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# Kinetic Modeling of Toxicity Evolution during Phenol Oxidation

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A previously proposed lumped pseudokinetic model has been improved and applied to analyze the literature toxicity evolution data for phenol oxidation using different abatement technologies, such as electrochemical (EC) treatment, photocatalysis (PC), Fenton's reagent (FR), and catalytic wet oxidation (CWO). It has been considered that phenol, P, reacts to a lumped intermediate species I, and the latter reacts to a lumped species

D. In this serial scheme,  $P \xrightarrow{r_1} I \xrightarrow{r_2} D$ , all species can contribute to the toxicity of the aqueous sample. The literature toxicity data found for the oxidation of phenol were analyzed by this model considering first-order kinetics for both reactions in the serial scheme. The ratios of effective nominal concentrations,  $EC_{50}(P)/EC_{50}(I)$  and  $EC_{50}(P)/EC_{50}(D)$ , were calculated from the fitting procedure. Values higher than unity were obtained in some cases, indicating that compounds more toxic than the parent pollutant are produced. Also, the pseudokinetic constants for the first and second reactions in the scheme were estimated. The lumping proposed adequately explains the literature data analyzed.

## 1. Introduction

Phenolic wastewaters are found in a great variety of industries, such as the pharmaceutical, petrochemical, and chemical industries.<sup>1–3</sup> As a result, phenol has probably been the most frequently targeted compound<sup>4–19</sup> in research on oxidation technologies to eliminate nonbiodegradable pollutants in wastewaters. The efficiency of each technology has usually been judged by considering only the pollutant abatement or chemical oxygen demand decrease. In contrast, toxicity evolution during phenol oxidation has scarcely been studied.<sup>20–28</sup> Nevertheless, it has been demonstrated that phenol is not directly oxidized to  $CO_2$ , as some toxic compounds, even more toxic than phenol, can be produced as first intermediates.<sup>29,30</sup> Therefore, conversions of phenol (P), total organic carbon (TOC), and/or chemical oxygen demand (COD) are not sufficient with regard to assessing the detoxification achieved for the original phenolic wastewater; other pollution indicators must be employed. The toxicity unit (TU) is one of the most recently used parameters for this detoxification evaluation. The normalized procedure commonly used to do this is the Microtox bioassay (AZUR Environmental, Carlsbad, CA; formerly Microbics Corporation).<sup>31</sup>

The standard Microtox test procedure is based on the decrease of light emission by *Photobacterium phosphoreum* resulting from its exposure to a toxicant, using a Microtox M500 Analyzer (AZUR Environmental). The inhibition of the light emitted by the bacteria is measured after contact times of 5 and 15 min. The parameter  $EC_{50}$  is defined as the effective nominal concentration of toxicant (in milligrams per liter) that reduces the intensity of light emission by 50%. The parameter  $IC_{50}$  is defined as the percentage of the initial volume of sample to the volume of the sample yielding, after the required dilution, a 50% reduction of the light emitted by the microorganisms. The toxicity units of a wastewater are calculated as

$$TU = \frac{100}{IC_{50}} \quad (1)$$

If the aqueous sample contains only compound *i* at concentration  $C_i$ , the toxicity unit can be predicted by the relationship

$$TU = \frac{C_i}{EC_{50,i}} \quad (2)$$

The toxicity of an aqueous sample containing a mixture of compounds can be predicted from the  $EC_{50}$  values corresponding to the individual components. Toxicity values, as TUs, can be predicted according to the following expression, which is based on the concept of concentration addition<sup>32,33</sup>

$$TU = \sum \frac{C_i}{EC_{50,i}} \quad (3)$$

where  $C_i$  is the concentration in the mixture, in milligrams per liter, of the individual pollutant *i*.

During the phenol oxidation process, toxicity can change; depending on the technology and operation conditions, toxicity can increase during initial stages, reaching a maximum with a further decrease.<sup>20,22,24–28,30</sup> A maximum in the toxicity profile over time means that the first oxidation intermediates are more toxic than the parent pollutant. On the other hand, if toxicity always decreases during the oxidation treatment, intermediates that are less toxic than the initial pollutant are produced.

## 2. Lumping Approach

One possible strategy to predict toxicity values versus time is by using eq 3; this approach requires the prediction of the change in the organic composition during the process.<sup>30</sup> Such an approach would require the discrimination of a complex kinetic model able to predict the evolution of the organic mixture during the oxidation process. To simplify this difficult task, a lumping approach for detoxification modeling has been proposed.<sup>28</sup> In this simplified approach, the following reaction scheme is considered



where P is the original pollutant (phenol, in this case) and I and D are the lumped species corresponding to the carbon-containing compounds produced in serial steps in the oxidation

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process. Species P, I, and D are expressed in terms of organic carbon content [milligrams of carbon per liter (mg<sub>C</sub>/L)].

In the previous study,<sup>28</sup> it was assumed that lumped species D had negligible toxic effects. In the present work, a more general approach is proposed, assuming that all species P, I, and D can contribute to the toxicity of the sample. Taking into account eqs 3 and 4, the toxicity units of a sample at a certain stage of the treatment can be calculated as

$$TU = \frac{C_P}{EC_{50}(P)} + \frac{C_I}{EC_{50}(I)} + \frac{C_D}{EC_{50}(D)} \quad (5)$$

where  $EC_{50}(P)$ ,  $EC_{50}(I)$ , and  $EC_{50}(D)$  are the effective nominal concentrations (mg<sub>C</sub>/L) of P, I, and D, respectively, that reduce the intensity of light emission by 50%. If the only initial pollutant is phenol, the  $EC_{50}(P)$  value can be experimentally determined or obtained from the literature. A value of  $EC_{50}(P) = 12$  mg/L (as carbon content) can be assumed.<sup>20</sup>

On the other hand, the effective nominal concentrations for the lumped species I and D,  $EC_{50}(I)$  and  $EC_{50}(D)$ , are unknown parameters that must be calculated from data fitting. The values of  $EC_{50}(I)$  and  $EC_{50}(D)$  provide an idea of the toxicity of the products generated with the progress of oxidation in relation to the toxicity of the original sample and can differ depending on the oxidation treatment or the operating conditions applied. The lower the  $EC_{50}$  value, the more toxic the compound or lumped species.

For the scheme in eq 4, the mass balances for species P, I, and D in a batch or plug-flow reactor can be written as

$$\frac{-dC_P}{d\tau} = r_1 \quad (6)$$

$$\frac{dC_I}{d\tau} = r_1 - r_2 \quad (7)$$

$$\frac{dC_D}{d\tau} = r_2 \quad (8)$$

where  $\tau$  is a time variable defined specifically for the reactor employed.

The disappearance rate of the toxicity units can be expressed by eqs 6–8, according to the relationship in eq 5.

If first-order pseudokinetic models are assumed for  $r_1$  and  $r_2$ , that is

$$r_1 = k_1 C_P \quad (9)$$

$$r_2 = k_2 C_I \quad (10)$$

then the following analytical solutions can be obtained by integration of eqs 6–8

$$C_P = C_{P0} \exp(-k_1 \tau) \quad (11)$$

$$C_I = C_{P0} \frac{k_1}{k_2 - k_1} [\exp(-k_1 \tau) - \exp(-k_2 \tau)] \quad (12)$$

$$C_D = C_{P0} \frac{1}{k_2 - k_1} [(k_2 - k_1) + k_1 \exp(-k_2 \tau) - k_2 \exp(-k_1 \tau)] \quad (13)$$

Substituting eqs 11–13 into eq 5 and taking into account the initial conditions

$$\tau = 0 \quad C_P = C_{P0}, TU = TU_0 = \frac{C_{P0}}{EC_{50}(P)} \quad (14)$$

gives the following dimensionless expression for toxicity units

$$\frac{TU}{TU_0} = \exp(-k_1 \tau) + \frac{EC_{50}(P)}{EC_{50}(I)} \frac{k_1}{k_2 - k_1} [\exp(-k_1 \tau) - \exp(-k_2 \tau)] + \frac{EC_{50}(P)}{EC_{50}(D)} \frac{1}{k_2 - k_1} [(k_2 - k_1) + k_1 \exp(-k_2 \tau) - k_2 \exp(-k_1 \tau)] \quad (15)$$

The contributions of P, I, and D to the toxicity of the sample correspond to the first, second, and third terms on the right-hand side of eq 15. The pseudokinetic parameters  $k_1$  and  $k_2$  can be expressed as functions of temperature by means of an Arrhenius expression of the form

$$k_i = \exp\left(\ln k_{i0} - \frac{E_{ai}}{RT}\right) \quad (16)$$

### 3. Results and Discussion

As previously discussed, the analysis of toxicity evolution with the oxidation progress has been little studied to date; however, increasing attention is being paid to this issue. The available data were published quite recently (during the past five years). In this study, toxicity data obtained in the photocatalyzed (PC) degradation of phenol,<sup>22</sup> the electrochemical (EC) oxidation of phenol,<sup>25</sup> the oxidation of phenol using Fenton's reagent (FR),<sup>26</sup> and the catalytic wet oxidation (CWO) of phenol using several catalysts and operating conditions<sup>20,23,24,27,30</sup> were analyzed. Experimental conditions used in the literature reports are summarized in Table 1.

In the case of phenol abatement using ozonation technology, no profile of the toxicity evolution but only data for the final stage are available in the literature.<sup>34,35</sup> Therefore, these ozonation results could not be analyzed using the kinetic approach proposed above.

Azevedo et al.,<sup>22</sup> in the photocatalyzed degradation of phenol, presented their results as  $LC_{50}$  profiles with irradiation time at several saline concentrations using a microcrustacean (*Artemia sp.*) different from that used in the Microtox bioassay (*Photobacterium phosphoreum*). From the reported  $IC_{50}$  values, the corresponding  $TU/TU_0$  data were calculated according to eq 1 and are summarized in Figure 1. Even though toxic organic intermediates (such as catechol, hydroquinone, etc.) were found in the reaction media by the authors, a continuous toxicity decrease is noticed, as can be seen from the results in Figure 1. If these data are fitted to eq 15, estimated parameters can be obtained, as summarized in Table 2. In this table, statistical values from the fitting are also given: the Fisher  $F$  value, the residual sum of squares (SQR), and the percentage of the variation that can be explained. The  $\tau$  variable in this case is the reaction time.

As can be seen, both lumped species I and D are less toxic than phenol. This accords with the toxicity profiles shown in Figure 1. Values predicted using the parameters in Table 2 are shown in Figure 1 as lines. A favorable agreement is obtained between the experimental and predicted values.

Yavuz and Koparal<sup>25</sup> presented results obtained in the electrochemical oxidation of phenol in terms of the relative toxicity index ( $TU/TU_0$ ) vs time measured by the Microtox bioassay at several phenol concentrations. A delay time is always noticed (40–50 min). Data reported at phenol concentrations of 100 and 200 mg/L are shown in Figure 2 (after correction of

Table 1. Literature Data from Phenol Oxidation Including Toxicity Profiles

ref	technology <sup>a</sup>	microorganism	C <sub>0</sub> <sup>b</sup>	T (°C)	catalyst	pH	operation	other variables
22	PC	Artemia sp.	100	25	TiO <sub>2</sub>	7 (initial)	batch, C <sub>cat</sub> = 0.5 g/L	C <sub>NaCl</sub> = 0, 2, 50 g/L
25	EC	Photobacterium phosphoreum	50–500	20–50	Ru mixed metal oxide electrode	3–11	batch	C <sub>Fe2+</sub> = 1–100 mg/L, C <sub>H2O2</sub> = 500–5000 mg/L
26	FR	Photobacterium phosphoreum	100	25	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	3	batch	P = 16 bar
20	CWO	Photobacterium phosphoreum	800	140	Engelhard Cu-0203T	3.5	batch, C <sub>cat</sub> = 180 g/L	P = 8, 12, 16 atm
23	CWO	Photobacterium phosphoreum	1000	127–160	Engelhard Cu-0203T	7–8	continuous	P = 16 bar
30	CWO	Photobacterium phosphoreum	1000	127–160	AC Industrial React FE01606A	3.5	continuous	P = 16 bar
24	CWO	Photobacterium phosphoreum	1000	160	AC Industrial React FE01606A	3.5 8 (buffered)	continuous	P = 8 bar
27	CWO	Photobacterium phosphoreum	1000	127	AC (Merck 102514), HNO <sub>3</sub> , and thermal pretreatment Fe impregnation	3.5	continuous	

<sup>a</sup> PC, photocatalytic; EC, electrochemical; FR, Fenton's reagent; CWO, catalytic wet oxidation. <sup>b</sup> C<sub>0</sub> in units of milligrams of compound per liter.

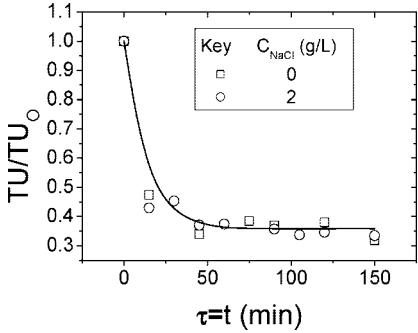


Figure 1. Experimental (points) and predicted (lines) values of toxicity evolution in the photocatalyzed degradation of phenol. Data from Azevedo et al.<sup>22</sup> fitted to eq 15. Estimated parameters in Table 2.

Table 2. Parameters Estimated by Fitting Data from Azevedo et al.,<sup>22</sup> Yavuz and Koparal,<sup>25</sup> and Zazo et al.<sup>26</sup>

parameter	ref 22	ref 25	ref 26		
			[Fe] = 1 mg/L	[Fe] = 5 mg/L	[Fe] = 10 mg/L
k <sub>1</sub> (1/min)	0.09	0.0053	0.074	2.03	8.71
k <sub>2</sub> (1/min)	0.21	0.151	0.042	1.33	2.71
EC <sub>50</sub> (P)/EC <sub>50</sub> (I)	<0.01	9.5	17.5	14.9	14.2
EC <sub>50</sub> (P)/EC <sub>50</sub> (D)	0.359	<0.01	1.98	1.77	1.14
SQR	0.01108	0.04646	6.15	0.8557	0.1338
F	1085.37	1364	46.413	236.38	332.514
% σ <sub>explained</sub>	98.43	94.2	92.0	96	99

the time by subtraction of the corresponding delay time). As can be seen, similar curves result, as expected from pseudo-first-order kinetics. Moreover, an initial increase in toxicity is noticed, and the toxicity reaches a maximum with a further decrease in the TU/TU<sub>0</sub> ratio. The data in Figure 2 were fitted to eq 15, and the parameters estimated are summarized in Table 2. It was found that the EC<sub>50</sub>(I) value is lower than that of the parent pollutant, phenol, which explains the maximum obtained in the toxicity profile.

Zazo et al.<sup>26</sup> studied the evolution of ecotoxicity upon Fenton's oxidation of phenol in water using Fenton's reagent. They reported TU profiles with time obtained at 25 °C using an initial phenol concentration of 100 mg/L and a dosage of hydrogen peroxide of 500 mg/L. The reported toxicity profiles correspond to runs carried out in a batch manner at catalyst (iron cation) concentrations of 1, 5 and 10 mg/L. From these toxicity values, the TU/TU<sub>0</sub> ratios were calculated and are shown in Figure 3. As can be seen, the catalyst concentration changes the obtained toxicity profiles.

Because few data were available at each iron concentration in the region near the maximum, the value of the pseudokinetic

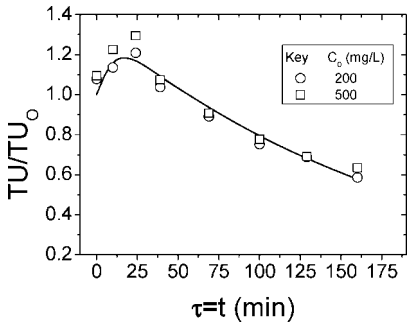
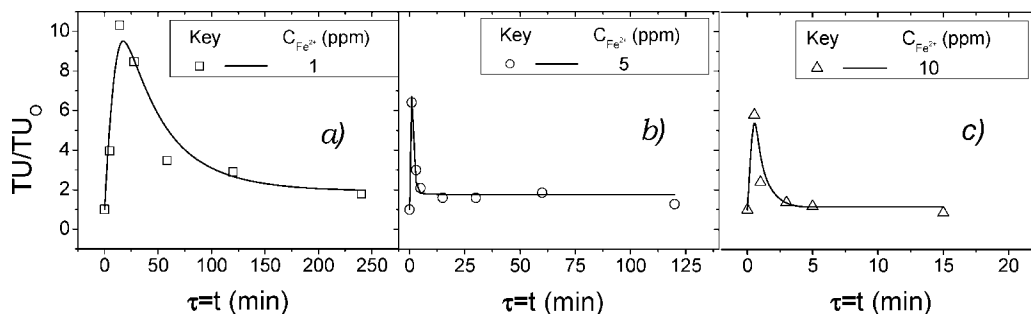
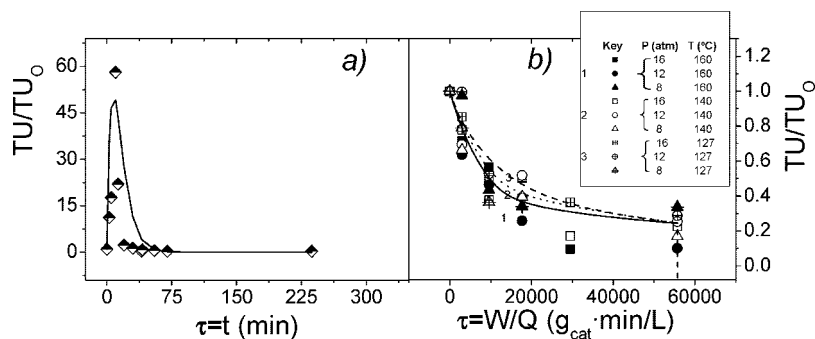


Figure 2. Experimental (points) and predicted (lines) values of toxicity evolution in the photocatalyzed degradation of 200 and 500 mg/L phenol. Data from Yavuz and Koparal<sup>25</sup> fitted to eq 15. Estimated parameters in Table 2.



**Figure 3.** Experimental (points) and predicted (lines) values of toxicity evolution in the Fenton's oxidation of phenol. Data from Zazo et al.<sup>26</sup> fitted to eq 15. Estimated parameters in Table 2.  $[\text{Fe}^{2+}]_0 =$  (a) 1, (b) 5, and (c) 10 mg/L.



**Figure 4.** Experimental (points) and predicted (lines) values of toxicity evolution in the catalytic wet oxidation of phenol with Cu-0203 catalyst at (a) acidic and (b) basic pH. Data from Santos et al.<sup>20,23</sup> fitted to eqs 15 and 16. Estimated parameters in Table 3.

**Table 3. Parameters Estimated by Fitting Data from Santos et al. for the Catalytic Wet Oxidation of Phenol with Cu-0203<sup>20,23</sup> and Activated Carbon (AC)<sup>30,24</sup> as Catalysts**

parameter	ref 20	parameter	ref 23	ref 30	parameter	ref 24
$k_1$ (1/min)	0.135	$k_{10}$ (L/g <sub>cat</sub> ·min)	$6.655 \times 10^{-3}$	0.95	$k_1$ (L/g <sub>AC</sub> ·min)	$6.5 \times 10^{-5}$
$k_2$ (1/min)	0.121	$k_{20}$ (L/g <sub>cat</sub> ·min)	—	$2.68 \times 10^6$	$k_2$ (L/g <sub>AC</sub> ·min)	—
$k_1'$ (L/g <sub>cat</sub> ·min)	$7.06 \times 10^{-4}$	$E_{a1}/R$ (K)	1993.5	3470	$\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{I})$	<0.01
$k_2'$ (L/g <sub>cat</sub> ·min)	$6.72 \times 10^{-4}$	$E_{a2}/R$ (K)	—	9450	$\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{D})$	<0.01
$\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{I})$	130	$\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{I})$	<0.01	75		
$\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{D})$	<0.01	$\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{D})$	<0.01	<0.01		
SQR	2775	SQR	0.741	974100	SQR	0.005811
$F$	21.549	$F$	543.053	49.504	$F$	3145.722
% $\sigma_{\text{explained}}$	15	% $\sigma_{\text{explained}}$	82	94	% $\sigma_{\text{explained}}$	97

constant  $k_1$  was previously obtained by fitting the corresponding phenol (P) profiles given by Zazo et al.<sup>26</sup> to eq 11. Using this  $k_1$  value, the parameter  $k_2$  was obtained by fitting the TU/TU<sub>0</sub> profiles in Figure 3 to eq 15. The values obtained are summarized in Table 2, and the TU/TU<sub>0</sub> values predicted using these estimated parameters are shown as lines in Figure 3. As can be seen, a favorable agreement is obtained in all cases. A value of  $\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{I})$  higher than the ratio  $\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{D})$  is obtained, which explains the maximum observed in the toxicity profile. Furthermore, both ratios  $\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{I})$  and  $\text{EC}_{50}(\text{P})/\text{EC}_{50}(\text{D})$  are higher than unity, but the values obtained decrease as the iron concentration increases. Moreover, as the catalyst concentration increases, the pseudokinetic constants  $k_1$  and  $k_2$  also increase. Therefore, the catalyst concentration has a remarkably positive effect on both the detoxification achieved and the time required. Moreover, Zazo et al.<sup>26</sup> also reported the TU values obtained at 4 h of reaction time, employing the higher iron concentration (up to 100 mg/L) and temperature ( $T = 50$  °C), and obtained a lower residual toxicity than the original value. These data could not be analyzed here as no profiles of TU vs time were reported under these conditions, although their results indicate that, by choosing an adequate iron concentration and temperature, suitable detoxification can be obtained using Fenton's reagent.

Santos et al.<sup>20,23</sup> studied the catalytic wet oxidation of phenol at acidic and basic pH values using a commercial catalyst based on copper (Engelhardt Cu-0203). The toxicity profiles obtained at acidic and basic pH are shown in Figure 4. A remarkable increase in toxicity in the first oxidation stages with a further decrease was found at acidic pH, corresponding to the maximum observed in Figure 4a.

By fitting the data obtained at acidic pH (Figure 4a) to eq 15, estimated parameters were obtained, as summarized in Table 3. Because the data at acidic pH were obtained in a batch run, the values of the pseudokinetic constants were also related to the catalyst concentration,  $k'$ , assuming the following linear dependence

$$k_i = k'_i C_{\text{cat}} \quad (17)$$

Parameters obtained from the data at neutral–basic pH (Figure 4b) are also summarized in Table 3. Although temperature changed at basic pH between 127 and 160 °C, the dependence of the pseudokinetic constant on this variable was taken into account by means of eq 16.

Santos et al.<sup>24,30</sup> also used a commercial activated carbon (AC) as a catalyst in the wet oxidation of phenol at acidic (A) and basic (B) pH (Industrial React FE01606A, kindly supplied

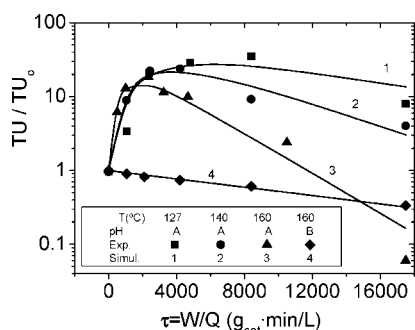


**Table 4. Parameters Estimated by Fitting Data from Quintanilla et al.<sup>27</sup> in the Catalytic Wet Oxidation of Phenol with Nonimpregnated (AC, AC-T, AC-N) and Iron-Impregnated (CAT, CAT-N) Activated Carbon from Merck as the Catalyst**

catalyst	AC	AC-T	AC-N	CAT	CAT-N
$k_1$ (L/g <sub>AC</sub> ·min)	$5.8 \times 10^{-5}$	$8.24 \times 10^{-5}$	$1.53 \times 10^{-4}$	$2.39 \times 10^{-4}$	$2.39 \times 10^{-4}$
$k_2$ (L/g <sub>AC</sub> ·min)	$1.1 \times 10^{-4}$	$8.33 \times 10^{-5}$	$2.89 \times 10^{-4}$	$2.16 \times 10^{-4}$	$7.03 \times 10^{-4}$
EC <sub>50</sub> (P)/EC <sub>50</sub> (D)	<0.01	<0.01	<0.01	<0.01	<0.01
EC <sub>50</sub> (P)/EC <sub>50</sub> (I)	23.0	22.2	34.8	14.9	125.5
SQR	5.273	2.034	4.179	0.248	13.45
$F$	32.35	137.7	117.4	813.39	181.32
% $\sigma_{\text{explained}}$	80.64	94.36	91.01	99.0	96.1

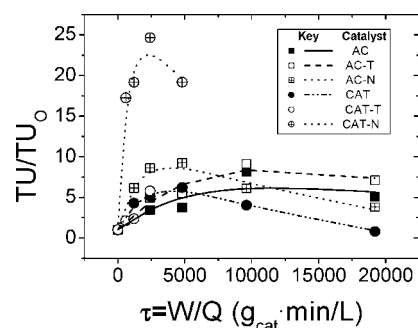
**Table 5. Comparison of EC<sub>50</sub>(P)/EC<sub>50</sub>(I),  $k_1$ , and  $k_2$  Values Estimated by Fitting Literature Data Obtained in the Catalytic Oxidation of Phenol<sup>a</sup>**

ref	catalyst	EC <sub>50</sub> (P)/EC <sub>50</sub> (I)	EC <sub>50</sub> (P)/EC <sub>50</sub> (D)	$k_1$ (L/g <sub>cat</sub> ·min)	$k_2$ (L/g <sub>cat</sub> ·min)
20	Cu-0203	137	<0.01	$7 \times 10^{-4}$	$7 \times 10^{-4}$
23	Cu-0203 (buffered)	<0.01	<0.01	$4.6 \times 10^{-5}$	—
30	AC Industrial React	75	<0.01	$1.62 \times 10^{-4}$	$1.47 \times 10^{-4}$
24	AC Industrial React (buffered)	<0.01	<0.01	$6.5 \times 10^{-5}$	—
27	AC from Merck	23.0	<0.01	$5.8 \times 10^{-5}$	$1.1 \times 10^{-4}$
27	AC-T from Merck	22.2	<0.01	$8.24 \times 10^{-5}$	$8.33 \times 10^{-5}$
27	AC-N from Merck	34.8	<0.01	$1.53 \times 10^{-4}$	$2.89 \times 10^{-4}$
27	CAT	14.9	<0.01	$2.39 \times 10^{-4}$	$2.16 \times 10^{-4}$
27	CAT-N	125.5	<0.01	$2.39 \times 10^{-4}$	$7.03 \times 10^{-4}$

<sup>a</sup>  $T = 127^\circ\text{C}$ .**Figure 5.** Experimental (points) and predicted (lines) values of toxicity evolution in the catalytic wet oxidation of phenol with AC Industrial React FE01606A as the catalyst at (A) acidic and (B) basic pH. Data from Santos et al.<sup>24,30</sup> fitted to eqs 15 and 16. Estimated parameters in the Table 3.

by Chemviron Carbon). Toxicity values obtained at acidic pH,<sup>30</sup> shown in Figure 5, were already analyzed elsewhere,<sup>28</sup> and the kinetic parameters obtained are summarized in Table 3. The results obtained using this AC and buffering the solution (500 mg/L of sodium bicarbonate was used to keep the pH between 7 and 8)<sup>24</sup> are also included in Figure 5, and the data were fitted to eq 15. The parameters obtained at neutral pH are listed in Table 3. As was observed with catalyst Cu-0203, a maximum in the toxicity profile is obtained at acidic conditions, but this maximum is not observed at neutral–basic pH. This corresponds to a value of EC<sub>50</sub>(P)/EC<sub>50</sub>(I) that is much higher at acidic pH than at basic pH and demonstrates a more toxic oxidation route at acidic conditions. Therefore, the control of pH plays an important role in toxicity evolution. If a solution is buffered with bicarbonate to keep the pH between 7 and 8, no toxic compounds appear, and the only toxic species seems to be phenol. On the other hand, if buffered conditions are used, the phenol disappearance rate is lower than that corresponding to the same catalyst under acidic conditions, as can be deduced from Table 3.

Quintanilla et al.<sup>27</sup> recently presented results on the detoxification of an aqueous phenol solution using a commercial activated carbon (AC) from Merck (102514) as the catalyst at 127 °C. The three activated carbons, AC, AC-T, and AC-N, were impregnated with iron cations (2.5 wt %) using the incipient-wetness impregnation method at ambient temperature. The corresponding catalysts obtained from AC, AC-T, and

**Figure 6.** Experimental (points) and predicted (lines) values of toxicity evolution in the catalytic wet oxidation of phenol by using nonimpregnated (AC, AC-T, AC-N) and iron-impregnated (CAT, CAT-T, CAT-N) activated carbon from Merck as catalysts. Data from Quintanilla et al.<sup>27</sup> fitted to eq 15. Estimated parameters in Table 4.

AC-N after iron addition are denoted CAT, CAT-T, and CAT-N, respectively. From toxicity data provided by the authors, the TU/TU<sub>0</sub> values were calculated and are shown in Figure 6. Because few data were available for each catalyst tested, the  $k_1$  value was determined separately by fitting the corresponding phenol profiles<sup>27</sup> to eq 11, as was done with the data from Zazo et al.<sup>26</sup> Subsequently, TU/TU<sub>0</sub> values were fitted to eq 15 to determine the pseudokinetic parameter  $k_2$  and the toxicity ratios. These are summarized in Table 4. Data from CAT-T were not considered because not enough experimental data were available. In Figure 6, the simulated values obtained using parameters in Table 4 are shown as lines. As can be seen, the model in eq 15 is also able to explain quite well the data obtained with the different catalysts tested by Quintanilla et al.<sup>27</sup> In all cases, the ratio EC<sub>50</sub>(P)/EC<sub>50</sub>(I) is higher than unity; the highest value was obtained for CAT-N, meaning that compounds more toxic than the original pollutant were produced in the phenol oxidation, as was observed with other catalysts.<sup>20,28</sup> In contrast, the ratio EC<sub>50</sub>(P)/EC<sub>50</sub>(D) is much lower than unity, meaning that the last refractory intermediates are not toxic. Therefore, if enough time were employed in the reactor, detoxification of the effluent would be achieved.

As data for different catalyst and pH conditions have been analyzed, a summary of estimated EC<sub>50</sub>(P)/EC<sub>50</sub>(I) and EC<sub>50</sub>(P)/EC<sub>50</sub>(D) ratios and pseudokinetic constants  $k_1$  and  $k_2$  (related to the catalyst weight) is provided in Table 5. The  $k_1$  and  $k_2$

values estimated in the catalytic wet oxidation of phenol with several catalysts at a temperature of 127 °C (the temperature for which the most data were available) are included in this table for comparison.

#### 4. Conclusions

Treatment of phenolic wastewaters using oxidation technologies must take into account the toxicity evolution with the oxidation progress. Although a relatively large number of oxidation species can be produced in the oxidation route, a simplified approach using lumping strategies can be a useful tool for designing the process in order to reach a specified detoxification of the initial wastewater.

From the data in Figures 1–6, it can be deduced that the serial scheme proposed elsewhere,<sup>28</sup> also including the final lumped product D as a possible toxic species, fits reasonably well the toxicity data available in the literature for phenol oxidation in the aqueous phase under the application of several technologies and varying operating conditions. Furthermore, literature data fitted to eq 15 allow the pseudokinetic constant for the disappearance rate of the original pollutant, phenol, and first intermediates, lumped as species I, to be estimated. Moreover, if the last oxidation products, lumped as D, are still toxic, the residual toxicity is obtained as an asymptotic value, as was observed in some oxidation technologies.

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#### Notation

AC = activated carbon

$C_i$  = concentration of species  $i$  (P, I, D) expressed as carbon content (mgC/L)

D = lumped species (sum of CO<sub>2</sub> and biodegradable short-chain acids) (mgC/L)

$E_a/R$  = activation energy/gas constant (K)

EC<sub>50</sub> = effective nominal concentration (mgC/L)

$F$  = Fisher  $F$  (statistical parameter of nonlinear regression)

I = lumped species corresponding to the toxic first organic intermediates (mgC/L)

IC<sub>50</sub> = ratio of the initial volume of the sample to the volume of the sample yielding a 50% reduction of the light emitted by the microorganisms

$k$  = pseudokinetic constant for pollutant oxidation (L/g<sub>cat</sub>·min)

P = lumped species for the pollutant or pollutant mixture in the initial aqueous sample (mgC/L)

$P_{O_2}$  = oxygen pressure (bar)

$Q$  = liquid flow rate (L/min)

$r$  = reaction rate (mgC/g<sub>cat</sub>·min)

SQR = residual sum of squares [ $\sum (TU_{exp} - TU_{calc})^2$ ]

$T$  = temperature (°C)

TU = toxicity unit

$W$  = catalyst weight in the reactor (g)

$\tau$  = time (batch) or  $W/Q$  ratio in the fixed-bed reactor

$\sigma$  = variance

#### Subscripts

0 = related to the initial conditions or pre-exponential factor

1,2 = related to reactions 1 and 2, respectively

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