastewaters, sludges, or contaminated soils:



Despite of its numerous advantages some limitations of this Fenton's reagent must also be taken into account: in order to avoid the

formation of iron hydroxides, initial pH needs to be acid and iron sludges are generated in the further neutralization step.

Besides, the reaction rate can be greatly influenced by the presence of free radical scavengers and/or iron chelants. Among these chelating agents the oxalic acid must receive a special attention.

This is because the original pollutants are not directly mineralized to  $\text{CO}_2$  but a big number of oxidation intermediates are produced. Phenol oxidation by using Fenton's reagent produces firstly aromatic intermediates (hydroquinone and catechol). Condensation products also appear, mainly at low dosages of hydrogen peroxide. Final organic intermediates are short chain organic acids such as oxalic acid, being these compounds refractory to the oxidation by the Fenton's reagent. [16,17].

As the oxalic acid is produced, the complexation of iron cation with this chelating intermediate decreases the availability of iron, stopping the radical generation by  $\text{H}_2\text{O}_2$  [18,19].

It is observed that the oxidation reaction does not continue or it occurs at very low rate because of the breakage of the catalytic cycle. As a consequence, an asymptotic value for mineralization grade is obtained, even if high dosage of hydrogen peroxide is employed.

As an example, it can be cited the results obtained in a previous work [20] where phenol, cresols and nitrophenols were oxidized by the Fenton's reagent. Several hydrogen peroxide percentages of amounts required according to stoichiometry for the total mineralization were used. High conversion of phenols (near the unity) was obtained, even at low concentrations of  $\text{H}_2\text{O}_2$ . On the contrary, the TOC percent removal obtained at times high enough to assure the end of the reaction reached an asymptotic value. This value was much lower than the unity and could be explained by the chelation of iron cation by organic acids produced. Therefore, if  $\text{H}_2\text{O}_2$

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### Nomenclature

<i>A</i>	oxidizable organic matter (mg CL <sup>-1</sup> )
<i>B</i>	refractory organic matter (mg CL <sup>-1</sup> )
<i>C</i> <sub>H<sub>2</sub>O<sub>2</sub></sub>	hydrogen peroxide concentration (mg H <sub>2</sub> O <sub>2</sub> L <sup>-1</sup> )
<i>C</i> <sub>(H<sub>2</sub>O<sub>2</sub>)<sub>0</sub></sub>	initial hydrogen peroxide concentration (mg H <sub>2</sub> O <sub>2</sub> L <sup>-1</sup> )
<i>k</i>	pseudokinetic constant for pollutant oxidation (L/mg H <sub>2</sub> O <sub>2</sub> s)
<i>ν<sub>g</sub></i>	empirical stoichiometric coefficient for hydrogen peroxide meaning the amount of H <sub>2</sub> O <sub>2</sub> required to get the asymptotic mineralization (mg H <sub>2</sub> O <sub>2</sub> /mg C)
<i>r</i>	reaction rate (mg CL <sup>-1</sup> s <sup>-1</sup> )
<i>SQR</i> <sub>TOC</sub>	residual sum of squares [ $\sum (TOC_{Exp} - TOC_{Calc})^2$ ] (mg CL <sup>-1</sup> ) <sup>2</sup>
<i>t</i>	time (s)
<i>TOC</i>	organic carbon concentration (mg CL <sup>-1</sup> )
<i>TOC</i> <sub>0</sub>	initial organic carbon concentration (mg CL <sup>-1</sup> )
<i>x</i>	fraction of the carbon content of specie <i>A</i> that reacts to specie <i>B</i>

**Table 1**

Radical reactions proposed in literature to describe the oxidation by Fenton's reagent.

Reaction	<i>k</i> (L/mol s)	Refs.
•OH + H <sub>2</sub> O <sub>2</sub> → HO <sub>2</sub> • + HO <sub>2</sub>	2.7 × 10 <sup>7</sup>	[9]
HO <sub>2</sub> • → O <sub>2</sub> • <sup>-</sup> + H <sup>+</sup>	1.58 × 10 <sup>5</sup> s <sup>-1</sup>	[10]
O <sub>2</sub> • <sup>-</sup> + H <sup>+</sup> → HO <sub>2</sub> •	10 <sup>10</sup>	[10]
•OH + Fe <sup>2+</sup> → Fe <sup>3+</sup> + OH <sup>-</sup>	3.2 × 10 <sup>8</sup>	[11]
HO <sub>2</sub> • + Fe <sup>2+</sup> (+H <sup>+</sup> ) → Fe <sup>3+</sup> + H <sub>2</sub> O <sub>2</sub>	1.2 × 10 <sup>6</sup>	[12]
HO <sub>2</sub> • + Fe <sup>3+</sup> → Fe <sup>2+</sup> + H <sup>+</sup> + O <sub>2</sub>	3.1 × 10 <sup>5</sup>	[13]
O <sub>2</sub> • <sup>-</sup> + Fe <sup>2+</sup> (+2H <sup>+</sup> ) → Fe <sup>3+</sup> + H <sub>2</sub> O <sub>2</sub>	10 <sup>7</sup>	[13]
O <sub>2</sub> • <sup>-</sup> + Fe <sup>3+</sup> → Fe <sup>2+</sup> + O <sub>2</sub>	5 × 10 <sup>7</sup>	[14]
•OH + •OH → H <sub>2</sub> O <sub>2</sub>	4.2 × 10 <sup>9</sup>	[15]
HO <sub>2</sub> • + HO <sub>2</sub> • → H <sub>2</sub> O <sub>2</sub>	8.3 × 10 <sup>5</sup>	[10]
•OH + HO <sub>2</sub> • → O <sub>2</sub> + H <sub>2</sub> O	10 <sup>10</sup>	[15]
•OH + O <sub>2</sub> • <sup>-</sup> → O <sub>2</sub> + OH <sup>-</sup>	10 <sup>10</sup>	[15]
HO <sub>2</sub> • + O <sub>2</sub> • <sup>-</sup> (+H <sup>+</sup> ) → O <sub>2</sub> + H <sub>2</sub> O <sub>2</sub>	9.7 × 10 <sup>7</sup>	[10]

amounts calculated by stoichiometry for total mineralization are used a loss of oxidant could takes place.

Oxidation of organic pollutants by using the Fenton's reagent is modeled considering both complex schemes of radical reactions or simplified approaches. As example, kinetic models for the oxidation and/or mineralization of phenols by using Fenton's reagent proposed in literature are shown in Table 2.

The complex mechanism by which hydroxyl radical is generated in the Fenton process (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) and Fenton-like process (Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>) takes place in serial stages, with most agreeing the outline based on reactions (1) and (2). Almost all of kinetic models proposed in literature used the evolution of the pollutant concentration as an indicator of the oxidation achieved and first order equations with respect to the concentration of hydroxyl radical and the pollutant.

**Table 2**

Kinetic model proposed in literature to describe the oxidation of phenolic compounds by Fenton's reagent.

Parameter	Outline	Kinetic equation	Refs.
Pollutant	P + H <sub>2</sub> O <sub>2</sub> → Prod.	$(-R_p) = kC_p^n$	[10,15–17]
	Radical	$(-R_p) = k_2 C_p C_{H_2O_2} + \frac{k_3 k_1 C_p C_{H_2O_2} C_{Fe^{2+}}}{k_5 C_p + k_3 C_{Fe^{2+}}}$	[12]
		$(-R_p) = \frac{k_5 k_2 C_p C_{H_2O_2} C_{Fe^{2+}}}{k_3 C_p + k_4 C_{H_2O_2} + k_5 C_{Fe^{2+}}}$	[13]
TOC	TOC → CO <sub>2</sub>	$(-R_{TOC}) = k C_{Fe} C_{TOC}^2$	[10]

The kinetic models based on complex radical reaction schemes [21–23] generally considered the equations proposed as stoichiometric irreversible elementary reactions where stoichiometric coefficients of reagents match with partial orders of reaction. Besides the hydroxyl radical concentration is assumed constant over time. Resulting model describes the kinetics of pollutant oxidation depending on the concentration of the reactants (organic pollutant and H<sub>2</sub>O<sub>2</sub>) and the catalyst (Fe<sup>2+</sup>) using a large number of kinetic constants [21–23]. Besides to these complex kinetic models, other approaches consider empirical equations for oxidation and/or mineralization rates. Kinetic parameters in these equations can be estimated empirically by adjustment of experimental data [24–27]. Simplified approaches proposed in literature for oxidation or mineralization commonly include the H<sub>2</sub>O<sub>2</sub> concentration effect in the kinetic constant [17,24–26], because data are obtained at oxidant dosages higher than the theoretically required by stoichiometry for the total mineralization of the initial pollutants. As and example, Zazo et al. [17], operating with excess hydrogen peroxide proposed an empirical kinetic model of second order with respect to organic pollutant, where the concentration of hydrogen peroxide is included in the kinetic constant.

However, it was observed, as cited before [20], that a high dosage of hydrogen peroxide does not improve the mineralization achieved because an asymptotic value of the TOC percent removal is obtained and therefore, an oxidant dosage lower than the theoretically required by stoichiometry should be more convenient from an industrial point of view. Moreover, these simplified kinetic models for mineralization rate in Table 2 do not predict the asymptotic mineralization achieved using this high dosage of oxidant.

The aim of the present work is to develop a pseudokinetic model to predict the mineralization of organic pollutants by Fenton's reagent. The model must be applied to the whole range of H<sub>2</sub>O<sub>2</sub> dosages (below the stoichiometric value or in excess). Validation of this lumped approach will be done by fitting experimental data obtained in the oxidation of phenol using the Fenton's reagent.

## 2. Experimental

The Fenton's reactions have been carried out by adding different amounts of hydrogen peroxide to three aqueous solution of phenol (PhOH) of 500, 1000 and 1500 mg/L. Taking into account the maximum concentration of iron cation permitted for the discharge of industrial wastewater in the region of Madrid (Spain), 10 mg/L of Fe<sup>2+</sup> was the amount selected to carry out the Fenton Runs (FR). This avoids having to add a further step for iron elimination. Analytical-reagent grade or better chemicals as well as Milli-Q water were used in the experiments. Phenol and hydrogen peroxide were purchased from Riedel - DeHaën. Acid pH initial values of solutions (3.5) were adjusted with H<sub>2</sub>SO<sub>4</sub>. Ferrous sulphate heptahydrate obtained from Fluka was used as the catalytic Fe(II) species. The concentration of H<sub>2</sub>O<sub>2</sub> was in the range of 250–7500 mg/L, corresponding to 10–100% approximately of the stoichiometric dosage theoretically required for the total mineralization of phenol. Initial pH was set to 3.5 with sulphuric acid. The pH was left free to vary during the experimental runs achieving an asymptotic value about

**Table 3**

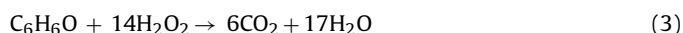
Experimental runs in the oxidation of phenol by Fenton's reagent ( $\text{pH}_0 = 3.5$ ,  $T = 50^\circ\text{C}$ ,  $C_{\text{Fe}^{2+}_0} = 10 \text{ mg/L}$ ).

$C_0$ (mg phenol/L)	% $\text{H}_2\text{O}_2$ <sup>a</sup>	$\text{H}_2\text{O}_2$ (mg/L)
500	10	250
	20	500
	40	1000
	100	2500
1000	10	500
	20	1000
	40	2000
	100	5000
1500	10	750
	20	1500
	40	3000
	100	7500

<sup>a</sup> Percentage of the stoichiometric value required for total mineralization, according to Eq. (3).

## 2.5. Experimental runs are summarized in Table 3.

The  $\text{H}_2\text{O}_2$  reagent was a solution 30% in weight provided by Riedel - DeHaën. The stoichiometric amount of  $\text{H}_2\text{O}_2$  theoretically required for total mineralization was calculated according to the following reactions:



Reaction has been carried out in a batch way at temperature value of  $50^\circ\text{C}$  as an increase in the temperature improves the pollutant oxidation rate but also yields into a higher thermal degradation of the  $\text{H}_2\text{O}_2$ . About 15% of the initial hydrogen peroxide was degraded after 2 h in absence of pollutant and using iron cation (10 mg/L). Temperature was controlled along the experiments with a temperature controller. The pH and oxidation–reduction potential were measured during the runs by means of pH and ORP electrodes, respectively, during a period of 6000 s, assuring that the reaction was finished. Samples drawn were immediately placed in ice and pH was changed to 8–9 by using NaOH in order to stop the oxidation reactions. Soluble iron concentrations were analyzed using a DR/890 colorimeter with the FerroVer Iron reagent, supplied by HACH. All values were close to 10 mg/L.

Total organic carbon (TOC) values in the liquid phase were determined with a Shimadzu TOC-V CSH analyzer by oxidative combustion at  $680^\circ\text{C}$  with platinum catalyzed, and using an infrared detector.

## 3. Kinetic model development

The kinetic model development has been done based on previous works [28,29] but considering the hydrogen peroxide disappearance. The following scheme is considered to describe the mineralization of the organic carbon with hydrogen peroxide to carbon dioxide and water:



$$\text{TOC} = A + B \quad (5)$$

This simplified pathway divides the total organic carbon (TOC) into two components, A and B, which correspond to the oxidizable and refractory organic matter, respectively. The stoichiometric coefficient  $x$  is the fraction of the carbon content of A that reacts to B and therefore is not mineralized. Both A and B are expressed as mg of carbon per liter.  $\nu_g$  corresponds to an empirical stoichiometric coefficient meaning the amount of  $\text{H}_2\text{O}_2$  required to achieve the asymptotic mineralization.

From Eqs. (4) and (5) the following relationships between  $C_A$  and TOC and  $C_{\text{H}_2\text{O}_2}$  and  $C_A$  are given, respectively, in Eqs. (6) and (7).

$$C_A = \frac{\text{TOC} - x \cdot \text{TOC}_0}{1 - x} \quad (6)$$

$$C_{\text{H}_2\text{O}_2} = C_{(\text{H}_2\text{O}_2)_0} - \nu_g \cdot (C_{A0} - C_A) \quad (7)$$

The mass balances for A and TOC species can be written as

$$(-R_A) = \frac{-dC_A}{d\tau} \quad (8)$$

$$(-R_{\text{TOC}}) = (1-x)(-R_A) = \frac{-d\text{TOC}}{d\tau} = \frac{d\text{CO}_2}{d\tau} \quad (9)$$

$$(-R_{\text{H}_2\text{O}_2}) = \nu_g(-R_A) = \frac{-dC_{\text{H}_2\text{O}_2}}{d\tau} \quad (10)$$

with the initial conditions:

$$\tau = 0 \therefore C_{A0} = \text{TOC}_0 \quad (11)$$

where  $\tau$  is a time variable defined specifically for the reactor employed (time in batch reactors, volume to liquid flow rate ratio in plug flow reactor).

The TOC profile as a function of  $\tau$  can be obtained by integration the corresponding mass balance.

$$\text{TOC} = \text{TOC}_0 - \int (1-x)(-R_A) d\tau \quad (12)$$

Assuming that the disappearance rate of A in Eq. (4) can be described by a pseudokinetic model first order for each reactant:

$$(-R_A) = k \cdot C_A \cdot C_{\text{H}_2\text{O}_2} \quad (13)$$

and taking into account the relationship between  $C_A$  and  $C_{\text{H}_2\text{O}_2}$  from Eq. (7), Eq. (13) can be written as follows:

$$\frac{-dC_A}{d\tau} = k \cdot C_A \cdot (C_{(\text{H}_2\text{O}_2)_0} - \nu_g \cdot (C_{A0} - C_A)) \quad (14)$$

By integration of Eq. (14) with further substitution of  $C_A$  by Eq. (6) the following relationship between TOC and time ( $\tau$ ) is obtained:

$$\tau = \frac{1}{k \cdot (C_{(\text{H}_2\text{O}_2)_0} - \nu_g \cdot C_{A0})} \cdot \ln \left[ \frac{C_{A0} [\nu_g (((\text{TOC} - x\text{TOC}_0)/1 - x) - C_{A0}) + C_{(\text{H}_2\text{O}_2)_0}]}{((\text{TOC} - x\text{TOC}_0)/1 - x) C_{(\text{H}_2\text{O}_2)_0}} \right] \quad (15)$$

The kinetic parameter  $k$  and the stoichiometric coefficient  $\nu_g$  can be calculated by fitting the experimental TOC vs time data to Eq. (15). The stoichiometric coefficient  $x$  can be determined from the asymptotic TOC value or calculated as fitting parameter in Eq. (15).

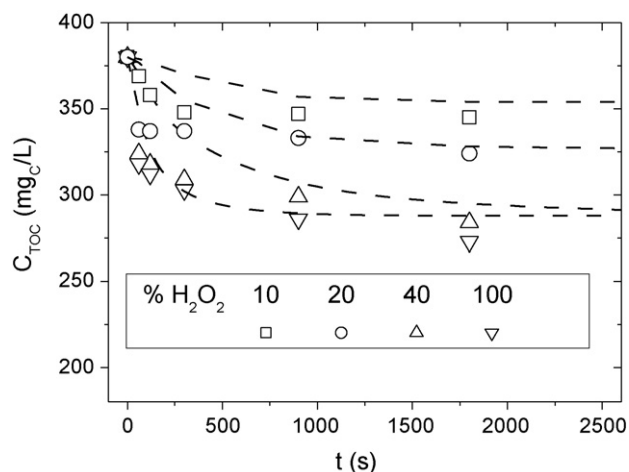
## 4. Results and discussion

Total organic carbon profiles obtained for runs in Table 3 are showed as symbols in Figs. 1–3 (initial phenol concentration 500, 1000 and 1500 mg/L respectively).

As can be seen in Figs. 1–3, the rate of disappearance of TOC is faster when higher dose of  $\text{H}_2\text{O}_2$  is used and the time to reach the asymptotic value decreases. As can be seen in Figs. 1 and 3, fixed a initial concentration of phenol, TOC asymptote obtained using 40% and 100% of  $\text{H}_2\text{O}_2$  of the stoichiometric dosage theoretically required for the total mineralization of phenol is very similar, reaching an asymptotic TOC percent removal close to 30% in both cases. So, an increase of hydrogen peroxide from 40% to 100% does not improve the results. The increase of hydrogen peroxide dosage

**Table 4**Pseudokinetic constant  $k$  and stoichiometric coefficients  $x$  and  $\nu_g$  as calculated by fitting of data obtained in the FR of Phenol (Table 3 using Eq. (15)).

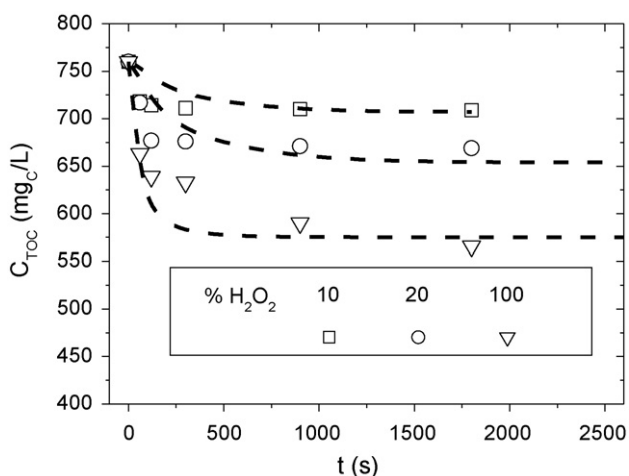
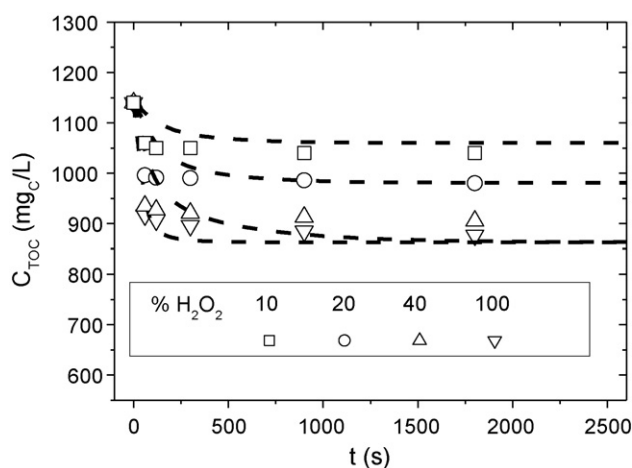
$k$ (L/mgH <sub>2</sub> O <sub>2</sub> s)	$\nu_g$ (mg H <sub>2</sub> O <sub>2</sub> /mg C)	$x$	$SQR_{TOC}$ (mg C/L) <sup>2</sup>	$\sum \left[ \frac{TOC_{EXP} - TOC_M}{TOC_{EXP}} \right]^2$ (mg C/L)	Percentage of variation explained
$2.66 \times 10^{-6}$	2.3	0.72	$6.96 \times 10^4$	0.1942	98.94

**Fig. 1.** Experimental (points) and predicted (lines) TOC values using FR in the PhOH oxidation. H<sub>2</sub>O<sub>2</sub> dosages: (□) 10%; (○) 20%; (△) 40%; (▽) 100% of the stoichiometric values required.  $T = 50^\circ\text{C}$ ;  $C_{Fe} = 10\text{ mg/L}$ ;  $C_{PhOH_0} = 500\text{ mg/L}$ .

from 40% to 100% only produces a shorter time to get the asymptotic TOC percent removal.

By fitting together all TOC vs time data to Eq. (15) the kinetic constant  $k$  and the stoichiometric coefficients  $\nu_g$  and  $x$  have been calculated. Marquardt algorithm was used to do this. Values obtained are reported in Table 4. Residual sum of squares (SQR) was calculated for TOC by comparison of experimental data to the predictions of the corresponding pseudokinetic models. This SQR value is also shown in Table 4. From statistical parameters in Table 4 it can be deduced that the proposed model fits properly the experimental data obtained.

As can be seen in Table 4, the coefficient for hydrogen peroxide consumption,  $\nu_g$ , is much lower (2.3 mg H<sub>2</sub>O<sub>2</sub>/mg C) than the expected if a total mineralization of phenol would happen (6.6 mg H<sub>2</sub>O<sub>2</sub>/mg C according to Eq. (3)). This yields that using a dosage of hydrogen peroxide over this value, 2.3 mg H<sub>2</sub>O<sub>2</sub>/mg C,

**Fig. 2.** Experimental (points) and predicted (lines) TOC values using FR in the PhOH oxidation. H<sub>2</sub>O<sub>2</sub> dosages: (□) 10%; (○) 20%; (△) 40%; (▽) 100% of the stoichiometric values required.  $T = 50^\circ\text{C}$ ;  $C_{Fe} = 10\text{ mg/L}$ ;  $C_{PhOH_0} = 1000\text{ mg/L}$ .**Fig. 3.** Experimental (points) and predicted (lines) TOC values using FR in the PhOH oxidation. H<sub>2</sub>O<sub>2</sub> dosages: (□) 10%; (○) 20%; (△) 40%; (▽) 100% of the stoichiometric values required.  $T = 50^\circ\text{C}$ ;  $C_{Fe} = 10\text{ mg/L}$ ;  $C_{PhOH_0} = 1500\text{ mg/L}$ .

better results would not be obtained in the TOC percent removal with the corresponding loss of oxidant reagent.

It is also obtained that only about 30% of the initial carbon is mineralized remaining the rest in solution as oxidation intermediates.

The simulated values of TOC vs time at different dosages of hydrogen peroxide (from 10% to 100% of the theoretical) and initial concentration of phenol of 500, 1000 and 1500 mg/L calculated by Eq. (15) with parameters in Table 4 are also shown as lines in Figs. 1–3 respectively. As is shown in Figs. 1–3 predicted values (lines) are quite close to the experimental data obtained (symbols), validating the model here developed to predict the TOC evolution.

## 5. Conclusions

The mineralization achieved in an oxidation process of a wastewater is one of the critical parameter to define the oxidation treatment effectiveness. Moreover, if Fenton's reagent is used to achieve this mineralization the hydrogen peroxide dosage is also a critical value from an economical point of view.

The simplified pseudokinetic model for mineralization by using Fenton's reagent proposed and validated in this work, allows predicting the mineralization evolution with time for a wide range of H<sub>2</sub>O<sub>2</sub> dosages (under the stoichiometric value or excess). The model includes an empirical stoichiometric coefficient,  $\nu_g$  that provides a value of the more convenient dosage of hydrogen peroxide in order to avoid the loss of this reagent. This value would have a remarkable impact on the cost of the process. Besides, asymptotic values obtained for the initial TOC percent removal are satisfactorily explained by the model.

## Acknowledgments

The authors thank the Spanish MICINN and Regional Government (Madrid) for financial support provided through Projects CTM2006-00317, CSD2006-00044T, and CM-S2009/AMB/1648.

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