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# Role of the intermediates in the degradation of phenolic compounds by Fenton-like process

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### Abstract

The degradation of three phenolic compounds, 4-chlorophenol, 4-nitrophenol and phenol by Fenton-like process was divided into three phases: the initiation phase, the fast phase and the termination phase. Compared with the initiation phase, the degradation of phenolic compounds, the consumption of  $H_2O_2$  and the generation of  $Fe^{2+}$  accelerated dramatically in the fast phase. At the end of the fast phase, about 80% phenolic compounds were removed. After then, the degradation rate slowed down sharply due to the lack of  $H_2O_2$ . The enhancement in the fast phase was caused by the role of some hydroquinone-like intermediates such as hydroquinone, catechol and 4-chlorocatechol, which were identified to reduce  $Fe^{3+}$  to  $Fe^{2+}$  quickly. The fast degradation of phenolic compounds promoted the formation of intermediates, thus the concentration of  $Fe^{2+}$  increased, and vice versa. A reaction pathway describing the role of the hydroquinone-like intermediates was suggested. © 2006 Elsevier B.V. All rights reserved.

Keywords: Fenton-like; Phenolic compounds; Intermediates; Fe<sup>3+</sup>reduction

### 1. Introduction

Phenolic compounds are common persistent organic contaminants, which show low biodegradability, posing serious risks to the environment once discharged into natural water. Some of the most toxic compounds of this class are those chlorinated and nitro-substituted phenolic compounds. The monochlorinated phenols are mainly used as intermediates in the synthesis of the higher chlorinated congeners and certain dyes and pesticides. The use of various nitrophenols includes the synthesis of aminophenol, nitroanisole and other dyestuff intermediates, photochemicals and leather preservatives. Phenolic compounds are released into the environment through their wide use [1].

Available technologies to deal with phenolic compounds include the advanced oxidation processes (AOPs) [2–4]. These processes base on the formation of very active hydroxyl radicals, which react quickly with the contaminant. Among the AOPs, Fenton ( $Fe^{2+}/H_2O_2$ ) process is one of the most attractive methods because the reagent components are easy to handle and environmentally benign [5]. The generation of hydroxyl radicals

0304-3894/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2006.01.022 and the degradation of the contaminant are described in Eq. (1) [6] and Eq. (2), respectively:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-,$$
  

$$k_1 = 51 M^{-1} s^{-1}[6]$$
(1)

•OH + 
$$P \xrightarrow{\star \circ_{OH}}$$
 intermediates (2)

According to reaction (1), ferrous ion is oxidized to ferric ion and then regenerated through the reduction of ferric ion by  $H_2O_2$ [7], as shown in Eq. (3):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+,$$
  

$$k_3 = 0.001 - 0.01 M^{-1} s^{-1}[7]$$
(3)

But because the reaction rate of Eq. (3) is much slower than that of Eq. (1), the ferrous ion is quickly consumed, but slowly regenerated [5]. The Fenton reaction slows down due to the low concentration of ferrous ion, which was reported in the literatures [8–12]. The decomposition of some pesticides and dyestuffs such as dichlorvos [8,9], atrazine [10], Procion Red H-E7B [11] and Disperse Red 354 [12] by Fenton process was a two-stage reaction. The first stage was a Fenton ( $Fe^{2+}/H_2O_2$ ) reaction in which the contaminant decomposed swiftly. But in

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the second stage, the decomposition was less rapidly for it was a Fenton-like (Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>) reaction. To degrade the contaminant quickly and effectively, the input of Fe<sup>2+</sup> should be enough comparing with that of H<sub>2</sub>O<sub>2</sub>. The optimal ratio of ferrous ion to hydrogen peroxide was found to be 2:1 for atrazine degradation [10].

However, it is interesting that the input of ferrous ion is much smaller for the treatment of phenolic compounds by Fenton system. The typical ratio of ferrous ion to hydrogen peroxide was 0.04–0.2 for chlorophenols [13,14], 0.01–0.1 for phenol [3,15] and 0.04–0.1 for nitrophenols [4]. Although the initial concentration of ferrous ion was low, the degradation of phenolic compounds was quick. Moreover, in our investigation into the treatment of phenolic compounds by Fenton-like system, the degradation rate increased quickly after an initiation phase.

It may be concluded that ferrous ion can be effectively generated during the degradation of phenolic compounds by Fenton and Fenton-like system. It was mentioned that some degradation intermediates of 4-chlorophenol, i.e. benzenediols could expedite the reduction of ferric ion [14]. However, more clear information is limited on the formation of the intermediates, the interaction among phenolic compounds, the intermediates and the ferrous ion. The objective of the paper was to reveal the relationship of the formation of the intermediates, which could reduce  $Fe^{3+}$ , with the degradation rate of the phenolic compounds in Fenton-like system. This study was useful for the application of Fenton-like system.

In this paper, the degradation of 4-chlorophenol (4-CP), 4-nitrophenol (4-NP) and phenol by Fenton-like process was investigated. The enhancement of the degradation, change of the concentration of  $H_2O_2$  and  $Fe^{2+}$  were measured. Reactions of  $Fe^{2+}/Fe^{3+}$  with inorganic species and intermediates were analyzed to find out the reason for  $Fe^{2+}$  generation. Formation of the hydroquinone-like intermediates was specially measured, which explained the enhancement of the degradation well. Finally, a pathway describing the interaction among the degradation of phenolic compounds, the formation of intermediates and the formation of  $Fe^{2+}$  was suggested.

### 2. Materials and methods

### 2.1. Materials

4-CP, 4-NP, phenol, hydroquinone catechol,  $Fe_2(SO_4)_3$  and hydrogen peroxide (30%) were purchased from Hangzhou Huadong Medicine Group Co. Ltd., and 4-chlorocatechol from Tokyo Kasei Kogyo Co. Ltd. They were all of analytical grade. Deionized and doubly distilled water was used throughout this study.

### 2.2. Procedures and analysis

Artificial wastewater (11) which contained 1 mol phenolic compounds was added into a flask, which was put in a thermostatic bath (T = 25 °C). Ferric ion was put into the solution after the pH adjusted to 3.0 by concentrated H<sub>2</sub>SO<sub>4</sub>. Then hydrogen peroxide was added to initiate the reaction. The ratio of

Fe<sup>3+</sup> to  $H_2O_2$  was chosen to be 1:20 referring to the literatures [13–15]. All experiments were carried out under the following conditions unless mentioned elsewhere: 1.0 mM phenolic compounds, 0.125 mM Fe<sup>3+</sup>, 2.5 mM H<sub>2</sub>O<sub>2</sub>, pH 3.0 and 25 °C.

At the given reaction time intervals, samples were taken out and analyzed. Analysis of phenolic compounds and their intermediates was performed with a Knauer HPLC unit with a reversed phase C18 column and UV detector setting wavelength at 278 nm. Mobile phase was prepared by methanol (A) and deionized water (containing 2‰ acetic acid) (B). The volume of A was defined as  $V_A$  and that of B was  $V_B$ . The ratio of  $V_A$ to  $V_B$  was 52:48 for 4-CP and 45:55 for 4-NP and phenol. A flow rate of 1.0 ml min<sup>-1</sup> was chosen. The potential reaction of the target by hydroxyl radical was prevented by adding 1.0 ml 1.0 M *tert*-butyl alcohol to the sample.

The H<sub>2</sub>O<sub>2</sub> concentration was determined by a spectrophotometric method using the potassium titanium (IV) oxalate method ( $\lambda = 400$  nm,  $\varepsilon = 935$  M<sup>-1</sup> cm<sup>-1</sup>) [16]. The concentration of ferrous ion was measured by the *o*-phenanthroline colorimetric method ( $\lambda = 510$  nm,  $\varepsilon = 1.1 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) [17].

### 3. Results and discussion

### 3.1. Degradation of phenolic compounds by Fenton-like process

Fig. 1 shows the degradation of phenolic compounds (4-CP, 4-NP and phenol) by Fenton-like process. The degradation of all three phenolic compounds by Fenton-like reaction was a three-phase reaction: the initiation phase, the fast phase and the termination phase. At the first 5 min, i.e. the initiation phase, the degradation of 4-CP was very slow and only 5% 4-CP removal was achieved. However, the degradation rate increased sharply after 5 min and the removal of 4-CP reached 80% at 20 min. After 20 min, the degradation rate slowed down and 90% 4-CP was removed at 40 min. The degradation of the phenolic compounds

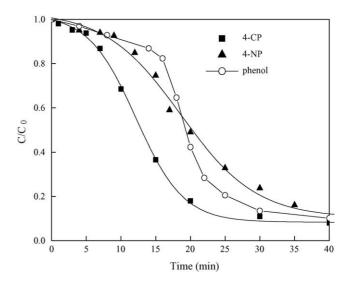


Fig. 1. The degradation of phenolic compounds by Fenton-like process: [4-CP, 4-NP, phenol]<sub>*i*</sub> = 1.0 mM, [Fe<sup>3+</sup>]<sub>*i*</sub> = 0.125 mM, [H<sub>2</sub>O<sub>2</sub>]<sub>*i*</sub> = 2.50 mM, pH 3.0, T = 25 °C.

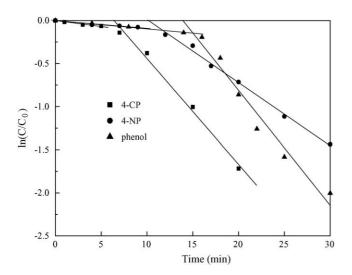


Fig. 2. Observed kinetics of phenolic compounds in two phases: [4-CP, 4-NP, phenol]<sub>i</sub> = 1.0 mM,  $[\text{Fe}^{3+}]_i = 0.125 \text{ mM}$ ,  $[\text{H}_2\text{O}_2]_i = 2.50 \text{ mM}$ , pH 3.0,  $T = 25 ^{\circ}\text{C}$ .

in the initiation phase and the fast phase fitted the following pseudo-first-order kinetics:

$$\ln\left(C/C_0\right) = -kt\tag{4}$$

where  $C_0$  and C is the concentration of phenolic compounds at the initial time (mM) and at the reaction time t, respectively; k is the pseudo-first-order reaction rate constant  $(min^{-1})$ . The plots of  $\ln(C/C_0)$  versus t are shown in Fig. 2. And it was found that at the beginning of the reaction, the plot of four data point of  $\ln(C/C_0)$  (A) versus time fitted linear. And the next several data points (B) versus time fitted another straight line. The interval including data A was defined as the initiation period. The slopes of the two linear plots were the observed rate constants in the initiation phase  $(k_A)$  and the fast phase  $(k_B)$ , respectively. Data of these observed kinetics for the degradation of 4-CP, 4-NP and phenol are shown in Table 1. For 4-CP,  $k_A$  was only  $0.0139 \min^{-1} k_{\rm B}$  was  $0.123 \min^{-1}$  in fast phase. Thus, the enhancement factor, i.e.  $k_{\rm B}/k_{\rm A}$ , which was an index to evaluate the acceleration of degradation in the fast phase, was calculated to be 8.85.

Degradation of 4-NP and phenol by Fenton-like process had a similar tendency to that of 4-CP, although the initiation period and the observed rate constants had some difference. Buxton et al. [18] reported that the rate constants for •OH with phenolic compounds were 4-CP>phenol>4-NP, with which the order of  $k_A$  was coincident. But the enhancement factor for phenol

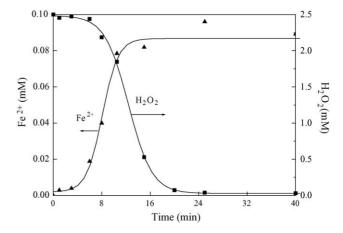


Fig. 3. Changes of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> during the 4-CP degradation by Fentonlike process: [4-CP] = 1.0 mM,  $[Fe^{3+}]_i = 0.125 \text{ mM}$ ,  $[H_2O_2]_i = 2.50 \text{ mM}$ , pH 3.0,  $T = 25 \degree$ C.

was much bigger than the other two, so the order of  $k_{\rm B}$  was phenol > 4-CP > 4-NP.

Generally speaking, in Fenton-like system,  $Fe^{2+}$  is slowly generated through the reduction of  $Fe^{3+}$  by  $H_2O_2$  (Eq. (3)) and Fenton reaction is initiated. But at the same time,  $Fe^{2+}$  is quickly reoxidized to  $Fe^{3+}$ . Therefore, the degradation of contaminant in Fenton-like process is slow. But it was interesting that the degradation of phenolic compounds was greatly improved after an initiation period.

### 3.2. Changes of the concentrations of $Fe^{2+}$ and $H_2O_2$

In Fenton-like process, the concentrations of  $Fe^{2+}$  and  $H_2O_2$ are the important parameters as they are the source of •OH. Therefore, changes of the concentrations of  $Fe^{2+}$  and  $H_2O_2$  were measured, which were similar for three phenolic compounds. As an example, changes of the concentrations of  $Fe^{2+}$  and  $H_2O_2$  in the degradation of 4-CP are shown in Fig. 3. The consumption of  $H_2O_2$  was also divided into three phases, just like the degradation of 4-CP. During the first 5 min, only 0.070 mM  $H_2O_2$ was consumed. However, the concentration of  $H_2O_2$  decreased rapidly after 5 min and  $H_2O_2$  became insufficient after 20 min, which led to the halt of 4-CP degradation.

The consumption rate of  $H_2O_2$  is closely related to the concentration of Fe<sup>2+</sup>. As shown in Fig. 3, ferrous ion was formed during the degradation. At the beginning of the reaction, the formation of Fe<sup>2+</sup> was slow and there was only  $3.90 \times 10^{-3}$  mM Fe<sup>2+</sup> at 3 min. After the initiation phase, the concentration of

 Table 1

 Kinetic data of three phenolic compounds degradation by Fenton-like process

	$k_{\bullet OH}^{a} (M^{-1} s^{-1})$	Initiation period (min)	$k (\mathrm{min}^{-1})$		Enhancement factor
			k <sub>A</sub>	kB	
4-CP	$7.6 \times 10^{9}$	5	0.0139 (R = 0.983)	0.1230 (R = 0.995)	8.85
4-NP	$3.8 \times 10^{9}$	9	$0.0091 \ (R = 0.973)$	0.0734 (R = 0.998)	8.02
Phenol	$6.6 \times 10^{9}$	14	$0.0097 \ (R = 0.997)$	$0.1459 \ (R = 0.982)$	15.0

<sup>a</sup> Cited from the literature [18].

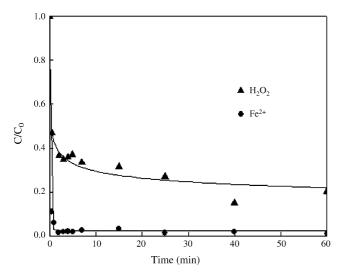


Fig. 4. Changes of  $Fe^{2+}$  and  $H_2O_2$  in the reaction of  $Fe^{2+}$  with  $H_2O_2$ :  $[H_2O_2]_i = 2.0 \text{ mM}, [Fe^{2+}]_i = 2.0 \text{ mM}, \text{ pH } 3.0, T = 25 \,^{\circ}\text{C}.$ 

 $Fe^{2+}$  increased rapidly and about 0.082 mM  $Fe^{2+}$  formed in the solution at 15 min. An amount of  $Fe^{2+}$  in the solution catalyzed  $H_2O_2$  to <sup>•</sup>OH quickly and hence, the degradation was accelerated.

## 3.3. Reasons for the quick formation of $Fe^{2+}$ —reduction of $Fe^{3+}$ by the intermediates

In Fenton-like process, the reactants with  $Fe^{2+}/Fe^{3+}$  are divided into two species. One is the inorganic species including  $H_2O_2$ , •OH,  $HO_2$ • and  $O_2^{-\bullet}$ . The other is the organic species involving the phenolic compounds and their degradation intermediates.

The principal reactions of the inorganic species with  $Fe^{2+}/Fe^{3+}$  are shown in Eqs. (1), (3) and (5)-(9). Eqs. (1) and (3) show that  $H_2O_2$  not only oxides Fe<sup>2+</sup>but also reduces Fe<sup>3+</sup>. But the rate constant of Fe<sup>2+</sup> with H<sub>2</sub>O<sub>2</sub>,  $k_1$ , is about 10<sup>4</sup>-10<sup>5</sup> times of  $k_3$ , which means Fe<sup>3+</sup> is the main iron species when only reactions (1) and (3) are considered. Also, the reaction rate of HO<sub>2</sub>• with Fe<sup>2+</sup> is quicker than that with Fe<sup>3+</sup>, as described in Eqs. (5) and (6) [19,20]. •OH is a strong oxidant, which can oxide  $Fe^{2+}$  quickly (Eq. (7) [21]) but not reduce  $Fe^{3+}$  to  $Fe^{2+}$ .  $O_2^{-\bullet}$  can react with Fe<sup>2+</sup> and Fe<sup>3+</sup>, as described in Eqs. (8) and (9) [20,22]. The rate constants,  $k_8$  and  $k_9$  show that Fe<sup>2+</sup> is the principal form of iron ions when only reactions with  $O_2^{-\bullet}$  are considered. However, the concentration of  $O_2^{-\bullet}$  in the solution is very low and the influence of  $O_2^{-\bullet}$  on the cycle of Fe<sup>2+</sup>/Fe<sup>3+</sup> can almost be ignored. This conclusion was confirmed by the following experiment. Fig. 4 describes changes of the concentration of  $Fe^{2+}$  and  $H_2O_2$  in Fenton reaction (without any organics). It was found that Fe<sup>2+</sup> decreased rapidly at the first 1 min, then kept almost unchangeable and only 2% Fe<sup>2+</sup> remained after 2 min. H<sub>2</sub>O<sub>2</sub> also decreased swiftly within 1 min and then it decreased slowly. All reactions of Fe<sup>2+</sup>/Fe<sup>3+</sup> with the inorganic species (Eqs. (1), (3) and (5)-(9)) happened in the solution, and the concentration of Fe<sup>2+</sup> was very low in

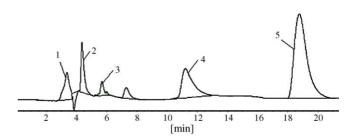


Fig. 5. Typical HPLC chromatogram during the Fenton-like oxidation of 4-CP. (1) Organic acids; (2) hydroquinone; (3) catechol; (4) 4-chlorocatechol; (5) 4-CP.

the solution, which was coincident with the conclusion drawn above.

$$HO_{2}^{\bullet} + Fe^{2+}(+H^{+}) \rightarrow Fe^{3+} + H_{2}O_{2},$$
  

$$k_{5} = 1.2 \times 10^{6} \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}[19]$$
(5)

HO<sub>2</sub>• + Fe<sup>3+</sup> → Fe<sup>2+</sup> + H<sup>+</sup> + O<sub>2</sub>,  

$$k_6 = 3.1 \times 10^5 \,\mathrm{M^{-1} \, s^{-1}}[20]$$
 (6)

•OH + Fe<sup>2+</sup> 
$$\rightarrow$$
 Fe<sup>3+</sup> + OH<sup>-</sup>,  
 $k_7 = 3.2 \times 10^8 \,\mathrm{M^{-1} \, s^{-1}}[21]$  (7)

$$O_2^{-\bullet} + Fe^{2+}(+2H^+) \rightarrow Fe^{3+} + H_2O_2,$$
  
 $k_8 = 1.0 \times 10^7 \,M^{-1} \,s^{-1}[20]$  (8)

$$O_2^{-\bullet} + Fe^{3+} \rightarrow Fe^{2+} + O_2,$$
  
 $k_9 = 5.0 \times 10^7 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}[22]$  (9)

Thus, reactions between the inorganic species and  $Fe^{2+}/Fe^{3+}$  cannot account for the quick formation of  $Fe^{2+}$  after the initiation period, as shown in Fig. 3. It is indicated that the cycle of  $Fe^{2+}/Fe^{3+}$  may involve the role of some intermediates.

HPLC analysis was used to identify the intermediates of phenolic compounds in Fenton-like reaction. Fig. 5 shows the typical HPLC chromatogram during the degradation of 4-CP. As could been seen, there were two species of the intermediates. One was the organic acid, it maybe formic acid, acetic acid, maleic acid and fumaric acid referred to the literature [14]. The other was the aromatic substance including benzoquinone and some hydroquinone-like intermediates. The intermediates were coincident with that reported in the literature [14]. In the degradation of 4-CP, the hydroquinone-like intermediates such as catechol, hydroquinone, and 4-chlorocatechol were found. The retention times of hydroquinone, catechol and 4-chlorocatechol were 4.40, 5.72 and 11.18 min, respectively. Also, catechol and hydroquinone were identified to be the intermediates of 4-NP and phenol. To find out the intermediates that could reduce Fe<sup>3+</sup>, a series of control experiments were conducted. Formic acid, acetic acid, maleic acid, fumaric acid and benzoquinone could not reduce the ferric ion because no ferrous ion was detected within 60 min when they reacted with Fe<sup>3+</sup>.

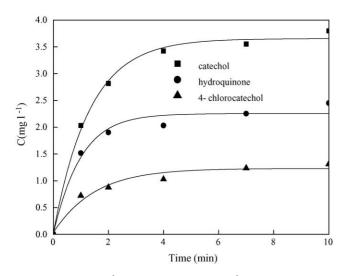


Fig. 6. Formation of Fe<sup>2+</sup> from the reduction of Fe<sup>3+</sup> by the intermediates: [4-chlorocatechol, catechol, hydroquinone]<sub>i</sub> = 5 mg l<sup>-1</sup>, [Fe<sup>3+</sup>]<sub>i</sub> = 5.6 mg l<sup>-1</sup>, pH 3.0,  $T = 25 \degree$ C.

Formation of Fe<sup>2+</sup> during the reaction between  $5 \text{ mg l}^{-1}$  hydroquinone-like intermediates and  $5.6 \text{ mg l}^{-1} \text{ Fe}^{3+}$  is shown in Fig. 6. All the hydroquinone-like intermediates reduced Fe<sup>3+</sup> to Fe<sup>2+</sup> quickly and the order was catechol > hydroquinone > 4-chlorocatechol. The concentration of Fe<sup>2+</sup> was 2.0, 1.5 and 0.7 mg l<sup>-1</sup> Fe<sup>2+</sup> at 1 min and rose to 3.4, 2.0 and 1.0 mg l<sup>-1</sup> at 4 min for catechol, hydroquinone and 4-chlorocatechol, respectively, then it remained unchangeable. Therefore, the reduction of Fe<sup>3+</sup> by these intermediates results in the quick formation of Fe<sup>2+</sup> during the degradation of phenolic compounds by Fenton-like process.

### 3.4. Role of the intermediates in the degradation process

To understand the role of hydroquinone-like intermediates clearly, the formations of hydroquinone-like intermediates in the degradation of phenolic compounds are shown in Fig. 7. In the initiation period, the slow degradation of 4-CP resulted in the slow formation of the hydroquinone-like intermediates. Concentrations of 4-chlorocatechol, hydroquinone and catechol were only 0.754, 0.125 and 0.154 mg  $l^{-1}$  at 5 min, respectively. Nevertheless, the hydroquinone-like intermediates took participate in the Fe<sup>2+</sup>/Fe<sup>3+</sup> cycle and led to the formation of Fe<sup>2+</sup>, as shown in Fig. 3. The formed Fe<sup>2+</sup> accelerated the consumption of H<sub>2</sub>O<sub>2</sub>, and the degradation of 4-CP. In consequence, the hydroquinone-like intermediates were quickly formed. At 12 min, concentrations of 4-chlorocatechol, hydroquinone and catechol increased to 2.01, 0.52 and  $1.83 \text{ mg} \text{ l}^{-1}$ , respectively. After then, the concentration of catechol decreased and that of 4-chlorocatechol and hydroquinone kept on increasing to reach the maximum of 5.0 and  $1.2 \text{ mg } l^{-1}$ , respectively.

Hydroquinone and catechol were formed in the decomposition of 4-NP and phenol. In the initiation period, the amount of them was small but rose in fast phase. After reaching the maximum, the concentrations of the intermediates decreased. The formation of the hydroquinone-like intermediates played

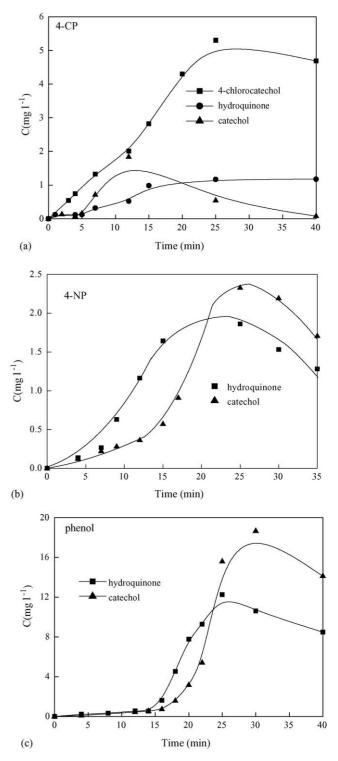


Fig. 7. Formation of intermediates during the process: (a) 4-CP, (b) 4-NP, and (c) phenol. [4-CP, 4-NP, phenol]<sub>*i*</sub> = 1.0 mM,  $[\text{Fe}^{3+}]_i = 0.125 \text{ mM}$ ,  $[\text{H}_2\text{O}_2]_i = 2.50 \text{ mM}$ , pH 3.0,  $T = 25 \,^{\circ}\text{C}$ .

an important role in the rapid degradation after the initiation phase.

In addition, the differences in the formation of hydroquinonelike intermediates agreed with the data listed in Table 1. At the time when the reaction was initiated,  $Fe^{3+}$  was only reduced by H<sub>2</sub>O<sub>2</sub>, thus the formation rates of Fe<sup>2+</sup> and the rate of Fenton reaction were all the same. Because the rate constants of  ${}^{\bullet}$ OH reacting with 4-CP, 4-NP and phenol ( $k_{{}^{\bullet}$ OH}) are 7.6 × 10<sup>9</sup>, 3.8 × 10<sup>9</sup> and 6.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively, the observed rate constants for the initiation phase ( $k_A$ ) are 4-CP > phenol > 4-NP. Nevertheless, in the fast phase, the total hydroquinone-like intermediates of phenol were much more than that of 4-CP or 4-NP. This may be due to the different reaction ways of  ${}^{\bullet}$ OH with phenolic compounds. The maximum of the total hydroquinone-like intermediates of phenol was 28.1 mg l<sup>-1</sup>, but that of 4-CP was only 7.0 mg l<sup>-1</sup>. In consequence, the reduction rate of Fe<sup>3+</sup> was much quicker in the oxidation of phenol than in the reaction of 4-CP and 4-NP. And the observed rate constant in the fast phase ( $k_B$ ) of phenol was larger than that of 4-CP.

During the Fenton-like process, the degradation of phenolic compounds, the formation of the hydroquinone-like intermediates and the generation of  $Fe^{2+}$  interact with each other. When Fenton-like reaction is initiated,  $Fe^{3+}$  is reduced to  $Fe^{2+}$  by  $H_2O_2$ , which lead to the occurrence of Fenton reac-

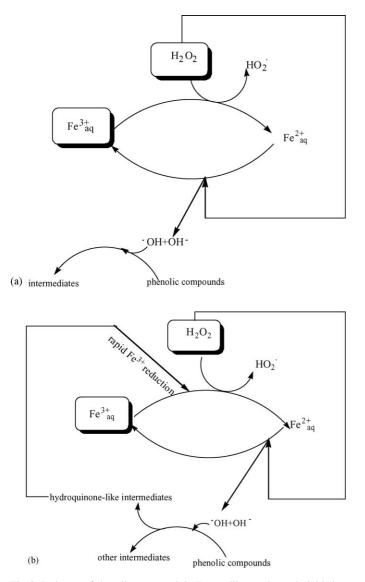


Fig. 8. Pathways of phenolic compounds by Fenton-like reaction at the initiation time (a) and in the fast phase (b).

tion. The reduction rate constant of  $Fe^{3+}$  by  $H_2O_2$  is only 0.001–0.01 M<sup>-1</sup> s<sup>-1</sup>, which is too small to generated  $Fe^{2+}$  quickly. In consequence, the degradation of the phenolic compounds in the initiation period is slow. But the hydroquinone-like intermediates produced in the initiation period reduce  $Fe^{3+}$  to  $Fe^{2+}$ , which results in the increase of the concentration of  $Fe^{2+}$  in the solution. Thus, the generation of  $Fe^{2+}$  promotes the degradation of phenolic compounds, as well as the formation of intermediates, and vice versa. When an amount of hydroquinone-like intermediates is formed in the solution, the generation of  $Fe^{2+}$  was very rapid, which caused the fast degradation. The reaction pathways at the initiation time and in the fast phase are described in Fig. 8.

The role of the hydroquinone-like intermediates keeps ferrous ion being generated quickly and changes the Fenton-like reaction into the Fenton reaction. Therefore, even a small amount of ferric ion  $(7.0 \text{ mg l}^{-1})$  input can make the phenolic compounds degrade effectively. Understanding of the role of the intermediates is helpful to the application of Fenton-like system.

Whether other aromatic compounds can generate hydroquinone-like intermediates and the relation of the molecular structure to the degradation will be subjected to future work.

### 4. Conclusion

- 1. For all of the three phenolic compounds (4-CP, 4-NP and phenol), the degradation was divided into three phases: the initiation phase, the fast phase and the termination phase. The degradation of phenolic compounds in the initiation phase and the fast phase both followed a first order law. The enhancement factors were 8.85, 8.02 and 15.0 for 4-CP, 4-NP and phenol, respectively.
- 2. In the fast phase, the consumption rate of  $H_2O_2$  and the formation rate of  $Fe^{2+}$  both increased rapidly. The quick formation of  $Fe^{2+}$  was not due to the reaction of  $Fe^{2+}/Fe^{3+}$  with the inorganic species ( $H_2O_2$ ,  $\bullet OH$ ,  $HO_2^{\bullet}$  and  $O_2^{-\bullet}$ ) but the reduction of  $Fe^{3+}$  by the hydroquinone-like intermediates.
- 3. The formation of the hydroquinone-like intermediates promoted the generation of ferrous ion, thus the degradation of phenolic compounds. Also, the different generation of hydroquinone-like intermediates accounted for the various enhancement factors of phenolic compounds. A pathway describing the role of the intermediates in the degradation was suggested.

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