



Reductive dissolution and oxidative catalysis of an immobilized iron oxide in the presence of catechol and phenol

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ABSTRACT

An original study of an immobilized iron oxide catalyst (SiG1) with one hydroxylation intermediate of phenol (catechol) in the reductive dissolution process was performed. Also, SiG1 was applied as the catalyst for the oxidation of phenol and catechol in the presence of hydrogen peroxide. The SiG1 used in this study reacted more efficiently with catechol than the other iron oxides. Only the hydroxylation intermediates of phenol (i.e. catechol and 1,4-hydroquinone) were able to reductively dissolve SiG1. However, there are no interactions between SiG1 and phenol. The reductive dissolution of SiG1 not only occurred at acidic solution but also occurred at alkali solution in the presence of catechol. Furthermore, the solution of pH 5 was found to be a critical condition in which the interactions of SiG1 and catechol were weak in the presence or absence of H₂O₂. The yields of Fe²⁺ from SiG1 in the presence of catechol were limited by the equilibrium of reduction and the oxidation rate of iron(III, II) species. A kinetic model was applied to obtain the estimated maximum concentration of Fe²⁺ produced by SiG1 and estimated proportional constant in the presence of catechol at different pH conditions by using a trial and error method. Catechol induced the reductive dissolution of SiG1 and then promoted its own oxidation along with that of phenol in the presence of hydrogen peroxide.

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1. Introduction

Advanced oxidation processes (AOPs) as well as Fenton-type processes have been widely applied for the treatment of phenolic wastewater. Iron salts applied in Fenton-type reactions including ferrous ions and ferric ions have been thoroughly studied, and it has been shown that the mineralization of organic compounds with the Fenton reaction is enhanced by inducing UV or solar light induction. Also, many studies have reported that the application of Fenton's reagent at near neutral pH conditions is feasible in the presence of some organic complexing ligands [1–9]. Organic compounds may act as ligands (L) or redox agents. Possible reactions include (i) the photolysis of Fe(III)-L complex [7], (ii) the formation of reactive high valent iron-oxo or iron-peroxo complexes stabilized by L [10], (iii) the reduction of Fe³⁺ by neutral organic molecules or radicals [11] and (iv) the oxidation of Fe²⁺ by radicals or carbocations [11]. The core thermal and photochemical inorganic reactions involved in •OH production and decay have been well established [11,12]. An understanding of these reactions is important for the

successful application and enhancement of Fenton-type remediation technologies. In 1954, Udenfriend and co-workers indicated that aromatic compounds are hydroxylated by O₂ or H₂O₂ when Fe(II), ascorbic acid, and ethylenediaminetetraacetic acid (EDTA) are present in a buffered solution around neutral pH [13]. In 1966, Hamilton and his co-workers reported that the hydroxylation of anisole by H₂O₂ in the presence of ferric ion and catechol involves two general types of mechanisms: (1) a free-radical chain reaction and (2) direct oxidation of the substrate by catechol with concomitant regeneration of Fe³⁺ [14]. Furthermore, aromatic pollutants have been the most frequently targeted compounds in the treatment of wastewater, and phenol, 1,2-hydroquinone (catechol) and 1,4-hydroquinone (1,4-HQ) have been found as the intermediates during AOP degradation [6,15,16]. It has been shown that catalytic amounts of catechol and 1,4-HQ greatly increases the rate of the Fe³⁺/H₂O₂ (Eq. (1)) degradation of substituted benzenes [17]

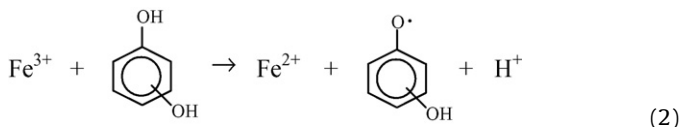


Also, polyphenols and particular catechols exist in many organisms, including plants and animals. These kinds of organic compounds have been found to easily reduce Fe(III) and to complex with Fe(II) (Eq. (2)) [18,19]. Moreover, it has been established that Fe³⁺ can be

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reduced to Fe^{2+} rapidly at a low pH in aqueous solution [19,20]



Hence, the acceleration of the rate of organic compound degradation is ascribed to the production of Fe^{2+} , which then generates $\bullet\text{OH}$ through the normal Fenton pathway (Eq. (3))



Hydroquinones have been used for the enhancement of homogeneous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems in the degradation of phenol [21]. Furthermore, iron oxides are popularly employed as catalysts in a heterogeneous Fenton reagent [12,22–29]. The major advantages for the application of iron oxides are that they are economical, plentiful and easy to obtain; as heterogeneous catalysts, they can also be easily separated from treated wastewater. Different types of iron oxides exhibit different activities. In our previous study, some immobilized iron oxides were found to be of high efficiency in the activation of hydrogen peroxide [22]. Furthermore, researchers have determined that the profound insolubility of ferric hydroxide and the low equilibrium concentrations of ferric ion in biological environments are overcome by the enormous stability and ion selectivity of ferric siderophore complexes [30]; this means that ferric hydroxide can be reductively dissolved in the presence of some quinone derivatives at a neutral pH. There are few reports that discuss the reductive dissolution of iron oxides in the presence of quinone derivatives. However, the cycling of iron is of great importance in the geochemical cycling of electrons in water–sediment systems, in soil systems, and in atmospheric waters. Iron oxides are reductively dissolved (both in dark and light reactions) to Fe(II) , which in turn is oxidized, and Fe(III) then precipitates to form iron oxides. Reductive dissolution of the Fe(III) of iron oxides has been demonstrated to be of interest in the storage and transfer of iron in biological cells, as well as in processes for the removal of iron corrosion products [31]. Reductive dissolution involves two stages: an induction period and an autocatalytic period. The dissolution process is affected by the initial solution pH, temperature, the exposure of solution to UV radiation and by the addition of bivalent iron in the solution [32]. Hence, an investigation of the reductive dissolution of iron oxides in the oxidative catalysis of phenol and catechol is meaningful and worthy of consideration.

The objective of this work is to compare the reductive dissolution abilities of commercial iron oxide and immobilized iron oxide (SiG1) in the presence of catechol and also to investigate the factors which may affect their reductive dissolution, such as the pH and the concentration of catechol. Also, a reasonable kinetic model was proposed to describe the formation of Fe^{2+} from SiG1 in the presence of catechol at different solution pH values. In addition, the pH effect on the oxidative catalyses of phenol and catechol were investigated. The reductive dissolution of SiG1 during the oxidative catalysis of phenol and catechol in the presence of H_2O_2 was also investigated.

2. Experiment

2.1. Materials and synthesis of SiG1

The commercial iron oxides catalysts, FeOOH_1 (30–50 mesh) and FeOOH_5 (50–80 mesh) were purchased from Aldrich and used as received. Catechol (99%+, Acros), Hydroquinone (99.5%, Acros) and NaClO_4 (99%, SHOWA) were of analytical reagent grade and used without further purification. An immobilized iron oxide on silica sand was developed in the following manner [23,33]: The ferrous

ion in ground water was oxidized by aeration, and the iron(III) oxyhydroxide was simultaneously immobilized on nonporous silica sand (SiO_2) at a neutral pH in a fluidized bed reactor. The immobilized iron oxide (SiG1) was withdrawn from the fluidized bed reactor after 1 month.

2.2. Characterization of SiG1 and analysis

About 17 mg/g of iron immobilized on SiG1 , the bulk density of which was about 1.52 g/cm^3 , and the mean particle diameter was approximately 0.99 mm. The surface elements distribution of SiO_2 and SiG1 were studied by an scanning electron microscope (SEM) (JEOL JSM-6700F) combined with an EDS (energy dispersive spectroscopy). The concentration of ferrous ions was measured using the 1,10-phenanthroline method [34]. The concentration of H_2O_2 was measured using titanium sulfate [35]. The concentrations of phenol and catechol were measured using high performance liquid chromatography (HPLC) (SHIMADZU SPD-10AP) with a TSK-GEL ODS-80TM column (4.6 mm \times 150 mm) and a UV detector at 225 nm. A mixture of methanol–water (50/50, v/v) was used as the mobile phase.

2.3. Experimental procedure

2.3.1. Reductive dissolution of different iron oxides

The SiG1 or commercial iron oxides were individually immersed in a 1-L aqueous catechol solution (200 mg/L) that contained 10 mM of NaClO_4 (ionic strength) at 30°C with an agitation speed of 150 rpm. The solution pH was adjusted to 4.0 ± 0.2 by HClO_4 or NaOH .

2.3.2. Reductive dissolution of SiG1

In this section, all the solutions were controlled at the same conditions (10 mM NaClO_4 , pH 4.0 ± 0.2 , 30°C and an agitation speed of 150 rpm). All the samples were withdrawn after a period of time and filtered using a $0.2\text{-}\mu\text{m}$ membrane filter. The production concentration of ferrous ions was the measured. The various amounts of SiG1 , 5, 10, 15 and 20 g, respectively were individually added to a 1-L aqueous catechol solution (50 mg/L); for the various concentrations of catechol, four 10 g portions of SiG1 were immersed in 50, 100, 200 and 400 mg/L of 1-L aqueous catechol solutions, respectively. For the test of reductively dissolved organic compounds, three 10 g portions of SiG1 were immersed in aqueous phenol, catechol and 1,4-HQ solutions, respectively. For the pH variation experiment, the operation procedure was similar to that mentioned above and the initial solution pH was adjusted by HClO_4 or NaOH . However, the pH condition was not controlled during the reaction to avoid Fe^{2+} oxidation or iron precipitation.

2.3.3. Catalytic oxidation process

Catalytic oxidation of phenol or catechol with H_2O_2 at different pH conditions was performed by the following procedure: SiG1 (10 g/L) was added into a 1-L beaker with either a phenol or catechol (100 mg/L, 1.06 mM) solution; H_2O_2 (68 mg/L, 2 mM) was then added to initiate the reaction at the adjusted pH (by HClO_4 or NaOH) at 30°C with an agitation speed of 150 rpm. The samples were withdrawn after a period of time and filtered using a $0.2\text{-}\mu\text{m}$ membrane filter. The concentration of ferrous ions, phenol or catechol was then measured by HPLC.

3. Results and discussion

3.1. Characterization of SiG1

Silica sand is abundant, cheap, has good mechanical properties and is easy to separate when used as a catalyst support. In terms

Table 1
Surface element compositions of SiO₂ and SiG1 by EDS.

Element	SiO ₂		SiG1	
	Weight %	Atomic %	Weight %	Atomic %
C	2.21	4.23	2.10	6.23
O	44.91	64.53	25.82	57.59
Al	0.3	0.26	0	0
Si	35.38	28.96	4.30	5.46
Ca	0	0	1.71	1.52
Fe	0	0	37.49	23.96
Pt	17.2	2.03	28.58	5.23

of catalyst recovery and separation, the immobilization of active species on the surface of silica sand is a concern. Nonporous silica sand (white) was chosen to be the support of iron oxide (brown) [36]. The major advantage of a nonporous catalyst in heterogeneous catalysis is that its internal mass transfer resistance is negligible as compared to a porous catalyst. A new technique for oxidizing Fe(II) and for the immobilization of Fe(III) at a neutral pH in a fluidized bed reactor has previously been developed [23,33]. After a small amount of iron oxides were immobilized on the silica sands, the particles became light brown. Table 1 lists the quantitative surface compositions of SiO₂ and SiG1, as determined by EDS. Obviously, iron oxides are successfully immobilized on the surface of SiO₂. Furthermore, it was demonstrated in this work that the immobilized iron oxides could not be easily removed from the surface of the silica sands by agitation. Hence, the iron oxides were firmly immobilized on the surface of the silica sand. The density and particle diameter properties show that SiG1 is easy to recover and separate after this application. Moreover, SiG1 is an amorphous and nonporous iron oxide, and its characteristics, such as its X-ray diffraction and morphology, have been reviewed in our previous work [22].

3.2. Reductive dissolution of different iron oxides

In our previous study, it was found that the immobilized iron oxide (SiG1) dissolved more easily in the presence of oxalic acid due to the fact that the bonding between iron oxide and silica sand (support) is weak [22]. In this work, it will be very interesting to investigate the reductive dissolution of different iron oxides in the presence of catechol. Fig. 1 shows that the immobilized iron oxide, SiG1, exhibits an easy progression to reductive dissolution (i.e. ferrous ion production). Moreover, the immobilized iron oxide, SiG1, is more reactive than the bulk iron(III) oxides (FeOOH_L and FeOOH_S) in the presence of catechol. The slopes of linear straight lines shown in Fig. 1 represent the formation rate of ferrous ions (Eq. (4))

$$R_f = \frac{[\text{Fe}^{2+}]}{t} \quad (4)$$

where R_f is the formation rate of Fe²⁺, [Fe²⁺] is the formation concentration of Fe²⁺, and t is the reaction time. Apparently, the formation rate of Fe²⁺ and the formation concentration of Fe²⁺ for SiG1 are greater than that of the commercial bulk iron oxides used in this study. The difference in the reactivity of the iron(III) oxides may be plausibly caused by the difference in the degree of polymerization of the oxides and as a result of the quantity of the active functional groups with various coordination arrangements on the surfaces of the these iron(III) oxides [37].

3.3. Reductive dissolution of SiG1

Firstly, the various amounts of SiG1 were individually immersed in 50 mg/L of catechol in order to investigate their reductive dissolution kinetics (Fig. 2a). When SiG1 is above 10 g, the formation rates of ferrous ions are close to each other (Table 2). Hence, the reductive dissolution of SiG1 is a diffusion control process. Fur-

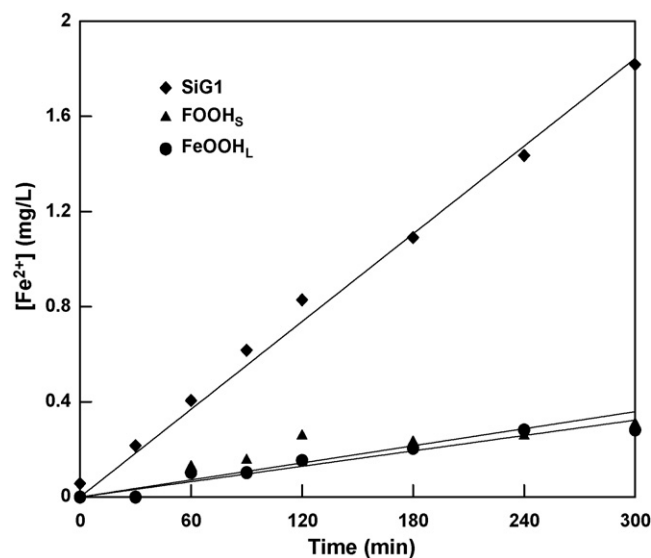


Fig. 1. Comparison of the reductive dissolution kinetics of iron oxide produced from immobilized of iron species ([SiG1]₀ = 10 g/L, iron contained = 170 mg/L) and commercial bulk iron oxide ([FeOOH]_{L,0} = [FeOOH]_{S,0} = 0.5 g/L, iron contained = 314 mg/L) (pH 4.0, [Catechol]₀ = 200 mg/L, 150 rpm, 30 °C, 10 mM NaClO₄).

thermore, the concentration of catechol in the solution relates to the saturated solubility and the reductive dissolution rate of the iron species. Secondly, 50, 100, 200 and 500 mg/L of catechol were prepared in different beakers, and then the SiG1 (10 g/L) samples were individually added into these beakers to study their reductive dissolution process. Fig. 2b shows that the formation rates of ferrous ions generated from SiG1 increase with increased concentration of catechol. Also, the yields of ferrous ions at 300 min are proportional to the concentration of catechol (Table 2). Based on the result, the higher the concentration of catechol that exists in the solution, the higher the saturated solubility and the faster the reductive dissolution rate of the iron species.

When ferrous ions and hydrogen peroxide (Fenton reagent) are combined for the degradation of phenol, ferric ions are formed by the oxidation of ferrous ions; catechol and 1,4-hydroquinone (1,4-HQ) are the initial products [21,30]. In a homogeneous system, a major interaction of iron ions and organic compounds is redox reaction. In contrast to a homogeneous system, the interactions of organic compounds and iron oxides should include adsorption, a reaction (redox) and a desorption (dissolution) process. Hence, the reductive dissolution of SiG1 in the presence of phenol, catechol and 1,4-HQ was compared. Fig. 3 shows that there was no reductive

Table 2

The formation concentration of Fe²⁺ at 300 min ([Fe²⁺]₃₀₀) and formation rate of Fe²⁺ (R_f) with different concentration of catechol (pH 4, 30 °C, 150 rpm, 10 mM NaClO₄).

Variables	[Fe ²⁺] ₃₀₀ (mg/L)	R_f (μM/min)
Iron oxides (Fig. 1)		
SiG1	2.72	0.172
FeOOH _S	0.31	0.021
FeOOH _L	0.28	0.019
[SiG1] ₀ (g/L) (Fig. 2a)		
20	1.46	0.087
15	1.23	0.080
10	1.31	0.083
5	0.87	0.054
[Catechol] ₀ (mg/L) (Fig. 2b)		
500	3.61	0.221
200	2.72	0.172
100	1.69	0.101
50	1.31	0.083

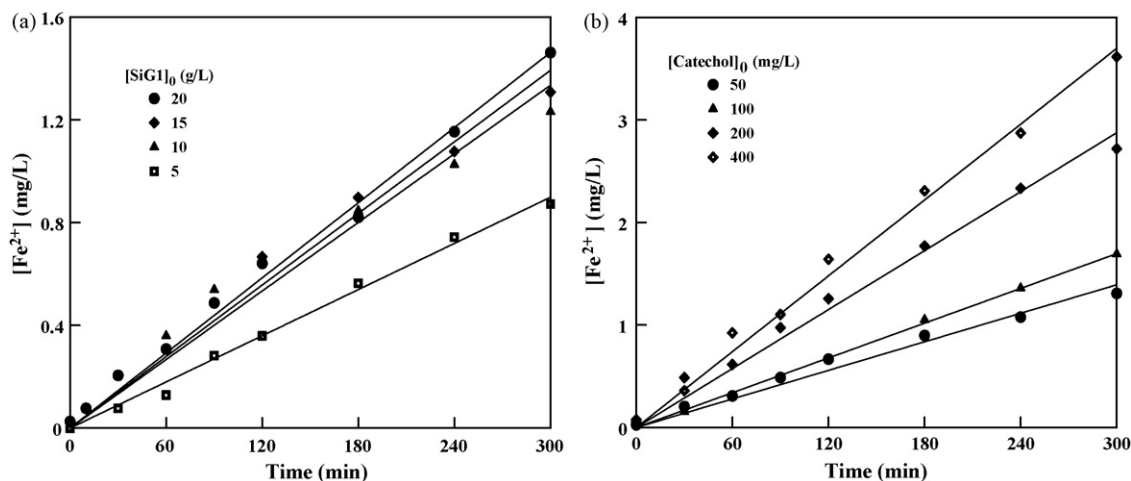


Fig. 2. Reductive dissolution kinetics of different concentrations of (a) SiG1 ($[\text{Catechol}]_0 = 50 \text{ mg/L}$) and (b) catechol ($[\text{SiG1}]_0 = 10 \text{ g/L}$) (pH 4.0, 150 rpm, 30°C , 10 mM NaClO_4).

dissolution of SiG1 in the presence of phenol. However, the catechol and 1,4-HQ are shown to be efficient for the reductive dissolution of SiG1. Furthermore, the reductive dissolution behavior of SiG1 was different in the presence of catechol and 1,4-HQ due to their difference in molecular structure. The initial reductive dissolution rate of SiG1 in the presence of catechol is faster than that in the presence of 1,4-HQ. However, the production of ferrous ions increases after 120 min in the presence of 1,4-HQ due to the autocatalytic mechanism (the initially formed 1,4-HQ-Fe(II) complex induces further reductive dissolution of SiG1). The reductive dissolution mechanism of SiG1 includes adsorption, iron(III) reduction and iron(II) dissolution in the presence of catechol or 1,4-HQ. Based on the results, the hydroxylation compounds of phenol (i.e. catechol and 1,4-HQ) were able to react with SiG1, rather than phenol. Generally, the active radicals produced on the surface of a catalyst can oxidize the organic compounds and are also adsorbed on the surface of the catalyst. However, in this case, phenol is not adsorbed by SiG1. If the active radicals were to be produced on the surface of SiG1 in the presence of H_2O_2 and then they were to diffuse to the aqueous solution, their short life would result in inefficiency in the oxidation of phenol or make it quite difficult. On the other hand, the production of Fe^{2+} from SiG1 via reductive dissolution can overcome this

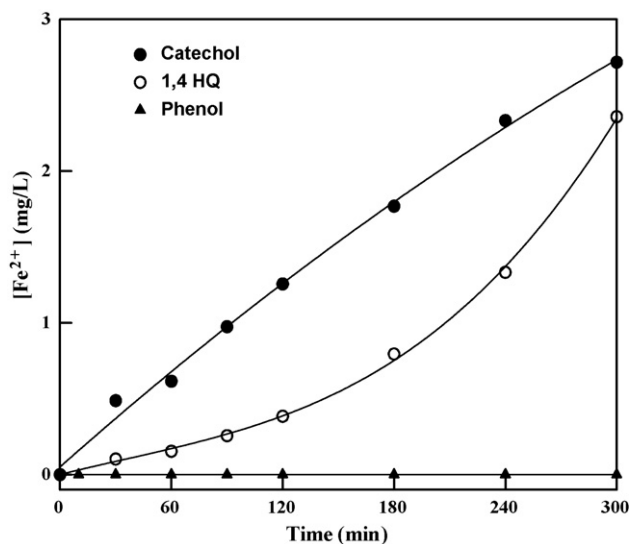


Fig. 3. Reductive dissolution kinetics with catechol, 1,4-HQ and phenol ($[\text{SiG1}]_0 = 10 \text{ g/L}$, pH 4.0, 150 rpm, 30°C ; $[\text{Catechol}]_0 = [\text{1,4-HQ}]_0 = 200 \text{ mg/L}$, $[\text{Phenol}]_0 = 100 \text{ mg/L}$, 10 mM NaClO_4).

problem. Hence, it is to be expected that catechol and 1,4-HQ play a significant role for the oxidation of phenol in the presence of SiG1 and H_2O_2 .

3.4. pH effect on the reductive dissolution of SiG1

Solution pH value is an important factor for the oxidation, dissolution and precipitation of iron species. Usually, the oxidation and precipitation rates of iron species are very fast at higher solution pH values (>5). The reduction and dissolution processes of iron species usually occur under acidic conditions. In this section, the reductive dissolution of SiG1 in the presence of catechol with various pH values was investigated. Firstly, it was confirmed that the SiG2 was not dissolved when the pH value of the solution was greater than 4.0. When the initial pH was adjusted below 5, the pH value remained constant during the reaction. However, when the initial pH was above 6, the pH value gradually decreased during the reaction. During the reaction, the alkali was not added into the system to avoid the oxidation and precipitation of ferrous ions. Fig. 4a shows that a pH of 4 is the optimum condition for yielding ferrous ions from SiG1 in the presence of catechol. When the initial solution pH was adjusted to 5.0, the yield of ferrous ions is lower than in other pH conditions. The yields of Fe^{2+} from SiG1 in the presence of catechol were limited by the equilibrium of reduction and the oxidation rate of the iron(III, II) species. Hence, the formation concentration of Fe^{2+} from SiG1 in the presence of catechol is expected to reach a plateau (equilibrium) or a maximum value (reduction and then oxidation periods) under different concentrations of catechol or under different solution pH values. One can see that the production of ferrous ions gradually reaches plateau at initial pH values of 4.5, 5.0, 6.0 and 9.0, respectively, as shown in Fig. 4a. The formation rate of Fe^{2+} from SiG1 in the presence of catechol is reasonably assumed to be proportional to the concentration gradient of Fe^{2+} between estimated maximum reductively dissolved concentration and the solution concentration (driving force), so the kinetic model can be expressed as

$$\frac{d[\text{Fe}^{2+}]}{dt} = -k_e([\text{Fe}^{2+}]_{\text{em}} - [\text{Fe}^{2+}]) \quad (5)$$

No Fe^{2+} is formed in the solution at time zero (i.e. $[\text{Fe}^{2+}]_0 = 0$). Therefore,

$$\ln \frac{[\text{Fe}^{2+}]_{\text{em}} - [\text{Fe}^{2+}]}{[\text{Fe}^{2+}]_{\text{em}}} = -k_e t \quad (6)$$

where k_e is the estimated proportional constant; t is time; $[\text{Fe}^{2+}]_{\text{em}}$ and $[\text{Fe}^{2+}]$ are the estimated maximum concentrations and solution

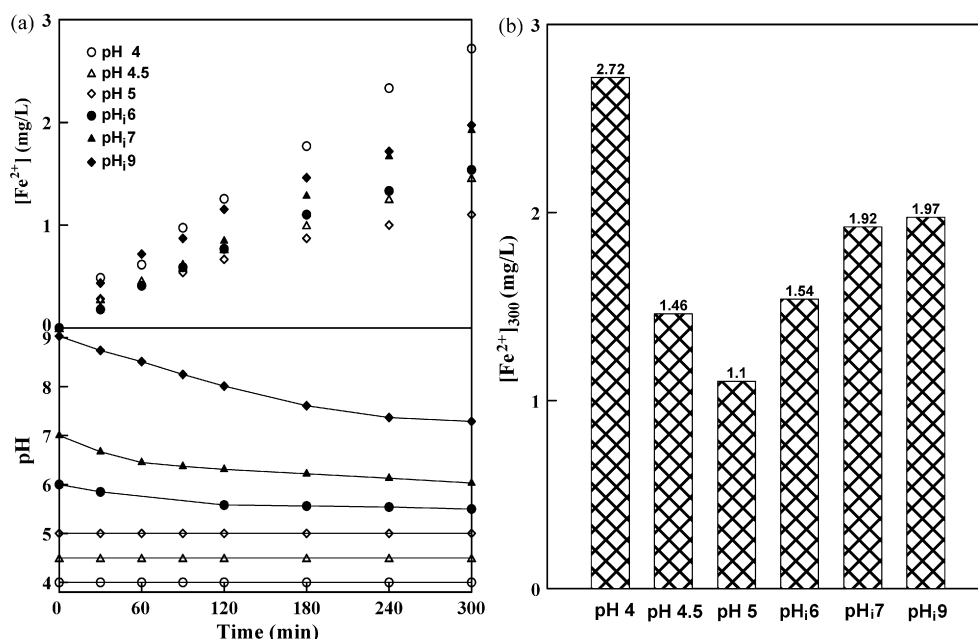


Fig. 4. (a) Reductive dissolution kinetics of SiG1 at different pH conditions; (b) the production of ferrous ions at 300 min at different pH conditions ($[SiG1]_0 = 10$ g/L, $[Catechol]_0 = 200$ mg/L, 150 rpm, 30 °C, 10 mM $NaClO_4$).

concentrations of Fe^{2+} . We can guess a value of $[Fe^{2+}]_{em}$, then k_e , and a straight regression line of $\ln([Fe^{2+}]_{em} - [Fe^{2+}])/[Fe^{2+}]_{em}$ vs. t (from 0 to 300 min) plot were obtained (trial an error method). When the R^2 of the regression line is close to 1, the values obtained for k_e and $[Fe^{2+}]_{em}$ are recorded in Table 3. The obtained values of $[Fe^{2+}]_{em}$ represent the estimated maximum Fe^{2+} formation concentrations in the presence of catechol at different pH conditions. Also, the formation of ferrous ions in the presence of catechol was recorded at 300 min under different pH conditions (Fig. 4b). Obviously, the reductive dissolution of SiG1 at a pH of 5 is the most inefficient (Fig. 4b and Table 3), so the solution of pH 5 is a critical condition for the interactions of SiG1 and catechol. Generally, the ferrous ions are rapidly oxidized to ferric ions by dissolved oxygen in solution at neutral or alkaline conditions [23,38]. However, the reductive dissolution of SiG1 at initial pH of 9 is also promoted in the presence of catechol. The results also mean that the ferrous ions produced were protected by catechol at higher solution pH conditions. Moreover, the color transformation of catechol-iron complexes in the solution was observed at different pH conditions during the reaction. It has been pointed out that the various solution colors were caused by the formation of different catechol-iron complexes [20,30].

3.5. Catalytic oxidation of phenol and catechol in the presence of H_2O_2

It is well known that the aromatic intermediates of phenol during the oxidation process are catechol and 1,4-HQ [6,39,40]. In this section, the catalysis of phenol and catechol at different pH conditions is a major concern. Also, the formation of ferrous ions was

Table 3

The estimated maximum concentration of Fe^{2+} ($[Fe^{2+}]_{em}$), estimated proportional constant (k_e) and R^2 ($[SiG1]_0 = 10$ g/L, $[Catechol]_0 = 200$ mg/L, 150 rpm, 30 °C, 10 mM $NaClO_4$).

pH	4.5	5.0	6.0 ^a	9.0 ^a
$[Fe^{2+}]_{em}$ (mg/L)	2.56	1.23	2.34	2.91
$k_e \times 10^3$ (1/min)	2.8	7.0	3.5	3.9
R^2	0.9978	0.9957	0.9972	0.9964

^a Represent the pH value decrease during the reaction.

observed during the reaction. Actually, the complete degradation of 1 mol of phenol to CO_2 consumed 14 mol of H_2O_2 . In this work, only 2 mol of H_2O_2 was applied to oxidize 1 mol of phenol and to further detect the hydroxylation intermediates of phenol. Fig. 5a shows the degradation of phenol at different pH conditions and the depletion of H_2O_2 at pH 4. The oxidation of phenol is observed at pH 4, but it is quite inefficient at both pH 5 and 9 in the SiG1/ H_2O_2 system. Lag periods in phenol oxidation and in H_2O_2 depletion (0–90 min) were found at pH 4. The lag phase of phenol actually represents a slow rate-limiting reduction of Fe^{3+} by H_2O_2 Eq. (1) to Fe^{2+} which sustains the Fenton reaction Eq. (2). Progression from the lag phase to the reaction phase is due to the buildup of Fe^{2+} through additional, more efficient reactions [21,41]. In the immobilized iron oxide, SiG1, which is a solid Fe(III) species, the role of the initiation mechanism for the activation of H_2O_2 is also considered similar to Fe^{3+} [22,42]. The tendency of H_2O_2 depletion is similar to that of the oxidation of phenol, which is also ascribed to the transformation of Fe(III) and Fe(II). Fig. 5a also demonstrates that H_2O_2 was decomposed, but the oxidation of phenol almost failed to occur at pH 5 and 9, because of the fact that H_2O_2 was decomposed to O_2 and H_2O by SiG1 at these pH conditions. Also, it is well known that H_2O_2 is easily decomposed to O_2 and H_2O under higher pH conditions, so the decomposition rate of H_2O_2 in the presence of SiG1 under pH 9 is faster than it is under pH 5. Furthermore, one of the initial products of phenol (i.e. catechol) and the formation of ferrous ions from SiG1 are presented in Fig. 5b. The products of catechol and Fe^{2+} were found after a 90 min reaction. As would be expected, the catechol is also oxidized during the reaction (after 180 min). The oxidation of phenol and the depletion of H_2O_2 occurred during the initiation periods (Fe^{2+} formation) before the 90 min reaction time. After a 90 min reaction time, the Fenton process is the dominative process for the oxidation of phenol and for the decomposition of H_2O_2 . Therefore, the reductive dissolution of Fe(III) by catechol was discussed in the previous sections, and this route has been shown to be much faster than that of the reduction of Fe(III) by H_2O_2 [21]. Hence, the initial intermediates of phenol are important species for promoting the oxidation process.

There were almost no reactions between catechol and H_2O_2 at both pH 4 and 5 without SiG1, but catechol exhibited an efficient reaction with H_2O_2 at pH 9 without SiG1. Actually, catechol

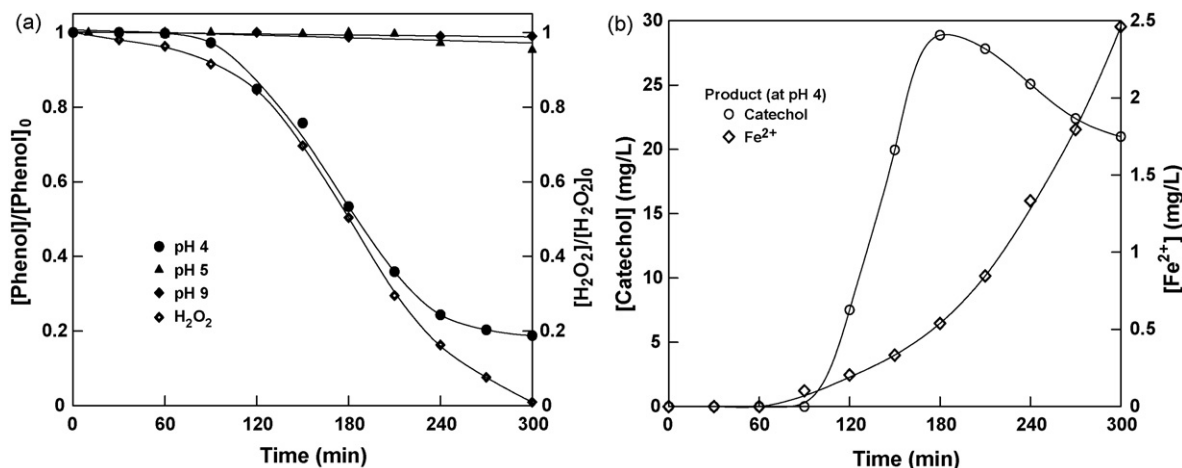


Fig. 5. (a) Catalytic oxidation of phenol with H_2O_2 at different pH conditions; (b) production of catechol and formation of ferrous ions during the oxidation of phenol at pH 4 ($[\text{SiG1}]_0 = 10 \text{ g/L}$, $[\text{Phenol}]_0 = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 68 \text{ mg/L}$, 150 rpm, 30°C , 10 mM NaClO_4).

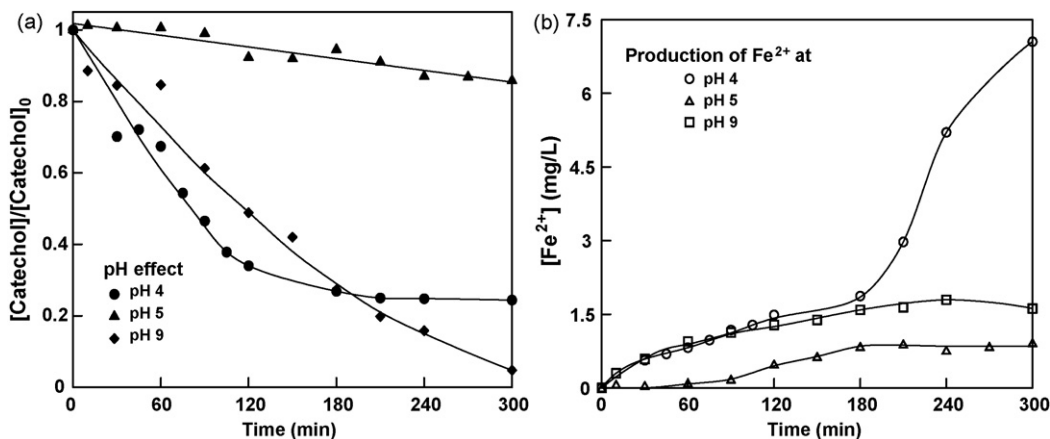


Fig. 6. (a) Catalytic oxidation of catechol with H_2O_2 at different pH conditions; (b) formation of ferrous ions during the oxidation of catechol; (c) decomposition of H_2O_2 during the oxidation of catechol ($[\text{SiG1}]_0 = 10 \text{ g/L}$, $[\text{Catechol}]_0 = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 68 \text{ mg/L}$, 150 rpm, 30°C , 10 mM NaClO_4).

is rapidly oxidized by dissolved oxygen and other oxidants at high pH conditions. The catalytic oxidation of catechol at different pH conditions is presented in Fig. 6a. No lag periods were observed during the oxidation of catechol because of the direct reductive dissolution of SiG1. The results show that catechol was dramatically oxidized at pH 4 and pH 9. The formation of ferrous ions dramatically increased after 180 min at pH 4 (Fig. 6b) due to the exhausting of H_2O_2 at this stage (Fig. 6c). The solution at pH 5 was also found to be a critical condition in which the interactions between SiG1 and catechol are small in the presence of H_2O_2 . The yields of Fe^{2+} from SiG1 in the solution with H_2O_2 (Fig. 6b) are higher than it in aqueous catechol solution without H_2O_2 (Fig. 4a), because some oxidative by-products of catechol (such as carboxylic acids or oxalic acid) may affect the dissolution of SiG1. The oxidation of catechol is very inefficient at pH 5 and the catechol may only be oxidized to an oxidative product without ring-opened reactions at pH 9, so the yields of Fe^{2+} were not dramatically increased at pH 5 and 9. Catechol was believed to be able to promote the oxidation of phenol in a homogeneous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system [21]. Hence, catechol and phenol were simultaneously oxidized in the SiG1/ H_2O_2 system, and the lag period for phenol degradation (0–10 min) was obviously improved due to the production of Fe^{2+} in the presence of catechol (Fig. 7). In the initial 10 min, catechol was oxidized in the SiG1/ H_2O_2 system, and then the concentration of catechol increased due to the oxidation of phenol during the period from 10 to 30 min; phenol and catechol were continuously oxidized until the H_2O_2 was exhausted

(about 150 min). SiG1 was reductively dissolved by the residue of hydroquinones to produce Fe^{2+} . Also some oxidative products such as hydroquinones and carboxylic acids may affect the dissolution of SiG1 in this stage. It can be concluded that catechol induces the

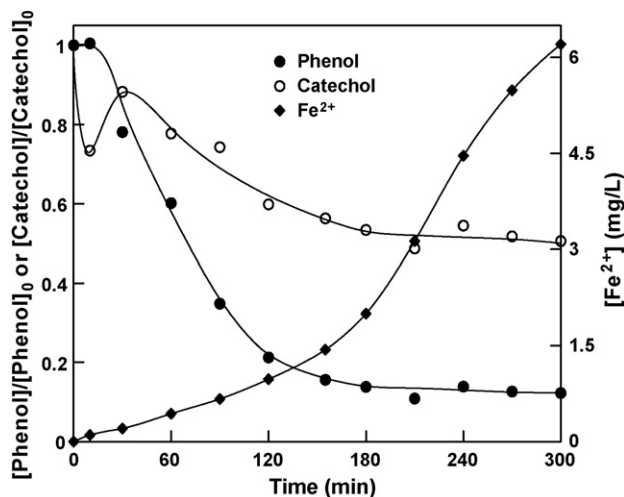


Fig. 7. Catalytic oxidation of catechol and phenol ($[\text{SiG1}]_0 = 10 \text{ g/L}$, $[\text{Phenol}]_0 = 50 \text{ mg/L}$, $[\text{Catechol}]_0 = 50 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 68 \text{ mg/L}$, 150 rpm, 30°C , pH 4, 10 mM NaClO_4).

reductive dissolution of SiG1 and then promotes its own oxidation and that of phenol in the presence of H₂O₂.

4. Conclusions

- The immobilized iron oxide (SiG1) used in this study exhibits high reactivity for the reductive dissolution process in the presence of catechol at pH 4.
- There are no interactions between phenol and SiG1, but the reductive dissolution process of SiG1 occurs in the presence of catechol or 1,4-HQ.
- A solution of pH 5 is found to be a critical condition in which the interactions between SiG1 and catechol are weak in the presence or absence of H₂O₂.
- The intermediates, catechol and 1,4-HQ, are able to induce the reductive dissolution of SiG1, and then in turn promote their own oxidation and that of phenol in the presence of H₂O₂.
- A kinetic model was applied to fit the reductive dissolution of SiG1, and the estimated maximum concentration of Fe²⁺ and estimated proportional constant were obtained.
- This study indicates that some of the heterogeneous (iron oxides) Fenton-type catalyses for the degradation of aromatic compounds also included the reductive dissolution route (homogeneous) during the reactions. Also, the hydroxylation compounds of phenol such as catechol and 1,4-HQ were oxidized not only by oxidants (*OH, H₂O₂, O₂, etc.) but also by iron(III) species.

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References

- [1] R. Alnaizy, A. Akgerman, *Adv. Environ. Res.* 4 (2000) 233–244.
- [2] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, *Catal. Today* 53 (1999) 51–59.
- [3] V. Kavitha, K. Palanivelu, *Chemosphere* 55 (2004) 1235–1243.
- [4] A. Mandal, K. Ojha, A.K. De, S. Bhattacharjee, *Chem. Eng. J.* 102 (2004) 203–208.
- [5] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, *Water Res.* 35 (2001) 3927–3933.
- [6] J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodriguez, *Environ. Sci. Technol.* 39 (2005) 9295–9302.
- [7] Y. Sun, J.J. Pignatello, *Environ. Sci. Technol.* 27 (1993) 304–310.
- [8] Y. Sun, J.J. Pignatello, *J. Agric. Food Chem.* 41 (1993) 308–312.
- [9] R.G. Zepp, B.C. Faust, J. Hoigne, *Environ. Sci. Technol.* 26 (1992) 313–319.
- [10] J.E. Cyr, B.H.J. Bielski, *Free Radic. Biol. Med.* 11 (1991) 157–160.
- [11] C. Walling, *Acc. Chem. Res.* 8 (1975) 125–131.
- [12] M.E. Balmer, B. Sulzberger, *Environ. Sci. Technol.* 33 (1999) 2418–2424.
- [13] S. Udenfriend, C.T. Clark, J. Axelrod, B.B. Brodie, *J. Biol. Chem.* 208 (1954) 731–739.
- [14] G.A. Hamilton, J.P. Friedman, P.M. Campbell, *J. Am. Chem. Soc.* 88 (1966) 5266–5268.
- [15] M. Neamtu, F.H. Frimmel, *Water Res.* 40 (2006) 3745–3750.
- [16] Z. Zhang, Q. Xiang, H. Glatt, K.L. Platt, B.D. Goldstein, G. Witz, *Free Radic. Biol. Med.* 18 (1995) 411–419.
- [17] G.A. Hamilton, J.W. Hanifin, J.P. Friedman, *J. Am. Chem. Soc.* 88 (1966) 5269–5272.
- [18] D. Naka, D. Kim, T.J. Strathmann, *Environ. Sci. Technol.* 40 (2006) 3006–3012.
- [19] P. Sanchez, N. Galvez, E. Colacio, E. Mirrones, J.M. Dominguez-Vera, *Dalton Trans.* (2005) 811–813.
- [20] M.J. Sever, J.J. Wilker, *Dalton Trans.* (2004) 1061–1072.
- [21] R. Chen, J.J. Pignatello, *Environ. Sci. Technol.* 31 (1997) 2399–2406.
- [22] C.P. Huang, Y.H. Huang, *Appl. Catal. A: Gen.* 346 (2008) 140–148.
- [23] Y.W. Lu, C.P. Huang, Y.H. Huang, C.P. Lin, H.T. Chen, *Sep. Sci. Technol.* 43 (2008) 1632–1641.
- [24] S. Chou, C. Huang, *Chemosphere* 38 (1999) 2719–2731.
- [25] S. Chou, C. Huang, Y.H. Huang, *Environ. Sci. Technol.* 35 (2001) 1247–1251.
- [26] C.L. Hsueh, Y.H. Huang, C.Y. Chen, *J. Hazard. Mater.* 129 (2006) 228–233.
- [27] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, *J. Mol. Catal. A: Chem.* 245 (2006) 78–86.
- [28] P. Mazellier, B. Sulzberger, *Environ. Sci. Technol.* 35 (2001) 3314–3320.
- [29] F. Shi, M.K. Tse, M.-M. Pohl, J. Radnik, A. Bruckner, S. Zhang, M. Beller, *J. Mol. Catal. A: Chem.* 292 (2008) 28–35.
- [30] A. Avdeef, S.R. Sofen, T.L. Bregante, K.N. Raymond, *J. Am. Chem. Soc.* 100 (1978) 5362–5370.
- [31] D. Suter, S. Banwart, W. Stumm, *Langmuir* 7 (1991) 809–813.
- [32] D. Panias, M. Taxiarchou, I. Paspaliaris, A. Kontopoulos, *Hydrometallurgy* 42 (1996) 257–265.
- [33] Y.H. Huang, L.T. Cho, C.Y. Chen, Republic of China, Taiwan Patent 200616902, 2006.
- [34] H. Tamura, K. Goto, T. Yotsuyanagi, M. Nagayama, *Talanta* 21 (1974) 314–318.
- [35] G.M. Eisenberg, *Ind. Eng. Chem. Anal.* 15 (1943) 327–328.
- [36] C.P. Huang, Y.F. Huang, H.P. Cheng, Y.H. Huang, *Catal. Commun.* 10 (2009) 561–566.
- [37] Y.W. Deng, W. Stumm, *Appl. Geochem.* 9 (1994) 23–36.
- [38] W. Stumm, G.F. Lee, *Ind. Eng. Chem.* 53 (1961) 143–146.
- [39] H.R. Devlin, I.J. Harris, *Ind. Eng. Chem. Fund.* 23 (1984) 387–392.
- [40] Y. Du, M. Zhou, L. Lei, *J. Hazard. Mater.* 136 (2006) 859–865.
- [41] H. Gallard, J. De Laat, *Water Res.* 34 (2000) 3107–3116.
- [42] M.C. Lu, *Chemosphere* 40 (2000) 125–130.