J. Braz. Chem. Soc., Vol. 23, No. 7, 1372-1377, 2012.
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0103 - 5053 $6.00+0.00

Article

Mechanistic Implications of Zinc(II) Ions on the Degradation of Phenol by the Fenton Reaction

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Um estudo da interferência de íons Zn^{2+} na reação de Fenton ($Fe^{2+}/Fe^{3+} + H_2O_2$) na degradação de fenol é relatado. Um dos intermediários formados inicialmente na reação, catecol, pode reduzir Fe^{3+} a Fe^{2+}, e na presença de H_2O_2 inicia um ciclo redox catalítico. Nas etapas iniciais da reação, este ciclo mediado por catecol torna-se a principal via de degradação térmica de fenol e seus produtos de oxidação. A adição de íons Zn^{2+} aumenta o tempo de persistência do catecol, provavelmente por estabilização do radical semiquinona via complexação.

A study of the interference of Zn^{2+} ions on phenol degradation by Fenton reaction ($Fe^{2+}/Fe^{3+} + H_2O_2$) is reported. One of the first intermediates formed in the reaction, catechol, can reduce Fe^{3+} to Fe^{2+} and, in the presence of H_2O_2 initiates an efficient catalytic redox cycle. In the initial stages of the reaction, this catechol-mediated cycle becomes the principal route of thermal degradation of phenol and its oxidation products. The Zn^{2+} ion addition enhances the persistence time of catechol, probably by stabilization of the corresponding semiquinone radical via complexation.

Keywords: phenol, Zn^{2+} ions, Fenton reaction

Introduction

More than a century ago, Fenton[1] showed that a mixture of H_2O_2 and Fe^{2+} in acidic medium had very strong oxidizing properties. Fenton reaction is an important source of hydroxyl radicals,[1-6] which oxidize organic substances,[1] in many cases to carbon dioxide and water.

A means of accelerating the rate of the Fenton reaction is via the use of phenolic compounds, especially dihydroxybenzene (DHBs), which have the ability to reduce Fe^{3+} to Fe^{2+}. Hamilton *et al.*[7] were the first to report that catalytic amounts of dihydroxybenzene (catechol or 1,4-hydroquinone), the primary initial intermediates in phenol degradation,[8,9] were able to increase the degradation rate of aromatic compounds in Fenton reactions. The same effect is observed when catechol is added to the reaction medium. Fe^{2+} forms a 1:1 complex with catechol that decomposes the *ortho*-semiquinone radical and Fe^{3+} ion. The semiquinone radical is unstable and is oxidized by another Fe^{3+} ion, leading to 1,2-benzoquinone. The 1,2-benzoquinone formed can interact with the superoxide ion to reform the semiquinone radical and molecular oxygen. This redox cycle, illustrated in Scheme 1, represents the Hamilton catalytic cycle.

In the technique of EPR (electron paramagnetic resonance), diamagnetic metal ions are used to complex semiquinone free radicals, increasing the kinetic stability of these radicals.[10] Thus, for example, Yamasaki and Grace[11] employed zinc ions as stabilizing agents to detect semiquinone radicals by EPR in the coupled system

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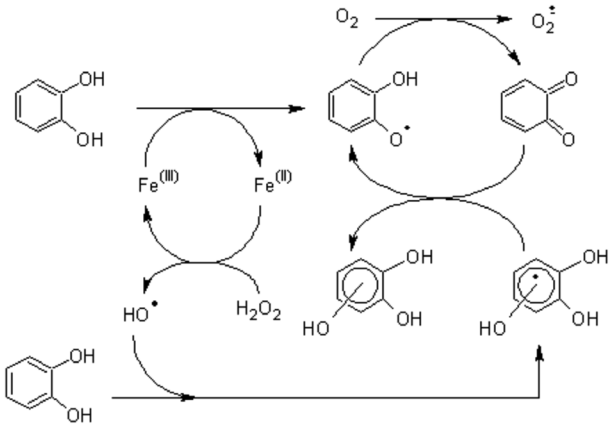

Scheme 1. Hamilton catalytic cycle for catechol (adapted from ref. 5).[8]

peroxidase/phenolic. This work aimed to study the mechanistic implications of zinc ions in the Fenton reaction using phenol as model compound.

Experimental

Materials

Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, Synth), zinc sulfate ($ZnSO_4$, Synth), hydrogen peroxide (H_2O_2, 30%, Synth), sulfuric acid (H_2SO_4, Synth), sodium hydroxide (NaOH, Merck), phenol (Aldrich), catechol (Acros), hydroquinone (Aldrich), oxalic acid (Aldrich) and acetonitrile (JT Baker) (all reagent grade or superior) were used as received.

General procedure for degradation experiments

The solutions of phenol were prepared by directly dissolving the desired amount of phenol in aqueous solution. The reactor used for the degradation of phenol was a batch reactor with an internal volume of 1.0 L, protected from incident light in order to minimize the influence of photochemical reactions. The solution temperature was controlled at 30 ºC by using a thermostatic bath and magnetic stirring.

Initially, a solution containing 10 mmol L^{-1} phenol, 0.5 mmol L^{-1} Fe^{2+} and different concentrations of Zn^{2+} at pH 3.0 was added to the reactor. Aqueous hydrogen peroxide was slowly added (3.33 mmol L^{-1} min^{-1}), with the aid of a peristaltic pump during the first 60 min of the reaction to minimize the formation of the hydroperoxide radical. At selected time intervals, 5 mL of sample solution were collected and 2 drops of a solution of 2.0 mmol L^{-1} NaOH immediately added, raising pH to ca. 12. The increase in pH precipitated Fe^{3+}, stopping the reaction. After filtration, the sample was reacidified to a pH around 3.0 to maintain the same conditions as in the reactor and total organic carbon (TOC) was analyzed with a Shimadzu Model TOC-5000A analyzer.

General procedure for high-performance liquid chromatography (hplc) analysis

Phenol and the main degradation products (hydroxyaromatics and aliphatic acids) were identified and quantified by high performance liquid chromatography (for hydroxyaromatics,a Shimadzu 2010A LC-MS with ionization in the APCI negative mode, and for aliphatic acids, a Shimazdu 20AD HPLC) using standard compounds for identification and calibration.

For the determination of aromatic intermediates, a Shim-pack C_{18} reverse phase column (5 μm, 4.6 × 150 mm) was used with detection at 270 nm. The mobile phase consisted of an aqueous solution containing 0.2% acetic acid (A) and acetonitrile containing 0.2% acetic acid (B). For 3 min, the mobile phase (flow rate 0.7 mL min^{-1}) was 18% B:82% A, followed by a gradient of 18-58% B over 10 min and completing the analysis by reverting for 1 min to 18% B:82% A. The main intermediates of the phenol degradation reaction were identified by their retention times and by their molecular masses. The retention times were 16.3 min for phenol, 13.5 min for catechol and 12.5 min for hydroquinone.

To determine the intermediate acids, a Hamilton PRP Brand-X300 ion exchange column was used with UV detection at 220 nm. The mobile phase consisted of an aqueous solution of H_2SO_4 (pH 2.00 ± 0.02), at a flow rate of 1 mL min^{-1} with the column temperature maintained at 30 ºC. Before being injected onto the ion exchange column, the samples were filtered through a C_{18} cartridge previously activated with methanol. This step removed the remaining aromatic compounds, this is necessary since these compounds are strongly retained on the ion exchange column, resulting in broad bands that hamper analysis.[12]

Results and Discussion

The efficiency of the Fenton reaction for the mineralization of phenol (reduction of the value of TOC) was determined as a function of time, as shown in Figure 1. The influence of the concentration of zinc ions on the oxidation of phenol was analyzed by fixing the concentrations of H_2O_2 and Fe^{2+} and varying the concentration of Zn^{2+}.

In the presence of Fe^{2+} ion, the system shows a high degradation rate, the beginning of the reaction reaching a

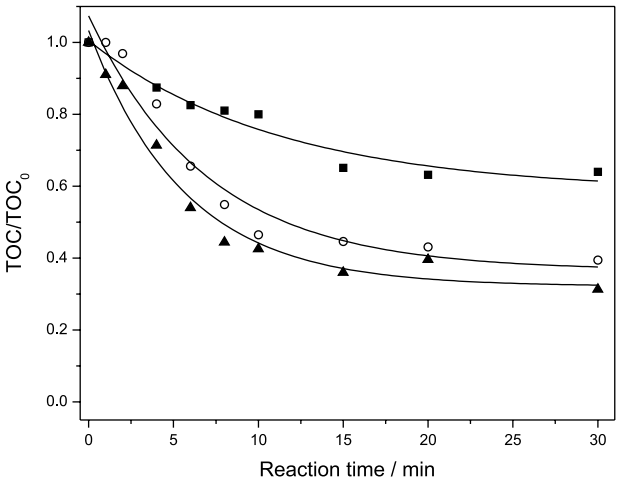

Figure 1. Effect of zinc ions on the degradation of phenol (10 mmol L^{-1} initial) by the Fenton reaction. Experimental conditions: $[Fe^{2+}]$ = 0.5 mmol L^{-1}, $[H_2O_2]$ = 200 mmol L^{-1}, T = 30 ºC and $pH_{initial}$ 3.0; $[Zn^{2+}]$: absence (■), 5 mmol L^{-1} Zn^{2+} (○) and 50 mmol L^{-1} Zn^{2+} (▲).

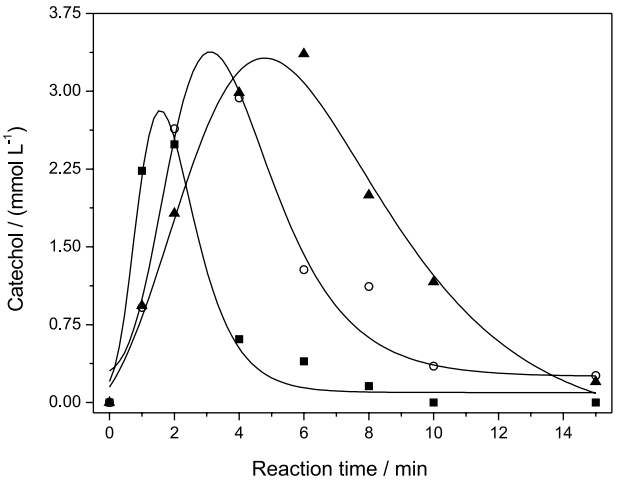

Figure 3. Formation and consumption of catechol as a function of the concentration of Zn^{2+} added to the system. Experimental conditions: $[Fe^{2+}]$ = 0.5 mmol L^{-1}, $[H_2O_2]$ = 200 mmol L^{-1}, T = 30 ºC and $pH_{initial}$ 3.0; $[Zn^{2+}]$: absence (■), 2 mmol L^{-1} (○) and 5 mmol L^{-1} (▲).

maximum of 25% degraded after 15 min, and then the TOC value remains constant. Joining the two reaction, Fenton and zinc, the degradation reaches 70% reduction at the end of the reaction (Figure 1). In both conditions, the mineralization was not completed due to the formation of intermediate compounds that interfere with the Fenton reaction.

Figure 2 shows that phenol was totally degraded in 10 min of reaction, both in the presence and absence of zinc ions. Zn^{2+} did not significantly influence the phenol disappearance rate, suggesting that zinc ions do not interfere with the formation of $HO^{\bullet}$ radicals. In contrast, the analysis of the intermediates initially formed in the degradation of phenol showed an increase in the persistence time of catechol in the reaction system in the presence of Zn^{2+} (Figure 3). In addition, as shown in Figure 4, there is

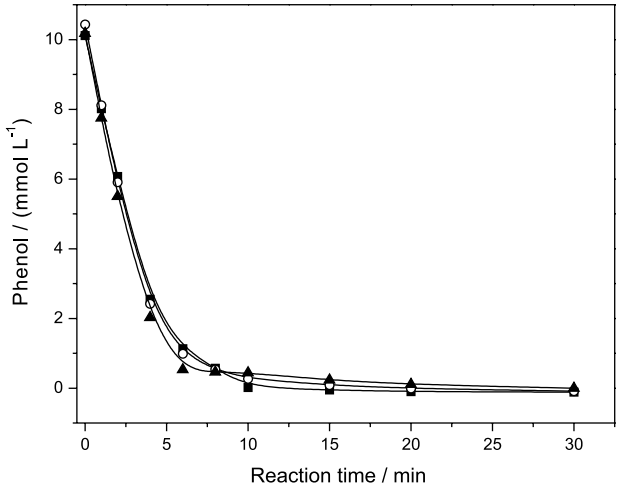

Figure 2. Degradation of phenol as a function of the concentration of Zn^{2+} added to the system. Experimental conditions: $[Fe^{2+}]$ = 0.5 mmol L^{-1}, $[H_2O_2]$ = 200 mmol L^{-1}, T = 30 ºC and $pH_{initial}$ 3.0; $[Zn^{2+}]$: absence (■), 5 mmol L^{-1} (○) and 50 mmol L^{-1} (▲).

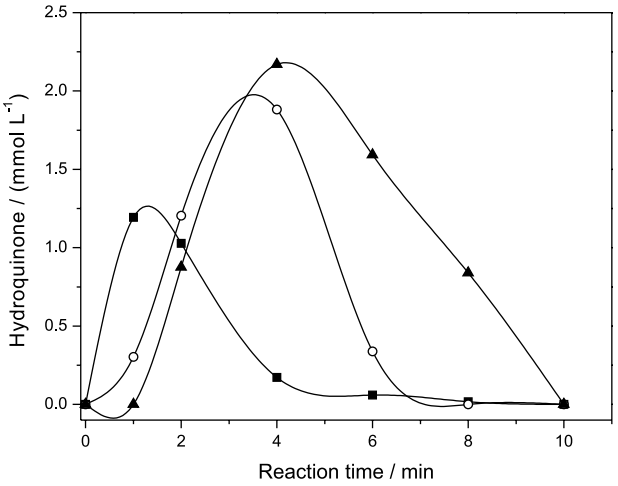

Figure 4. Formation and consumption of hydroquinone as a function of the concentration of Zn^{2+} added to the system. Experimental conditions: $[Fe^{2+}]$ = 0.5 mmol L^{-1}, $[H_2O_2]$ = 200 mmol L^{-1}, T = 30 ºC and $pH_{initial}$ 3.0; $[Zn^{2+}]$: absence (■), 2 mmol L^{-1} (○) and 5 mmol L^{-1} (▲).

also a decrease in the formation and consumption rates of hydroquinone with increasing zinc concentration.

In these experiments, it was used 0.5 to 200 mmol L^{-1} H_2O_2. This ratio would yield a maximum of 0.5 mmol L^{-1} of hydroxyl radicals, and when all of the Fe^{2+} was oxidized to Fe^{3+}, the degradation process should become slow since the reduction reaction of Fe^{3+} to Fe^{2+} by H_2O_2 is slow. As shown in Figure 2, the amount of phenol was greater than 0.5 mmol L^{-1}. Therefore, there must be another process capable of recycling Fe^{3+} to Fe^{2+} with high efficiency. It is known that catechol can form a complex with Fe^{3+} produced by thermal Fenton reaction. This complex is capable of reducing Fe^{3+} to Fe^{2+} by an electron transfer mechanism and Fe^{2+} regenerated could be used again in the thermal Fenton reaction to continue the oxidation process. Therefore, there

is an increased lifetime of the catechol after the addition of zinc ions to the system as shown in Figure 3.

According to Hamilton *et al.*,[7] the acceleration rate of hydroxylation of aromatic compounds when Fe^{2+}, H_2O_2 and a dihydroxy benzeno (DHB) like catechol are present in the system is due to a ternary DHB-Fe-H_2O_2 complex, which is then the active oxidizing agent, rather than hydroxyl radicals. However, it is also known that catechol (H_2cat) is able to reduce Fe^{3+} to Fe^{2+} rapidly at low pH,[13,14] resulting in the complex $[Fe^{2+}(cat^{\bullet})]^+$, which is unstable at pH < 2.0 and dissociates to the free semiquinone radical (Hcat$^{\bullet}$). The disproportionation of Hcat$^{\bullet}$ regenerates catechol and forms *o*-benzoquinone (equations 1-3). Thus, the regeneration of Fe^{2+} could be responsible for the observed acceleration of the decomposition rate.

$$Fe^{2+} + H_2cat \rightleftarrows [Fe^{2+}(cat^{\bullet})]^+ + 2\,H^+ \quad (1)$$

$$[Fe^{2+}(cat^{\bullet})]^+ + H^+ \rightleftarrows Fe^{2+} + Hcat^{\bullet} \quad (2)$$

$$2\,Hcat^{\bullet} \rightleftarrows H_2cat + \textit{o}\text{-benzoquinone} \quad (3)$$

The analysis of the organic compounds present at the end of the reaction showed principally the formation of oxalic acid (OA) (Figure 5). The ferrioxalate complex removes free Fe^{3+} from the solution, decreasing the efficiency of the Fenton reaction.

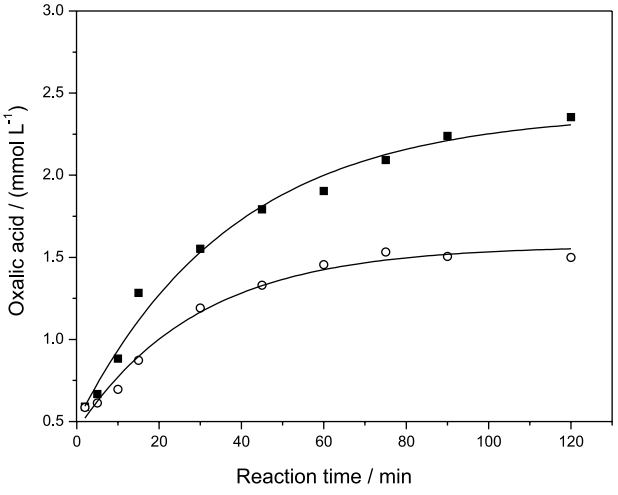

Figure 5. Variation of the concentration of oxalic acid (OA) with time. Effect of addition of inorganic ions on the degradation of 10 mmol L^{-1} phenol. Experimental conditions: $[H_2O_2]$ = 200 mmol L^{-1}, T = 30 ºC and $pH_{initial}$ 3.0. Addition of ions 0.50 mmol L^{-1} Fe^{2+} (■) or 0.50 mmol L^{-1} Fe^{2+} + 0.50 mmol L^{-1} Zn^{2+} (○).

In EPR studies, the addition of Zn^{2+} is used as a technique to increase the persistence of the semiquinone radical of catechol in aqueous media.[11, 15-17] Therefore, if the semiquinone radical is present in the system, an effect of Zn^{2+} ion is expected. In fact, the addition of Zn^{2+} to the system increased the persistence time of catechol in the reaction medium, as shown in Figure 3.

Using phenol as substrate for degradation, it was performed a kinetic modeling of the experimental curves for the disappearance of phenol and formation and degradation of catechol and hydroquinone. The differential equations for the variation of the concentration of the species were solved by numerical integration techniques, employing the software COPASI 4.6.[18]

In this model, the organic reactions involving the hydroperoxyl radical were assumed to be insignificant because the dissolved oxygen was consumed in a few seconds after the start of the Fenton reaction in the absence of light.[18] It was used a generic reaction for H_2O_2 production to simulate the gradual addition of this reagent during the first 60 min of reaction, with an addition rate of 1 mL min^{-1}. Reactions R01 to R08, listed in Table 1, represent the main inorganic reactions in the Fenton system.

Table 1. Minimal set of inorganic reactions for the description of the Fenton reaction

	Reaction	k / (mmol L^{-1} s^{-1})	Reference
R01	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^-$	$k_1 = 63$	19
R02	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$	$k_2 = 0.01$	19
R03	$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2$	$k_3 = 6 \times 10^9$	14
R04	$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$	$k_4 = 2.7 \times 10^7$	19
R05	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	$k_5 = 8.3 \times 10^5$	20
R06	$HO_2^{\bullet} + H_2O_2 \rightarrow HO^{\bullet} + O_2 + H_2O$	$k_6 = 0.5$	20
R07	$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2$	$k_7 = 2 \times 10^3$	2
R08	$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + H_2O_2$	$k_8 = 1.2 \times 10^6$	2

The rate constants of reactions R01 to R08 are widely known and discussed in the literature.[2,14,19,20] The reaction R01 is the crucial stage of the Fenton reaction due to the formation of the hydroxyl radical, which is a strong oxidant.

The initial step involves the exchange of one water molecule of hydration of hexaaquoiron(II) by a molecule of peroxide. This complex of Fe^{2+} with H_2O_2 decomposes, generating the hydroxyl radical and Fe^{3+}. Although it is possible to produce large quantities of hydroxyl radicals from reaction R01 stoichiometrically, reactions R03 and R04 efficiently consume hydroxyl radicals. Therefore, in practical applications of the Fenton reaction, catalytic amounts of iron salts (below 10^{-4} mol L^{-1}) are typically used and hydrogen peroxide added slowly to the system.

The addition of the hydroxyl radical to phenol is represented by reactions R09 and R10, forming hydroxycyclohexadienyl radicals by addition of HO$^{\bullet}$ radical

in the *ortho* and *para* positions of phenol. The *meta* position is less favored because the hydroxycyclohexadienyl radical formed by attack at the *meta* position is less stable. These radicals may undergo subsequent oxidation, reforming the Fe^{2+} ion. Reactions R11 and R12 form catechol and hydroquinone, respectively, and these intermediaries were identified and quantified by HPLC analysis. The proposed kinetic model for phenol oxidation consists of the ten reactions listed in Table 2 and the steps involving zinc complexation are listed in Table 3.

Table 2. Kinetic model for the initial steps of the Fenton degradation of phenol

	Reaction	k / (mmol L^{-1} s^{-1})	Reference
R09	phenol + $HO^{\bullet}$ → *o*-DHCR$^{\bullet}$[a]	$k_9 = 2 \times 10^{10}$	19
R10	phenol + $HO^{\bullet}$ → *p*-DHCR$^{\bullet}$[b]	$k_{10} = 1 \times 10^{10}$	19
R11	*o*-DHCR$^{\bullet}$ + Fe^{3+} → cat[c] + Fe^{2+}	$k_{11} = 1.4 \times 10^{4}$	19
R12	*p*-DHCR$^{\bullet}$ + Fe^{3+} → hq[d] + Fe^{2+}	$k_{12} = 7 \times 10^{3}$	19
R13	cat + $HO^{\bullet}$ → THCD$^{\bullet}$[e]	$k_{13} = 1 \times 10^{10}$	21
R14	hq + $HO^{\bullet}$ → THCD$^{\bullet}$	$k_{14} = 1 \times 10^{10}$	21
R15	THCD$^{\bullet}$ + Fe^{3+} → Fe^{2+} + THB[f]	$k_{15} = 7 \times 10^{3}$	19
R16	THB + $HO^{\bullet}$ → poliphenol	$k_{16} = 2.5 \times 10^{8}$	20
R17	polyphenol + $HO^{\bullet}$ → poliphenol$^{\bullet}$	$k_{17} = 1 \times 10^{10}$	20
R18	poliphenol$^{\bullet}$ + Fe^{3+} → Fe^{2+} + products	$k_{18} = 1 \times 10^{4}$	20

[a]*o*-DHCR$^{\bullet}$: *ortho*-dihydroxycyclohexadienyl radical; [b]*p*-DHCR$^{\bullet}$: *para*-dihydroxycyclohexadienyl radical; [c]cat: catechol; [d]hq: hydroquinone; [e]THCD$^{\bullet}$: trihydroxycyclohexadienyl radical; [f]THB: trihydroxybenzene.

Table 3. Additional kinetic steps involving zinc complexation with the intermediate initially formed in phenol degradation

	Reaction	k / (mmol L^{-1} s^{-1})[d]
R19	*o*-DHCR$^{\bullet}$ + Zn^{2+} ⇄ Zn (*o*-DHCR)$^{2+}$[a]	$k_{19} = 1 \times 10^{3}$ $k_{-19} = 0.01$
R20	*p*-DHCR$^{\bullet}$ + Zn^{2+} ⇄ Zn (*p*-DHCR)$^{2+}$[b]	$k_{20} = 1 \times 10^{2}$ $k_{-20} = 0.005$
R21	THCD$^{\bullet}$ + Zn^{2+} ⇄ Zn(THCD)$^{2+}$[c]	$k_{21} = 10$ $k_{-21} = 1 \times 10^{-4}$
R22	Zn(THCD)$^{2+}$ + Fe^{3+} → Fe^{2+} + THB + Zn^{2+}	$k_{22} = 1 \times 10^{-4}$

[a]Zn (*o*-DHCR)$^{2+}$: zinc complex of the *ortho*-dihydroxycyclohexadienyl radical; [b]Zn (*p*-DHCR)$^{2+}$: zinc complex of the *para*-dihydroxy-cyclohexadienyl radical; [c]Zn(THCD)$^{2+}$: zinc complex of the trihydroxy-cyclohexadienyl radical; [d]this work.

The reaction of $HO^{\bullet}$ with the radical intermediates reduces Fe^{3+} to Fe^{2+}. However, these intermediates, initially formed in the process of phenol degradation, are consumed during the Fenton reaction, possibly disrupting the iron redox cycle and stopping the reaction. The first intermediate, the *o*- hydroxycyclohexadienyl radical (*o*-DHCR•), is the main intermediate that reduces the Fe^{3+} ion in the decomposition of phenol to form catechol. Several authors have suggested that Fe^{2+} is regenerated only by organic intermediates.[22-26]

The kinetic model fits the decomposition of phenol by Fenton reaction and the generation and decay of the dihydroxybenzene intermediaries reasonably well, highlighting the importance of the regeneration of Fe^{2+} by the reaction intermediates in the degradation of phenol, as shown in Figure 6.

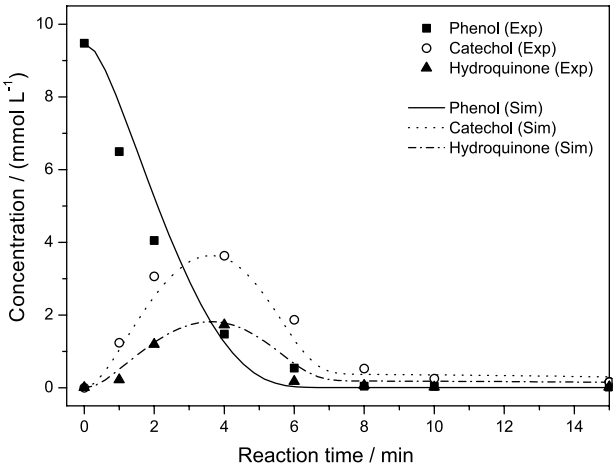

Figure 6. Comparison between the kinetic model and the experimental data for phenol degradation by the Fenton reaction in the absence of Zn^{2+}.

The experimental results show that there is an increase in the disappearance rate of organic carbon depending on the concentration of Zn^{2+}. Due to the increased persistence of the semiquinone radical of catechol in aqueous solution, Fe^{2+} is regenerated for a longer time and more $HO^{\bullet}$ radicals are generated.

The kinetic modeling of the formation and consumption of catechol and hydroquinone during the phenol degradation in the presence of zinc ions required the inductions of reactions R19 and R20, which correspond to the complexation of zinc with the *ortho*- and *para*-dihydroxycyclo hexadienyl radicals, respectively. Figure 7 shows the comparison between the experimental data and the simulation in the presence of zinc ions.

Figures 6 and 7 show a reasonable correlation between the modeling results and the experimental results. The difference between the curves of consumption of phenol is due to small variations in the initial concentrations of this compound, which do not affect the reaction mechanism. The reactions involving the reduction of Fe^{3+} by the di- and trihydroxycyclohexadienyl radicals are indispensable for the modeling process and explain the high extent of phenol degradation, considering the stoichiometry of the process. The results underscore the importance of the regeneration of Fe^{2+} in the degradation of organic compounds that form intermediates capable of reducing Fe^{3+}.

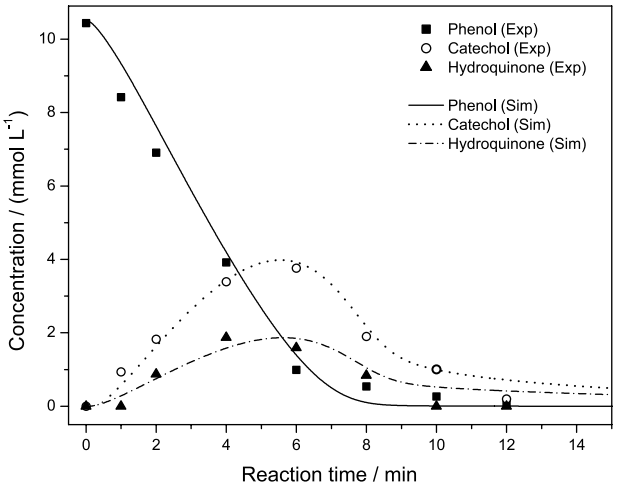

Figure 7. Comparison between experimental data and the kinetic model for phenol degradation by Fenton reaction in the presence of Zinc ions ($[Zn^{2+}]$ = 5 mmol L^{-1}).

Conclusions

This study confirms the existence of an effect of Zn^{2+} ion on persistence time of the formed intermediates on the phenol degradation by the Fenton reaction. Catechol, one of the main initial intermediates in the Fenton oxidation of phenol, can complex with Fe^{3+}. This complex is capable of reducing Fe^{3+} to Fe^{2+}, here by catalyzing the overall process of oxidation. In the initial stages of the Fenton reaction, the presence of zinc ions exerted a beneficial effect on the phenol degradation since it enhances the persistence of catechol, probably via stabilization of the corresponding semiquinone radical. Our results provide further indications that the reduction of Fe^{3+} to Fe^{2+} in the presence of H_2O_2 and catechol is an important catalytic pathway for the Fenton reaction in our system.

Acknowledgments

L. C. F. thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brasília, for graduate research fellowship support , and LSCP. C. L. P. S. Z. thanks FAPEAL, M. A. M. thanks ALCOA Foundation, A. M. Jr. thanks FUNDECT for financial support of the work at UFMS, V. O. S. and F. H. Q. thank the CNPq and INCT-Catalysis for fellowships and funding.

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Submitted: November 28, 2011
Published online: June 28, 2012

FAPESP has sponsored the publication of this article.