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Evolution of Ecotoxicity upon Fenton's Oxidation of Phenol in Water

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This work deals with the evolution of intermediates and ecotoxicity upon Fenton's oxidation of phenol in aqueous solution. The EC_{50} values of the intermediates identified in the oxidation pathway of phenol have been measured. Some of these compounds, mainly hydroquinone and *p*-benzoquinone, showed toxicity levels much higher than phenol itself. Depending on the operating conditions, these intermediates could be completely transformed into organic acids, mainly oxalic and formic. Ecotoxicity values substantially lower than those expected from the chemical composition were measured in the reaction samples. This is explained by a reduction of the concentration of aromatic intermediates when the pH was adjusted at 6–8 (according to what is required by the standard bioassay ISO 11348-3). Formation of complexes between hydroquinone and *p*-benzoquinone at increasing pH can remove from solution those highly toxic intermediates whose very low EC_{50} values give rise to a high ecotoxicity even at fairly low concentrations. This together with the enhanced decomposition of residual H_2O_2 at increasing pH represent important beneficial effects of the neutralization step following Fenton treatment which allow a complementary cleaning of the effluent.
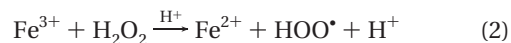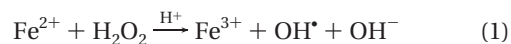
Introduction

The wastewaters resulting from the widespread use of phenols in chemical, coke, paper, and pharmaceutical industries represent a serious pollution problem. Use of conventional biological treatments is limited to low-phenol concentration waste streams and other treatments, such as incineration, wet air oxidation (WAO), or catalytic wet air oxidation (CWAO) which require high-energy consumption. Therefore, new solutions are being investigated for wastewaters with relatively low organic contents. Use of advanced oxidation processes (AOP) has been claimed to be an efficient solution to remove phenolic contaminants from aqueous off-streams. AOP's have been defined as near-ambient temperature and pressure water treatment processes which involve generation of hydroxyl radicals (OH•) in sufficient quantity to allow water purification (*1*). This radical is a strong ($E°$ 2.8 V) and nonselective oxidant. For instance, oxidation rate constants for most organic compounds are usually several orders of magnitude higher than those reported for other oxidants such as ozone (*2*). Due to the fact that hydroxyl radicals are so reactive, they are very unstable and must be continuously produced in situ by means of chemical or photochemical

reactions. The most widely known methods of generating OH• radicals include O_3/catalyst, O_3 at high pH (>8.5), O_3/ H_2O_2, Fenton's Reagent (Fe^{2+}/H_2O_2), and photoprocesses such as O_3/UV, O_3/H_2O_2/UV, H_2O_2/UV, photo-Fenton, or photocatalytic oxidation (UV/TiO_2) (*3–5*).

Use of Fenton's reagent is one of the most effective ways for OH• radical generation. In addition, due to the simplicity of equipment and mild operation conditions (atmospheric pressure and room temperature) it has been postulated as the most economic AOP alternative (*6–8*).

The mechanism of OH• generation, which has been well established in the literature (*9–12*), is quite complex. Briefly, H_2O_2 decomposes catalytically by means of Fe^{2+} at acid pH giving rise to hydroxyl radicals. Fe^{3+} can react, at acid pH, with H_2O_2 in the so-called Fenton-like reaction, regenerating the catalyst and thus sustaining the process. Moreover, in phenols oxidation some intermediates are also able to reduce Fe(III) to Fe(II) (*9*)

$$Fe^{2+} + H_2O_2 \xrightarrow{H^+} Fe^{3+} + OH^\bullet + OH^- \qquad (1)$$

$$Fe^{3+} + H_2O_2 \xrightarrow{H^+} Fe^{2+} + HOO^\bullet + H^+ \qquad (2)$$

Most commonly works reported on this topic follow the efficiency of this process through the evolution of residual phenol concentration, chemical oxygen demand (COD), or total organic carbon (TOC) (*11, 13–15*). Nevertheless, due to a higher social and political concern on environmental risk, new parameters (i.e., ecotoxicity) are being considered in order to achieve an environmentally safe effluent.

Evolution of toxicity of phenolic wastewaters upon different oxidation treatments (i.e., ozonation, photocatalytic treatment, CWAO) has been studied (*16–19*), although few works have been reported in this respect relative to Fenton's oxidation (*20*). In previous work we established the route of phenol oxidation by Fenton's reagent (*21*), and the aim of this work now is to learn about the evolution of intermediates and toxicity at different operating conditions. Ecotoxicity according to a normalized test, Microtox Acute Toxicity Test (*22*), has been used as the main parameter to follow.

Materials and Methods

The oxidation runs were carried out in 100 mL stirred glass bottles placed in an orbital shaker (200 rpm). The reaction volume was 50 mL. The starting concentrations were 100 mg/L of phenol and 500, 2500, and 5000 mg/L of H_2O_2, which correspond to 1, 5, and 10 times the theoretical stoichiometric amount of H_2O_2 necessary to completely oxidize phenol up to CO_2 and H_2O. The Fe^{2+} dose was varied between 1 and 100 mg/L. All reactants were added simultaneously at the beginning of the runs. The initial pH was 3.0, which has not been controlled along the process. In these conditions phenol oxidation with H_2O_2 alone was negligible. Temperature was varied between 25 and 50 °C.

Reaction samples were immediately analyzed to avoid further evolution. Phenol and aromatic byproducts were identified and quantified by means of HPLC (Varian Pro-Start 240) using a diode array detector (330 PDA). A Microsorb C_{18} 5 μm column (MV 100, 15 cm long, 4.6 mm diameter) was used as the stationary phase and 1 mL/min of 4 mM aqueous sulfuric solution as the mobile phase. A UV detector was used at a wavelength of 210 nm to quantify phenol, catechol, and hydroquinone and at 246 nm for *p*-benzoquinone. Short-chain organic acids were analyzed by ion chromatography with chemical suppression (Metrohm 790 IC) using a

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TABLE 1. Results Obtained after 4 h of Reaction at Different Initial Experimental Conditions ([phenol]$_0$ = 100 mg/L; TOC$_0$ = 76.6 mg/L; pH$_0$ = 3)

experimental conditions			results					
Fe^{2+} dose (mg/L)	H$_2$O$_2$ dose (mg/L)	T (°C)	$X_{TOC}{}^a$	$X_{H2O2}{}^b$	$\Sigma_{aromatics}{}^c$ (mg/L)	$\Sigma_{acids}{}^d$ (mg/L)	$\Sigma_{carbon}{}^e$ (mg/L)	TU (15 min)
1	500	25	0.06	0.32	12.67	40.2	21.4	9.2
5			0.23	0.50	0.00	54.0	16.2	6.8
10			0.26	0.63	0.00	65.5	18.3	5.5
100			0.27	1.00	0.00	136.0	36.2	1.4
100	2500	25	0.37	0.98	0.00	127.3	33.9	6.5
	5000		0.56	0.97	0.00	118.4	32.7	18.2
1	500	50	0.21	0.56	1.13	43.1	13.1	3.9
10			0.39	0.74	0.00	64.3	18.4	2.6

^{a} X_{TOC}: fraction of organic carbon oxidized up to CO$_2$. ^{b} X_{H2O2}: fraction of H$_2$O$_2$ decomposed. ^{c} $\Sigma_{aromatics}$: sum of the concentrations (expressed in mg/L) of phenol, catechol, hydroquinone, and p-benzoquinone. ^{d} Σ_{acids}: sum of the concentrations (expressed in mg/L) of muconic, maleic, fumaric, malonic, acetic, oxalic, and formic acid. ^{e} Σ_{carbon}: sum of the amount of carbon (expressed in mg/L) computed from aromatics and acids
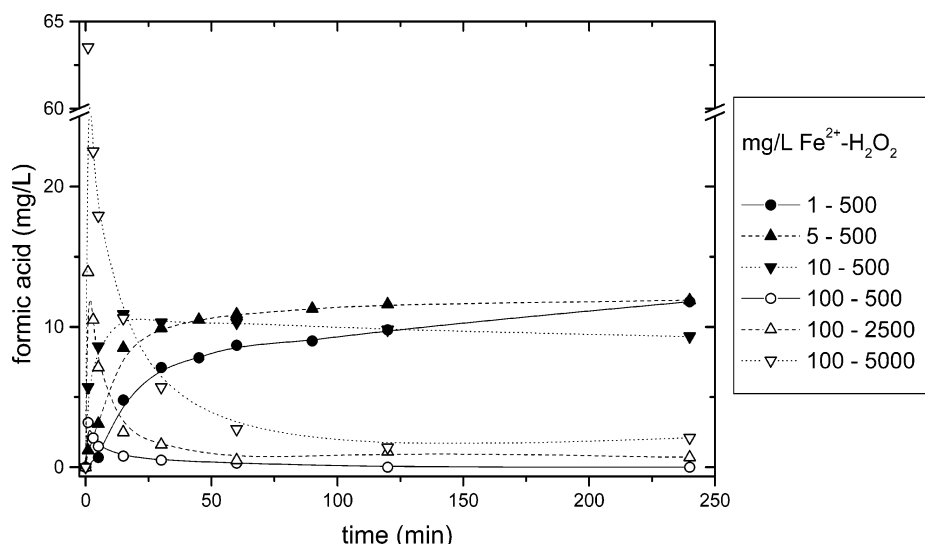

FIGURE 1. Formic acid production upon phenol oxidation by Fenton's reagent at different H$_2$O$_2$ and Fe^{2+} doses (pH$_0$ = 3, T = 25 °C).

conductivity detector. A Metrosep A supp 5−250 column (25 cm long, 4 mm diameter) was used as the stationary phase and 0.7 mL/min of an aqueous solution 3.2 mM of Na$_2$CO$_3$ and 1 mM of NaHCO$_3$ as the mobile phase. Values of 0.01 and 0.1 mg/L detection limits have been established for aromatic compounds and short-organic acids, respectively. TOC was measured with an OI TOC Analyzer (model 1010). The sample is injected in an oven at 90 °C where it is oxidized to carbon dioxide using a sodium persulfate solution (200 g/L). Previously, the samples were acidified with phosphoric acid (1 M) to remove inorganic carbon from carbonates and bicarbonates. The amount of CO$_2$ produced is measured with an infrared detector. Residual H$_2$O$_2$ concentration was determined by colorimetric titration using the titanium sulfate method (23).

Toxicity measurements were carried out in triplicate by the Microtox toxicity text, a standard bioassay (ISO 11348-3, 1998) which was a luminescent marine bacteria *Vibrio fisheri* (*Photobacterium phosphoreum*). A Microtox M500 Analyzer (Azur Environmental) was employed. The difference between the light emitted before and after addition of the sample serves to measure the toxicity. To prevent pH effects, the pH of each sample has to be adjusted into the range 6−8 using a NaOH solution (1 N). Moreover, these marine bacteria require adjusting the osmotic pressure of the sample to approximately 2% NaCl.

The EC$_{50}$ is used to quantify the ecotoxicity of a compound. It is defined as the effective nominal concentration (mg/L) of the compound that reduces the intensity of light emission by 50% after 15 min contact time (19). For complex samples

IC$_{50}$ is used, defined as the dilution ratio of the sample that yields this 50% reduction. The EC$_{50}$ and IC$_{50}$ values are inversely proportional to the biological toxicity expressed as toxicity units (TU). They are related by eq 3, where C_0 corresponds to the concentration of the compound used to obtain its EC$_{50}$ value.

$$TU = \frac{C_0 (mg/L)}{EC_{50}} = \frac{100}{IC_{50}} \tag{3}$$

Phenol oxidation by Fenton's reagent takes place through a complex pathway, which includes aromatic intermediates, condensation products, and organic acids (21). These compounds show a quite different behavior with respect to this oxidation process. Hence, to assess the ecotoxicity upon Fenton oxidation it is necessary not only to know the toxicity of each of them but also their evolution throughout the process depending on the influence of the operating conditions (pH, Fe^{2+} and H$_2$O$_2$ doses, temperature).

Results and Discussions

Influence of the Operating Conditions. Evolution of phenol oxidation with Fenton's reagent depends on different variables. The pH is one of the most important. An initial pH of 3 has been used in all experiments without further control. In these conditions phenol was rapidly oxidized, reaching 85% conversion after 5 min when 1 mg/L Fe^{+2} and the stoichiometric amount of H$_2$O$_2$ were used. Moreover, a slight reduction of pH was observed as a consequence of the organic
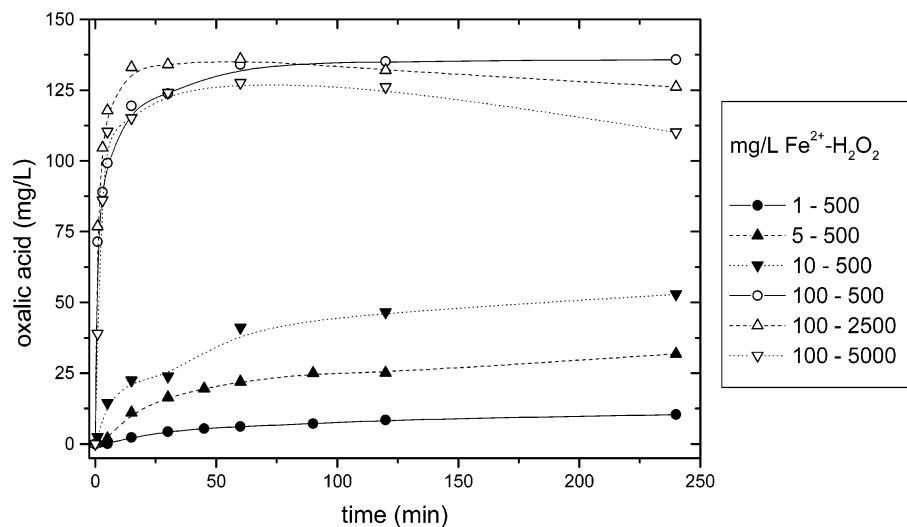
FIGURE 2. Oxalic acid production upon phenol oxidation by Fenton's reagent at different H_2O_2 and Fe^{2+} doses ($pH_0 = 3$, $T = 25\ °C$).
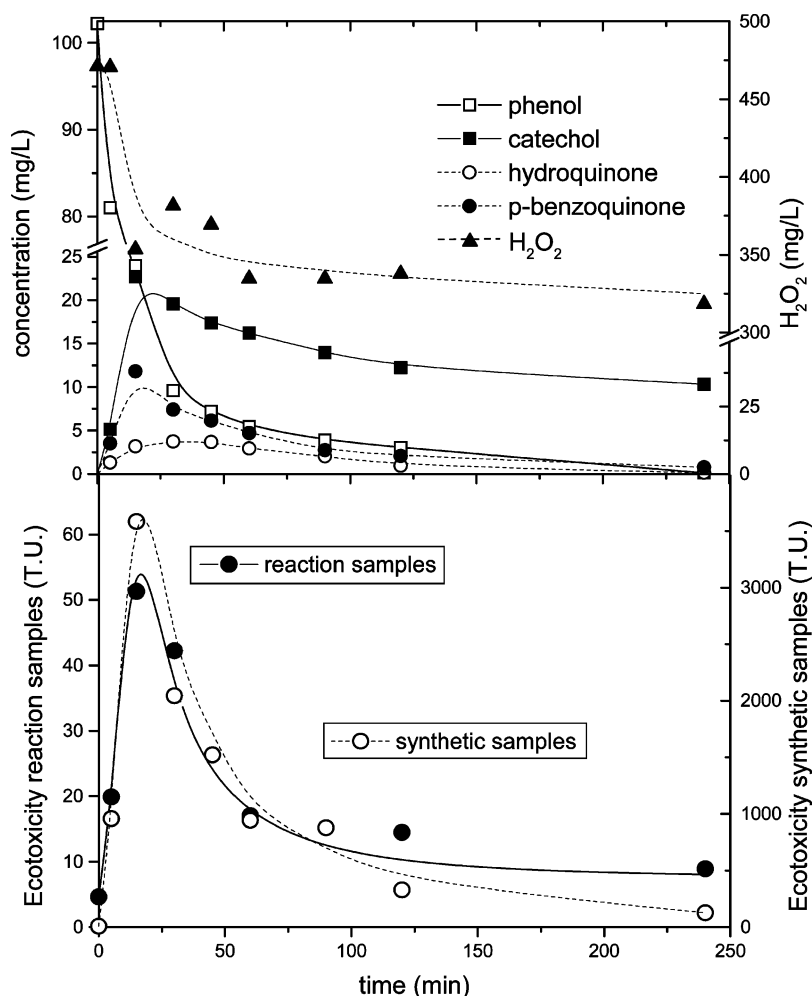

FIGURE 3. Evolution of aromatics, H_2O_2, and ecotoxicity upon Fenton's oxidation of phenol using 1 mg/L Fe^{2+} ([Ph]$_0$= 100 mg/L, [H_2O_2]$_0$= 500 mg/L, $pH_0 = 3$, $T = 25\ °C$).

acids generated, evolving down to around 2.5 at the end of the experiments.

The optimum pH range is 3–3.5 (*24–26*), although some authors have reported a wider range, up to 2–4 (*27–29*). The effect of pH is related to the oxidation state of iron, which influences the production of hydroxyl radicals. At pH values lower than 3, the decrease of OH• production is attributed to formation of the complex species $[Fe(H_2O)_6]^{2+}$, which reacts

more slowly with H_2O_2 than $[Fe(OH)(H_2O)_5]^+$, thus producing a smaller amount of OH• radicals (*30*). At higher pH, Fe^{3+} precipitates as $Fe(OH)_3$, which decomposes H_2O_2 into O_2 and H_2O (*31*). Due to the pH influence, some authors maintain this value constant (*24*).

The Fe^{2+} and H_2O_2 doses also show a great influence in the evolution of the process. There is a relationship between both. The initial H_2O_2 concentration needed is related to
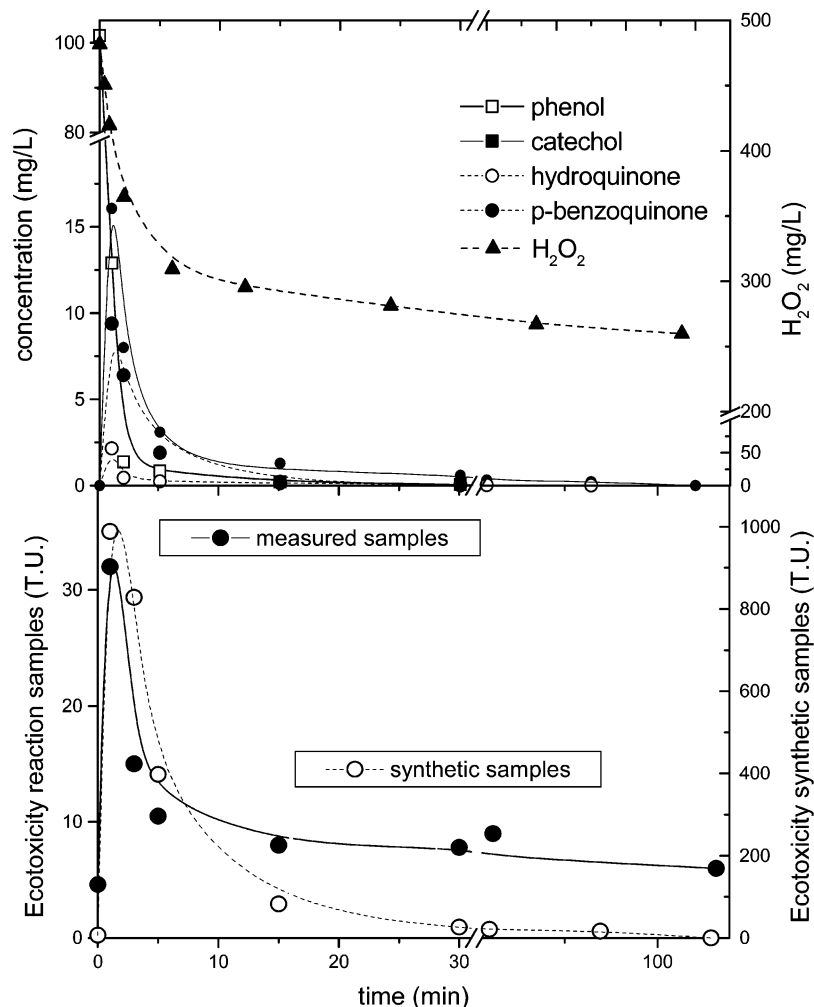
FIGURE 4. Evolution of aromatics, H_2O_2, and ecotoxicity upon Fenton's oxidation of phenol using 5 mg/L Fe^{2+} ([Ph]$_0$= 100 mg/L, [H_2O_2]$_0$= 500 mg/L, pH$_0$ = 3, T = 25 °C).

that of the substrate. It is usually expressed relative to the stoichiometric ratio, namely, the theoretical amount for complete oxidation of the organic species to CO_2 and H_2O. With regard to the Fe^{2+} dose, a higher amount favors a higher phenol conversion and enhances the oxidation rates of the intermediates, mainly the aromatic byproducts (Table 1). The reaction time needed to achieve complete depletion of 100 mg/L of phenol using the stoichiometric amount of H_2O_2 was around 4 h at 1 mg/L of Fe^{2+}, whereas it decreased to 60 min, 5 min, and less than 1 min when using 5, 10, and 100 mg/L of Fe^{+2}, respectively. The aromatic byproducts initially formed are slowly transformed when 1 mg/L of Fe^{2+} is used with significant concentrations after 4 h of reaction remaining in solution. However, their complete depletion was achieved after 90 min, 15 min, and less than 1 min when using 5, 10, and 100 mg/L of Fe^{2+}, respectively. Nevertheless, in spite of the complete disappearance of aromatic compounds, TOC conversion (X_{TOC}), that is, the fraction of organic carbon oxidized up to CO_2, is relatively low since these compounds were transformed into low weight acids, among them acetic, oxalic, and formic acids. Oxalic acid is refractory to this oxidation, remaining in solution even when fairly severe conditions (100 mg/L Fe^{2+}, 5000 mg/L H_2O_2) were used. These results are in agreement with those reported by other authors. Potter and Roth (*24*) reached an 80% chlorophenol conversion after 230 min using 1.3 mg/L Fe^{2+} and a 90% conversion after 25 min using 2.5 mg/L Fe^{2+}. Esplugas et al. (*3*) raised the phenol conversion from 58% to 84.7% after 9 min, increasing the Fe^{2+} dose from 3 to 7.25 mg/L.

Nevertheless, as can be seen in Table 1, the TOC conversion was not increased using a higher Fe^{2+} dose at the stoichiometric H_2O_2 initial concentration and 25 °C. To obtain a higher TOC reduction it was necessary to increase the H_2O_2 dose, although this effect has a limit since the oxalic acid produced in the oxidation process remains in solution. Moreover, a higher initial H_2O_2 concentration means a higher cost and higher amount of residual H_2O_2 which needs to be removed prior to final discharge.

As can be appreciated in Table 1, when 1 mg/L of Fe^{2+} and the stoichiometric amount of H_2O_2 are used, there is a great difference between the TOC measured and the amount of carbon computed from the identified byproducts and residual phenol. The differences can be explained by formation of polymeric species resulting from condensation of aromatics and Fe−aromatic complexes (*21*). These species are measured as TOC but were not identified by HPLC or ion chromatography. Formation of those species is supported by the appearance of a brown color in the reaction medium and a dark solid residue after evaporation. This solid was insoluble under the experimental conditions (pH 3) but soluble in basic medium (1 N aqueous NaOH).

These unidentified compounds are oxidized to low weight acids (formic or oxalic acids) depending on the operating conditions, making necessary to use sufficiently severe conditions (10 times the stoichiometric amount of H_2O_2 and 100 mg/L Fe^{2+}) to reach their complete degradation. As can be seen in Figure 1, formic acid production hardly depends on the Fe^{2+} dose. It reaches a maximum value around 10
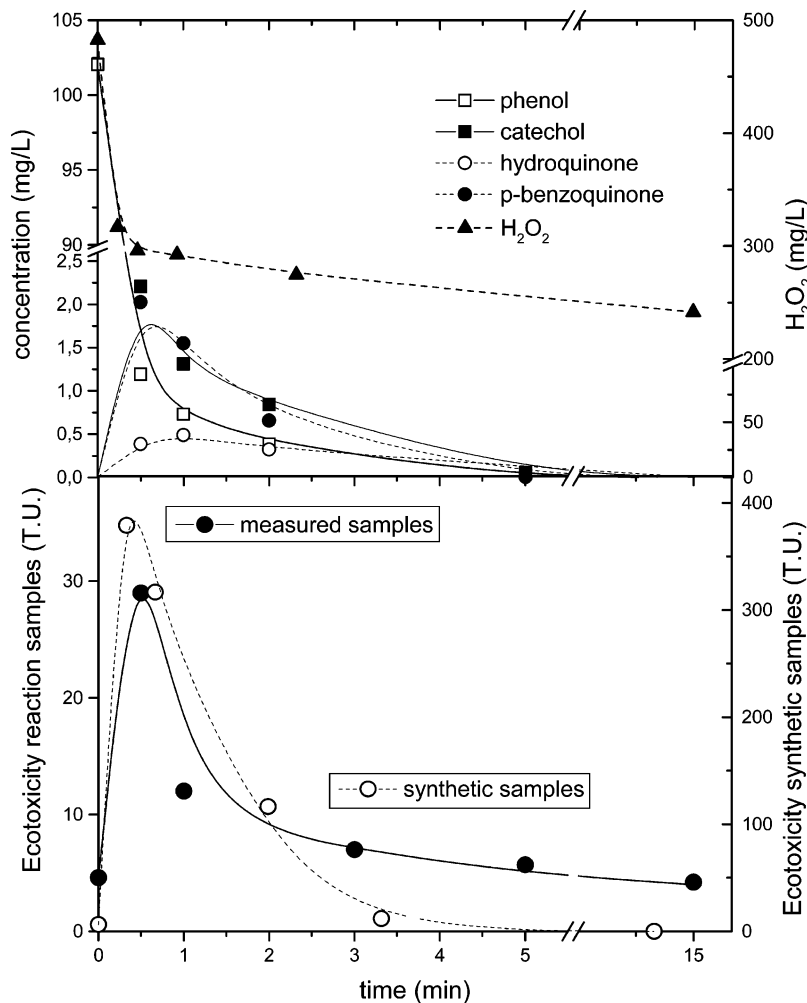
FIGURE 5. Evolution of aromatics, H_2O_2, and ecotoxicity upon Fenton's oxidation of phenol using 10 mg/L Fe^{2+} ([Ph]$_0$= 100 mg/L, [H_2O_2]$_0$= 500 mg/L, pH$_0$ = 3, T = 25 °C).

mg/L, and from this concentration it is oxidized up to CO_2 at increasing Fe^{2+} dose (using the same initial H_2O_2 concentration). In the case of oxalic acid, its concentration increased at increasing Fe^{2+} dose, as can be seen in Figure 2. This fact can be explained by the oxidation of the aforementioned unidentified intermediates (polymer-like) whose oxidation rate is much lower than that of the identified aromatic oxidation intermediates.

These results explain the higher amount of carbon detected in identified intermediates at increasing the Fe^{2+} dose, whereas reduction of measured TOC remains almost constant (Table 1, results at 25 °C and 500 mg/L H_2O_2). Unidentified compounds that are not detected by chromatography (polymer-like species) are oxidized up to oxalic acid that can be analyzed. As oxalic acid is quite refractory it remains in solution. Nevertheless, there is still a difference between the amount of carbon in identified compounds and the TOC measured. To match the carbon balance it is necessary to increase also the H_2O_2 dose (up to 10 times the stoichiometric ratio). In these conditions the oxalic acid concentration hardly varied, whereas a higher formic acid production was detected (Figure 1). This indicates that the unidentified intermediates are in part oxidized to this acid. Moreover, in contrast to oxalic acid, formic acid is completely oxidized up to CO_2 and H_2O (*21*), which explains the higher TOC reduction at increasing H_2O_2 dose (Table 1).

The temperature is also an important variable. It shows two opposite effects. Higher temperatures favor the oxidation rate but also diminish the H_2O_2 stability. H_2O_2 decomposition

into O_2 and H_2O increases approximately 2.3 times for each 10 °C (*25*). In the range investigated (25−50 °C) phenol, aromatic intermediates, and TOC removal increased when increasing the temperature (Table 1). The H_2O_2 conversion is also higher, which can be explained by both a higher TOC conversion and a higher decomposition into O_2 and H_2O. In any case, the residual H_2O_2 concentration was always higher than 100 mg/L, which indicates that this reactant was not limiting in these conditions.

Evolution of Ecotoxicity. Figures 3−5 show the time−concentration curves of phenol and aromatic intermediates as well as evolution of ecotoxicity at three different Fe^{2+} doses. Phenol is rapidly transformed into catechol, hydroquinone, and *p*-benzoquinone, which are further oxidized into organic acids, the oxidation rate being related to the initial Fe^{2+} concentration. In the case of the ecotoxicity, the values obtained for the reaction samples were lower than those expected from the presence of significant concentrations of highly ecotoxic compounds in solution, such as hydroquinone or *p*-benzoquinone.

To confirm this we measured the ecotoxicity values of synthetic samples having the same composition as the reaction samples analyzed along the oxidation process at different reaction times (phenol, aromatic byproducts, and low weight acids). The pH was set at 3, and the corresponding Fe^{2+} dose was also added. Before measuring the toxicity the pH was readjusted to 6 according to the Microtox protocol. These values are included in Figures 3−5 where it can be appreciated that the directly measured values of ecotoxicity

TABLE 2. EC$_{50}$ (mg/L) Values Obtained for Phenol, H$_2$O$_2$, and Oxidation Byproducts (data at 15 min)

	EC$_{50}$ (mg/L)		EC$_{50}$ (mg/L)
phenol	16	maleic acid	250
catechol	7	fumaric acid	260
hydroquinone	0.04	acetic acid	130
p-benzoquinone	< 0.01	oxalic acid	> 450
H$_2$O$_2$	17	formic acid	160

TABLE 3. Concentrations of Hydroquinone and p-Benzoquinone As Determined Before and After Neutralization (Fe^{2+} = 1 mg/L, H$_2$O$_2$ = 500 mg/L, pH$_0$ = 3, pH$_{after\ neutralization}$ ≅ 6.5)

reaction time (min)	hydroquinone (mg/L) before	hydroquinone (mg/L) after	p-benzoquinone (mg/L) before	p-benzoquinone (mg/L) after
5	1.32	1.04	3.55	0.83
15	3.19	1.99	11.82	1.13
30	3.75	2.76	7.42	0.65
60	2.95	1.98	4.71	0.35
120	0.97	0.65	2.09	0.08
240	0.15	0.0	0.78	0.0
standard				
50 mg/L hydroquinone	50.2	46.1	0	5.2
50 mg/L p-benzoquinone	0	0	49.7	49.5

are lower although the differences become smaller and even inexistent as the Fe^{2+} concentration and reaction time increase. The EC$_{50}$ values of Table 2 show that p-benzoquinone and hydroquinone are by far the most critical compounds in the phenol oxidation pathway in terms of toxicity. Both yield ecotoxicity values 4 orders of magnitude higher than that of phenol, whereas the organic acids are at least 1 order of magnitude less toxic than phenol. This is consistent with the shape of the toxicity curves which show an initial steep rise due to the rapid transformation of phenol into p-benzoquinone and hydroquinone up to a maximum followed by a decrease which corresponds to disappearance of aromatic intermediates giving rise to organic acids of low toxicity.

Fenton oxidation is carried out at low pH (≈ 3), whereas the ecotoxicity test requires adjusting the pH of the samples within the 6−8 range. During this neutralization step some transformations take place affecting the composition of the samples, which would explain the unexpected low toxicity values. To check this samples from the oxidation experiments were adjusted to pH 6 and analyzed. The results are reported in Table 3, which shows the concentrations of hydroquinone and p-benzoquinone (the two critical intermediates with regard to the ecotoxicity) at different reaction times before and after neutralization.

As can be seen, the neutralization step reduces the concentration of these two highly toxic aromatic intermediates, thus decreasing the ecotoxicity. However, in the case of phenol and catechol, their concentrations hardly varied upon neutralization. This reduction may be caused by the interaction between hydroquinone and p-benzoquinone, generating quinhydrones-like complexes (*32−33*), which could also explain the change of color of the solution (to a darker brown color) when the pH of the solution is adjusted to around 6. Due to the low EC$_{50}$ values of hydroquinone and p-benzoquinone removal of small amounts of them from the reaction media would cause a substantial reduction of the ecotoxicity of the resulting solution. Nevertheless, the change in both color and concentration at increasing pH was observed neither when the experiments were carried out using synthetic samples nor in the case of hydroquinone

and p-benzoquinone standards, even when using higher concentrations (Table 2).

These findings have an important practical implication since neutralization of a Fenton-treated phenolic stream prior to discharge leads to a significant complementary cleaning of the final effluent in terms of such an important parameter like ecotoxicity.

From the data shown in Table 1, the toxicity values (reaction samples after 4 h) are reduced at increasing Fe^{2+}. However, these values increased significantly when increasing the initial H$_2$O$_2$ concentration as a result of a higher residual amount of H$_2$O$_2$. This indicates that the final toxicity values are quite related to the residual H$_2$O$_2$ concentration in the reaction medium. Nevertheless, increasing the pH enhances decomposition of H$_2$O$_2$ into O$_2$ and H$_2$O. Therefore, this represents another beneficial effect of the neutralization step subsequent to a Fenton oxidation treatment.

This effect of the neutralization step on the evolution of toxicity represents an advantage of the Fenton process with respect to other oxidation treatments (i.e., ozonation, photocatalytic treatment, CWAO). This step not only removes Fe but also traces of toxic intermediates and residual H$_2$O$_2$ concentration, thus improving the relative position of Fenton's oxidation in the pool of alternative advanced oxidation processes.

Supporting Information Available

Two tables showing the individual concentration of each compound included under aromatics and acids terms in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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