Heterogeneous Fenton oxidation of catechol and 4-chlorocatechol catalyzed by nano-Fe₃O₄: Role of the interface

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HIGHLIGHTS

- Catechol or 4-chlorocatechol was removed within 3 h in nano-Fe₃O₄/H₂O₂ system.
- 4-Chlorocatechol was removed faster than catechol, with a minor mineralization.
- The oxidation of (chloro-)catechols obeyed Eley–Rideal mechanism.
- Carboxyl acids and ethers or dimers were generated and also adsorbed on nano-Fe₃O₄.

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ABSTRACT

The nano-Fe₃O₄ catalyzed Fenton oxidations of catechol and 4-chlorocatechol in aqueous solution were comparably investigated to elucidate the interface reaction mechanism of the heterogeneous Fenton reactions. Nano-Fe₃O₄ were synthesized as quasi-spherical particles with specific surface areas of 57.84 m²/g. Almost all the catechol or 4-chlorocatechol was oxidized within 3 h after the addition of H₂O₂, while about only 10% of the parent compounds adsorbed onto nano-Fe₃O₄ without H₂O₂. And the oxidation curves followed the pseudo-second order kinetic model. 4-Chlorocatechol was oxidized faster than catechol, but with only 40% of mineralization. The contribution of homogeneous reaction induced by the leaching iron was limited. The surface generated reactive oxygen species were ·OH and HO₂/O₂^{·−}, which were further reacted to generate oxygen-centered radicals in both systems, and carbon-centered radicals only in catechol system. In-situ flow-cell ATR-FTIR spectroscopy further confirmed that the adsorbed catechol or 4-chlorocatechol remained on the nano-Fe₃O₄ surface, indicating an Eley–Rideal mechanism. Meanwhile, the generated carboxyl acids and some intermediates like ethers or dimers were also adsorbed. Accordingly, schematic diagrams of oxidation mechanisms of catechol and 4-chlorocatechol in nano-Fe₃O₄/H₂O₂ system were proposed.

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1. Introduction

Advanced oxidation processes (AOPs) utilize reactive oxygen species (ROS), especially hydroxyl radicals (·OH), to remove organic compounds from water effectively. The classic homogeneous Fenton reaction, one of the AOPs, could generate unselectively strong oxidant of ·OH ($E^0 = 2.73$ V [1]) through a Haber–Weiss

mechanism (Eq. (1) shows the initiating reaction [2]), to achieve the degradation of refractory organics.

A heterogeneous Fenton reaction generates ROS from the active decomposition of H₂O₂ catalyzed by solid catalyst, and can be used in neutral pH range without sludge disposal problems as Fenton process. Most researches of heterogeneous Fenton reactions focus on the preparation of high efficient catalysts, the optimum operating conditions, and possible degradation mechanisms. However, compared to the classic Fenton reaction, the mechanism of the heterogeneous Fenton reaction is still unclear, including the oxidation

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kinetic process, the places where the oxidation happened, the identification of ROS [3,4], etc. The unaccomplished fundamental knowledge of mechanisms, to some extent, inhibits the wide application of heterogeneous Fenton reactions.

Based on whether the sorbed target organic compound is attacked or not, the heterogeneous Fenton reaction is usually analyzed using two main bimolecular kinetic models, the Langmuir–Hinshelwood (L–H) model and the Eley–Rideal (E–R) model. Liang et al. [5] proposed that the degradation of cationic dye methylene blue (MB) and anionic dye acid orange II (AOII) by chromium substituted magnetite ($\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$) and H_2O_2 followed different kinetic mechanisms. With a certain amount of adsorption, the oxidation kinetics of MB were fitted with the zero-order equation and followed the L–H mechanism (i.e., reaction of adsorbed MB molecule with $\cdot\text{OH}$ engendered on magnetite surface). The oxidation kinetics of AOII, on the other hand, were best described by the second-order reaction and were proposed to follow the E–R mechanism (i.e., reaction of dissolved AOII molecule with $\cdot\text{OH}$ produced on magnetite surface) due to the lack of adsorption. Furman et al. [6] proposed that the reaction between sorbed superoxide and aqueous hexachloroethane (HCA) obeyed E–R mechanism, based on the correlation of first-order rate constants for HCA degradation with different H_2O_2 concentrations catalyzed by MnO_2 . Xue et al. [7] found that the correlation between the degradation kinetic constant of pentachlorophenol (PCP) and the initial concentrations of PCP could be fitted by L–H model. Raman spectroscopy of the aqueous suspension before and after reaction showed the disappearance of sorbed PCP from magnetite surface after oxidation, suggesting the L–H mechanism. However, none of the above researches have provided direct evidence of molecular level. The different chemistry environments between the reaction and examination could influence the test results. Considering the wide application of in-situ ATR-FTIR technology in the fields of adsorptions, like gas–solid interface reactions [8] and photocatalytic reactions [9], an in-situ ATR-FTIR with a horizontal flow-cell was used to monitor the interface reaction in the heterogeneous system.

Catechol (1,2-dihydroxybenzene) and chlorocatechols occur as intermediary metabolites during the degradation of naturally occurring and synthetic aromatic compounds [10,11]. For example, catechol is the starting material for insecticides, perfumes, drugs, polymerization inhibitors, etc., and is also used as an antiseptic in photography, dyestuffs, electroplating, etc. [12]. Chlorocatechols, like 4-chlorocatechol (4-chloro-1,2-benzenediol), are major pollutants in the effluents of saw and pulp mills [13]. (Chloro-)catechols have already been reported to be toxic for bacteria and higher organisms, and catechol is even more toxic than phenol [13]. Moreover, catechols can form stable complexes with various di- and trivalent metal ions especially iron [12]. And ortho-diphenolic compounds adsorb on metal oxides more strongly than other diphenols and phenols [14]. In addition, iron based materials are a predominant class of heterogeneous catalysts due to their abundance in nature and the reactivity in redox reactions. Therefore, the interaction between (chloro-)catechols and iron oxides is representative of the interfacial mechanisms of a heterogeneous Fenton reaction.

In the current study, the respective oxidation of catechol and 4-chlorocatechol in the synthesized nano- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system was compared and measured thoroughly, including the adsorption and oxidation kinetics, the corresponding pH change and iron leaching, the ROS identification, and the generation of degradation products. In-situ flow-cell ATR-FTIR experiments were conducted to observe the interface reactions in situ. The main objective is to understand the mechanisms, especially the role of the interface, of the heterogeneous Fenton reaction catalyzed by nano- Fe_3O_4 .

2. Materials and methods

2.1. Chemicals

Catechol and 4-chlorocatechol were purchased from Acros Organics and Tokyo chemical industry company. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) and α -(4-Pyridyl N-oxide)-N-tert-butyl nitron (POBN) were purchased from J&K and Sigma. All chemicals were of analytical reagent grade and used as received. Milli-Q water was used throughout the study.

2.2. Preparation and characterization of nano- Fe_3O_4

Nano- Fe_3O_4 was prepared by the chemical coprecipitation method [15] (detailed in [Supporting information](#)). The crystal phase was identified by XRD (PANalytical, Netherlands) and transmission Mössbauer spectra at room temperature. The morphology and size distribution were examined by TEM (Hitachi, Japan). The BET surface area was determined as $57.84 \pm 0.20 \text{ m}^2/\text{g}$ with ASAP 2000 (Micromeritics, USA). The point of zero charge of nano- Fe_3O_4 in NaNO_3 (0.01 mol/L) was measured to be around 7.5 (Zetasizer Nano ZS, Malvern, U.K.).

2.3. Adsorption and oxidation experiments

Batch experiments were carried out in duplicate using 50 mL polypropylene centrifuge tubes containing 40 mL 0.01 mol/L NaNO_3 solution and 1 g/L nano- Fe_3O_4 at room temperature ($25 \pm 2^\circ\text{C}$) in dark. Certain amount of freshly prepared catechol or 4-chlorocatechol stock solution were added to initiate the adsorption. pH was adjusted within 6.5 ± 0.2 by NaOH and HNO_3 solutions. Samples at certain time intervals were immediately separated by an external magnetic field, and followed by high speed centrifugation and filtration. The amount of the adsorbed organic compound (q_t , mg/m^2) was calculated by the following equation:

$$q_t = \frac{(C_0 - C) \cdot V}{M_s \cdot SA} \quad (2)$$

where C_0 and C (mg/L) are the initial concentration and the concentration at a specific time of the residual target organics in solution, respectively. V (L) is the volume of the solution, M_s (g) and SA (m^2/g) are the mass and surface area of Fe_3O_4 in solution.

The oxidation reactions were started by adding H_2O_2 to the suspension after pre-adsorption equilibrium at $\text{pH } 6.5 \pm 0.2$. During the oxidation, pH was not controlled but monitored to prevent any potential interference. Samples were divided into two equal parts. One was added with n-butanol to quench excess $\cdot\text{OH}$ [16] for the concentration analysis of the residual organics. The other parallel part was added with NaOH (4 mol/L) to terminate reactions for dissolved organic carbon (DOC) determination.

2.4. In-situ ATR-FTIR experiments

In situ ATR infrared measurements were performed using the flow-cell technique described by Hug and Sulzberger [17] and others [17–19]. The preparation of the nano- Fe_3O_4 film was described in [Supporting information](#). The FTIR Spectra were acquired using the Nicolet 8700 FTIR spectrometer equipped with a DTGS detector and ATR accessory, and were recorded by averaging 128 scans at a resolution of 4 cm^{-1} under ambient temperature in dark. After the equilibration of the magnetite film under the flow of 0.01 mol/L NaCl, a certain amount of catechol or 4-chlorocatechol stock solution was added to start the adsorption experiments. The oxidation experiments were subsequently performed by adding H_2O_2 to the solution.

2.5. Analytical determinations

The concentration of catechol and 4-chlorocatechol was analyzed by HPLC with a Waters 2487 UV Detector and a C₁₈ column (5 μ m, 250 mm $\times$ 4.6 mm). The mobile phase was water/acetonitrile (80:20 for catechol and 60:40 for 4-chlorocatechol) at pH 3 (adjusted with phosphate acid), with a flow rate of 1.0 mL/min. The wavelengths were set at 275 nm for catechol and 283 nm for 4-chlorocatechol. The corresponding DOC was analyzed by a Fusion analyser (Tekmar Dohrmann, USA).

The concentration of total iron in solution was measured by ICP-OES on an Optima 2000 instrument (PerkinElmer, USA). The formed organic acids and the released chloride ions were quantified by ion chromatography (Dionex, USA). Degradation intermediates were identified by ESI-Q-TOF-MS and GC-MS (detailed in Supporting information).

ROS were identified by electron spin resonance (ESR) spectroscopy (Bruker model ESP 300E), operating at 3514 G center field and 9.85 GHz microwave frequency. After the addition of spin trap agent, DMPO or POBN, the ESR spectra of the reaction filtrate were recorded.

3. Results and discussion

3.1. Characterization of synthesized Fe₃O₄

Fig. 1a shows that the characteristic reflections of synthesized sample were assigned to the (220), (311), (400), (511) and (440) planes of the cubic spinel structure, corresponding to the standard card of Fe₃O₄ (JCPDS No. 19-0629). With the cations occupying both tetrahedral and octahedral interstices, Fe₃O₄ is usually represented by the formula (Fe³⁺)_{tet}[Fe²⁺Fe³⁺]_{oct}O₄. So its

Table 1

Hyperfine parameters of synthesized Fe₃O₄.

Component	Isomer shift δ (mm/s)	Magnetic hyperfine field H (T)	Q splitting (mm/s)	Line width (mm/s)	Relative content (%)
(Fe ³⁺) _{tet}	0.325	48.27	−0.012	0.465	37.8
[Fe ²⁺ Fe ³⁺] _{oct}	0.535	44.23	0.0126	1.014	62.2

Mössbauer spectra is commonly interpreted as a superposition of two patterns associated with (Fe³⁺)_{tet} and [Fe²⁺Fe³⁺]_{oct}. The Mössbauer spectra of synthesized sample were fitted by two sextets (Fig. 1b), and the hyperfine parameters were in agreement with literature values for Fe₃O₄ [20] (Table 1). The fitted relative area ratio of the two spectral components is close to 1:1.65. Both the broad XRD peak and the broad line width of the Mössbauer spectra indicated the small poorly crystallized powders [20]. Moreover, the binding energies (BE) of Fe 2p_{3/2} (710.5 eV) and Fe 2p_{1/2} (723.7 eV) of the synthesized nano-Fe₃O₄ (Fig. 1c) was in good agreement with the reported values [21]. There was no obvious shake-up satellite peak at around 719.0 eV, further suggesting the pure Fe₃O₄ phase [22] on the surface. The typical TEM image (Fig. 1d) shows that the synthesized magnetite particles were quasi-spherical with an average diameter of about 40 nm.

3.2. Adsorption and oxidation kinetics

Prior to the addition of H₂O₂, only about 10% of catechol or 4-chlorocatechol adsorbed onto the nano-Fe₃O₄. However, on the addition of H₂O₂, the parent organic compounds were rapidly removed within 3 h (Fig. 2). Meanwhile, only 9.82% and 0.17% of catechol and 4-chlorocatechol were oxidized by H₂O₂ after 3 h in

Fig. 1. (a) XRD pattern, (b) Mössbauer spectra, (c) XPS spectra of Fe 2p and (d) TEM image of synthesized Fe₃O₄.

Fig. 2. Adsorption and oxidation curves of catechol or 4-chlorocatechol. Circles represent catechol, squares represent 4-chlorocatechol, solid forms represent oxidation reaction, and hollow forms represent adsorption process. All the lines are pseudo-second order fitting results. The insert illustrates the change of adsorbed amount. $[\text{catechol}]_0 = [\text{4-chlorocatechol}]_0 = 10^{-3} \text{ mol/L}$, $[\text{Fe}_3\text{O}_4] = 1 \text{ g/L}$, and $[\text{H}_2\text{O}_2]_0 = 0.05 \text{ mol/L}$.

the absence of nano- Fe_3O_4 , indicating the significance of nano- Fe_3O_4 as catalyst in the heterogeneous Fenton reaction.

Adsorption processes of both catechol and 4-chlorocatechol were best described by the pseudo-second order kinetic model (Insert of Fig. 2 and Table 2). In accordance with the experimental data, the calculated q_e is 0.15 and 0.14 mg/m^2 for catechol and 4-chlorocatechol, respectively. The slightly lower adsorption amount of 4-chlorocatechol is attributed to the substitution of donor group $-\text{Cl}$. Meanwhile, the nano- Fe_3O_4 surface is positively charged when pH is lower than 7.5, and more phenolic hydroxyl group ($\text{pH}-\text{OH}$) of 4-chlorocatechol was deprotonated at pH 6 than catechol due to its lower pK_{a1} value [11,23] (Fig. S1). However, the adsorption capacity was not enhanced by the electrostatic attraction between the 4-chlorocatechol anion and the positively charged surface, compared to catechol. To more acidic pH, less favorable adsorption of catechol on iron oxides was observed by previous studies [23–26]. Therefore, both adsorptions of catechol [23] and 4-chlorocatechol on nano-magnetite should involve chemical reaction between the $\text{pH}-\text{OH}$ and surface sites, forming inner-sphere complex. In addition, the steric effect of the larger 4-chlorocatechol molecule may hinder its inner-sphere complexation.

As shown in Fig. 2, the catalytic oxidation of catechol and 4-chlorocatechol exhibited similar kinetic features. Nearly all the catechol or 4-chlorocatechol were removed within 3 h. The pseudo-second order kinetic model best fitted the oxidation curves of cat-

Fig. 3. DOC and Cl^- change during the oxidation of catechol or 4-chlorocatechol. $[\text{catechol}]_0 = [\text{4-chlorocatechol}]_0 = 10^{-3} \text{ mol/L}$, $[\text{Fe}_3\text{O}_4] = 1 \text{ g/L}$, and $[\text{H}_2\text{O}_2]_0 = 0.05 \text{ mol/L}$.

echol and 4-chlorocatechol (Table 2). The fitted apparent rate constant (k) for catechol and 4-chlorocatechol oxidation was 6.71 and 15.04 $\text{h}^{-1} (\text{mmol/L})^{-1}$. The observed faster degradation of chlorinated catechol than catechol was opposite to the refractory of chlorophenols than phenols [27]. Similar reverse degradable laws of chlorocatechols and chlorophenols were also observed by Cheng et al. [10]. The slightly lower adsorption amount of 4-chlorocatechol probably led to more active surface sites participating in the catalyzed decomposition of H_2O_2 , so that more ROS were generated and contributed to the faster oxidation of 4-chlorocatechol. In addition, it was reported that para-diphenolic compounds, 2,5-dichlorohydroquinone and tetrachlorohydroquinone were able to undergo autooxidation to produce corresponding chlorosemiquinone anion radicals at pH 7.4 [28,29]. Catechol, however, formed semiquinone radicals and ortho-benzoquinone through redox reactions [12]. Similar to chlorohydroquinone, 4-chlorocatechol seemed more reactive in a heterogeneous Fenton system than catechol.

DOC removal reached a steady plateau within 1 h for both systems, that was nearly 65% and 40% for the catechol and 4-chlorocatechol systems, respectively, while the parent organics were almost removed. As an indicator of 4-chlorocatechol degradation, the concentration of Cl^- was also measured and increased with time, following a similar trend as the oxidation of 4-chlorocatechol (Fig. 3). However, complete dechlorination was not yet reached, and about 60% of chlorine ion was released after 3 h based on the initiated concentration of 4-chlorocatechol, suggesting the generation of chlorinated organic compounds other than

Table 2
Kinetic parameters for the adsorption and oxidation of catechol or 4-chlorocatechol.

	Kinetic model	Simulation equation	Catechol			4-Chlorocatechol		
			R^2 ^a	q_e ^b	k ^c	R^2	q_e	k
Adsorption	Pseudo-1st	$q_t = q_e - q_e \cdot \exp(-kt)$	0.919	0.15 ± 0.01	82.77 ± 27.95	0.991	0.13 ± 0.00	14.37 ± 1.87
	Pseudo-2nd	$q_t = \frac{kq_e^2 t}{1 + kq_e t}$	0.945	0.15 ± 0.01	870.85 ± 407.55	0.995	0.14 ± 0.00	284.01 ± 67.62
Oxidation	Pseudo-1st	$\frac{C}{C_0} = \exp(-kt)$	0.916	–	3.20 ± 0.46	0.907	–	8.79 ± 1.94
	Pseudo-2nd	$\frac{C}{C_0} = \frac{1}{ktC_0 + 1}$	0.971	–	6.71 ± 0.85	0.970	–	15.04 ± 2.43
	Pseudo-3rd	$\frac{C}{C_0} = \frac{1}{\sqrt{2ktC_0^2 + 1}}$	0.936	–	18.54 ± 5.28	0.954	–	45.40 ± 13.73

^a R^2 is the coefficients of determination for the fit of adsorption and oxidation curves to kinetic models.

^b q_e (mg/m^2) is the amount of adsorbed organic compounds at equilibrium.

^c k is the apparent pseudo first-order rate constant (h^{-1}) and pseudo second-order rate constant ($\text{m}^2 \text{ h/mg}$) of adsorption kinetics, and the pseudo first-order rate constant (h^{-1}), pseudo second-order rate constant ($\text{L}/(\text{mmol h})$) and pseudo third-order rate constant ($\text{L}^2/(\text{mmol}^2 \text{ h})$) of oxidation kinetics.

Fig. 4. (a) pH change and (b) iron leaching in the nano- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system with and without organic compounds. $[\text{catechol}]_0 = [\text{4-chlorocatechol}]_0 = 10^{-3}$ mol/L, $[\text{Fe}_3\text{O}_4] = 1$ g/L, and $[\text{H}_2\text{O}_2]_0 = 0.05$ mol/L.

4-chlorocatechol. Therefore, more analysis were performed to further understand the mechanisms of the observed different kinetic processes.

As shown in Fig. 4, the solution pH decreased slightly without addition of organic compounds, and the corresponding iron leaching was hardly detected although the decomposition of H_2O_2 occurred. However, the solution pH decreased dramatically from 6.5 to below pH 4 for catechol and to about pH 3 for 4-chlorocatechol (Fig. 4a), suggesting the generation of organic acids. Meanwhile, the total dissolved iron remained at a relatively low level (0.3 mg/L) for catechol, but reached 3 mg/L for 4-chlorocatechol with the lower pH. However, according to previous studies [7,30], the contribution of homogeneous reactions induced by the leaching iron at such level was limited. Therefore, the ROS were mainly generated from the active decomposition of H_2O_2 catalyzed by nano- Fe_3O_4 surface, i.e., the heterogeneous mechanism.

3.3. Identification of oxidation products and intermediates

GC-MS analysis of samples taken at different oxidation reaction time was performed. The mass spectra shows that all the derived compounds occurred as trimethylsilyl derivatives characterized by the m/z 73 peak, but some derivatives were hardly identified from the NIST library. For example, the compound with the retention time of 43.86 min in 4-chlorocatechol system was poorly matched with the NIST library and might be assigned as 4,5-dichlo-

rocatechol. However, most compounds, such as carboxylic acids and alcohols, could still be identified. Table S1 shows all the identified products after 30 min of oxidation. Among all the detected intermediates, 2-furanylglycolic acid and 1,2-benzenedicarboxylic acid were only existed in catechol system. Tartronic acid, 2,2-dihydroxymalonic acid, and 4,5-dichlorocatechol only appeared in the 4-chlorocatechol system.

Ion chromatography was used to further quantify the detected carboxylic acids with low molecular weight, namely formic acid, oxalic acid, maleic acid, and succinic acid. Fig. 5 shows that the concentrations of the four organic acids increased during the oxidation. Formic acid and oxalic acid were the two main products in both systems, and succinic acid was in trace amounts. While more maleic acid was generated in catechol system, the other three organic acids were generated more in 4-chlorocatechol system, in accordance with the lower pH.

ESI-Q-TOF-MS was also performed to analyze the intermediates in solution. After 30 min of oxidation, a base ion peak at m/z 229 $[\text{M}-\text{H}]^-$ and fragment ions at m/z 201 $[\text{M}-\text{H}-\text{CO}]^-$, 173 $[\text{M}-\text{H}-2\text{CO}]^-$, 157 $[\text{M}-\text{H}-4\text{H}_2\text{O}]^-$, and 141 $[\text{M}-\text{H}-2\text{O}-2\text{CO}]^-$, was detected in catechol system, which was assigned to a dimer with a proposed formula of $\text{C}_{12}\text{H}_6\text{O}_5$ (Fig. S2c, hereafter called intermediate A). In 4-chlorocatechol system, a base ion peak at m/z 285 $[\text{M}-\text{H}]^-$ with an isotopic characteristic pattern of two chlorines (m/z 285, 287, 289), and fragment ions at m/z 213 $[\text{M}-\text{H}-2\text{HCl}]^-$, was assigned to a dimer with a proposed formula

Fig. 5. Concentrations of some acids during the oxidation of (a) catechol or (b) 4-chlorocatechol. $[\text{catechol}]_0 = [\text{4-chlorocatechol}]_0 = 10^{-3}$ mol/L, $[\text{Fe}_3\text{O}_4] = 1$ g/L, and $[\text{H}_2\text{O}_2]_0 = 0.05$ mol/L.

of $C_{12}H_8O_4Cl_2$ (Fig. S2d, hereafter called intermediate B). A base ion peak at m/z 299 $[M-H]^-$ with an isotopic characteristic pattern of two chlorines (m/z 299, 301, 303), and fragment ions at m/z = 263 $[M-H-Cl]^-$ with an isotopic ion cluster of one chlorine (m/z = 263 and 265), 227 $[M-H-2HCl]^-$, 199 $[M-H-2HCl-CO]^-$, 171 $[M-H-2HCl-2CO]^-$, was assigned to a dimer $C_{12}H_6O_5Cl_2$ (Fig. S2e, hereafter called intermediate C). All of them disappeared after 1 h of oxidation.

In addition, the transparent liquid phase of both systems turned reddish brown at first and then turned light yellow in the end, implying the generation of unstable 1,2-benzoquinone and its transformation to 1,4-benzoquinone, according to the observation of Zazo et al. [30]. However, these compounds were not detected in the present work, possibly due to their fast transformation under the tested conditions and the limited testing techniques.

In the nano- Fe_3O_4/H_2O_2 system, the typical four-line signal with a peak height ratio of 1:2:2:1 and hyperfine coupling constant ($a_N = a_H = 15.0$ G) of DMPO-OH adduct was observed (Fig. 6a), confirming the generation of $\cdot OH$. However, in the systems containing catechol or 4-chlorocatechol, the formed $\cdot OH$ was quickly consumed, especially for 4-chlorocatechol. HO_2/O_2^- were also detected in the nano- Fe_3O_4/H_2O_2 system in methanol (Fig. 6b), since the DMPO-OOH/ O_2^- readily decompose to DMPO-OH [31] in aqueous medium and are more stable in organic-rich media [32]. In the presence of catechol or 4-chlorocatechol, oxygen-centered radicals with the hyperfine coupling constant of $a_N = 14.17$ G and $a_H = 8.79$

G [33] were predominant instead of DMPO-OOH/ O_2^- . These oxygen-centered radicals may act as ROS and were probably generated from the reactions between the organics and HO_2/O_2^- , because their signals decreased as the concentration of catechol or 4-chlorocatechol increased (Fig. S3). Therefore, $\cdot OH$ quickly oxidized 4-chlorocatechol, while the oxygen-centered radicals were gradually consumed contributing to the limited mineralization. Moreover, the sextet characteristic peaks of POBN-carbon-centered radical adducts, with hyperfine coupling constant of $a_N = 13.17$ G and $a_H = 1.7$ G, were only detected in the catechol system (Fig. 6c). So the carbon-centered radicals were probably generated from the reactions between catechol and $\cdot OH$ or oxygen-centered radicals, which might contribute to the more complete mineralization of catechol.

3.4. Identification of interface species

To further investigate the interface mechanism of heterogeneous Fenton oxidation, in-situ flow-cell ATR-FTIR spectral measurements and the XPS spectra of the nano- Fe_3O_4 surface were performed. The evolution of adsorbed organic compounds during the oxidation were recorded by ATR-FTIR spectra (Fig. 7). The assignment of IR bands were summarized in Table S2 based on second-derivative spectra analysis.

Both the spectra of adsorbed catechol and 4-chlorocatechol were dominated by two main bands. The band at 1480 cm^{-1} could

Fig. 6. ESR spectra of (a) DMPO-OH in aqueous dispersion, (b) DMPO-OOH/ O_2^- , DMPO-OR in methanol dispersion, and (c) POBN-carbon-centered radical adducts in aqueous dispersion: 1 nano- Fe_3O_4 only, 2 H_2O_2 only, 3 nano- $Fe_3O_4 + H_2O_2$, 4 nano- $Fe_3O_4 + H_2O_2 +$ catechol, 5 nano- $Fe_3O_4 + H_2O_2 +$ 4-chlorocatechol. Experiments in each graph were conducted under identical instrument parameters.

Fig. 7. Evolution of ATR-FTIR spectra upon addition of H_2O_2 into (a) catechol solution and (b) 4-chlorocatechol solution: $[\text{catechol}]_0 = [\text{4-chlorocatechol}]_0 = 10^{-3}$ mol/L, $[\text{H}_2\text{O}_2]_0 = 0.05$ mol/L, $\text{pH} = 6.5 \pm 0.2$, $[\text{NaCl}] = 0.01$ mol/L, the dashed lines are the pre-adsorption spectra.

be assigned to the $\nu(\text{CC})$ modes of the aromatic ring [34,35], and the other band at around 1260 cm^{-1} was assigned to $\nu(\text{CO})$ modes of phenyl-O groups [11,35]. Other peaks were also observed, such as C–H bending at 1213 and 1102 cm^{-1} for catechol, and at 1216 , 1115 and 1070 cm^{-1} for 4-chlorocatechol, and the OH deformation and bending band at 1195 cm^{-1} (catechol) and 1405 cm^{-1} (4-chlorocatechol). And the relatively weak band at 1398 cm^{-1} should be related to $\nu(\text{CC})$ [36].

Upon the addition of H_2O_2 , the two main bands at 1480 and 1260 cm^{-1} in the pre-adsorption spectra were broadened with shoulders (Fig. 7). The 1480 cm^{-1} band of adsorbed catechol species could be resolved into two bands at 1490 and 1466 cm^{-1} , and the 1257 cm^{-1} band shifted slightly to 1255 cm^{-1} with growing shoulder bands at 1277 and 1225 cm^{-1} . In 4-chlorocatechol system, the 1481 and 1262 cm^{-1} bands also shifted to 1487 and 1258 cm^{-1} , respectively. Because the solution pH was carefully maintained at 6.5 ± 0.2 , these shifts should not be attributed to the protonation or deprotonation of interfacial species. Changes of the spectral features might result from the different micro-environment of the adsorbed organics upon addition of H_2O_2 and also from the generation of some new ph-O compounds, such as 3,4-dihydroxybenzoic acid, according to the GC–MS analysis. During the oxidation, $\nu_a(\text{COO})$ band at 1533 (catechol) and 1532 cm^{-1} (4-chlorocatechol) [34] and $\nu_s(\text{COO})$ band at 1398 (catechol) [34] and 1389 cm^{-1} (4-chlorocatechol) [35,37] arose and increased in intensity, indicating the adsorption of generated carboxylic compounds. The shoulder at 1277 cm^{-1} and 1195 cm^{-1} , arising in the oxidation of catechol, were assigned to the overlapping peaks of asymmetric vibrations of C–O–C linkage and C–OH vibrations [35,38,39], and symmetric vibrations of C–O–C linkage [35,38].

According to Araujo et al. [34], the peak arising at 1428 cm^{-1} might be assigned to C–O stretching and O–H deformation vibrations in the dimer. So ethers or dimers containing C–O and O–H might be generated and adsorbed on the nano- Fe_3O_4 surface during the oxidation of catechol. Besides, in plane $\delta(\text{CH})$ at 1213 cm^{-1} (catechol) and 1216 cm^{-1} (4-chlorocatechol) decreased. And $\delta(\text{OH})$ at 1225 and 1349 cm^{-1} (catechol) and at 1222 and 1348 cm^{-1} (4-chlorocatechol) arose [34,35,39]. Above all, the characteristic peaks of adsorbed catechol or 4-chlorocatechol still existed during the oxidation, indicating that the adsorbed target organics were not mainly attacked by ROS. Therefore, the heterogeneous Fenton oxidation of (chloro-)catechol probably obeyed the E–R kinetic mechanism, i.e., the surface generated ROS mainly attacked the unadsorbed organic compounds near the interface region.

The nano-magnetite surface, on the other hand, was also observed to be oxidized by the analysis of XPS spectra of Fe 2p (Fig. 1c). The obvious shake-up satellite peak on the higher-binding-energy side (ca. 719 eV) arose in the spectra of the sample after the reaction with catechol or 4-chlorocatechol, indicating the existence of Fe(III) on the surface. Besides, Fe $2p_{3/2}$ peak was shifted slightly to 710.7 eV in both catechol and 4-chlorocatechol system, and the Fe $2p_{1/2}$ peak was also shifted to 724.4 eV , suggesting the oxidation of surface iron, too. Therefore, the structural Fe(II) on the surface of the catalyst was oxidized to Fe(III) during the heterogeneous Fenton reaction.

3.5. Possible oxidation mechanism of catechol and 4-chlorocatechol

Based on the information obtained above, a possible reaction mechanism of the oxidation of catechol or 4-chlorocatechol in such

Fig. 8. Schematic diagram of the reaction mechanism of the oxidation of (a) catechol or (b) 4-chlorocatechol in nano- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system.

a heterogeneous system was proposed in Fig. 8. Firstly, the ROS were generated by the catalytic reactions of H_2O_2 on the nano- Fe_3O_4 surface, mainly $\cdot\text{OH}$ as also proved by other researchers [16,40]. The electron transfer between the surface Fe species ($\equiv\text{Fe}^{\text{II}}$ and $\equiv\text{Fe}^{\text{III}}$) and the adsorbed H_2O_2 led to the generation of the radicals, which initiated the subsequent chain reactions (Eqs. (3) and (4)). More $\equiv\text{Fe}^{\text{II}}$ species could be produced through the reactions of the formed $\equiv\text{Fe}^{\text{III}}$ species with H_2O_2 (Eq. (4)) and HO_2/O_2^- (Eq. (6)). Secondly, though part of catechol and 4-chlorocatechol adsorbed onto nano- Fe_3O_4 , the surface generated $\cdot\text{OH}$ and HO_2/O_2^- mainly attacked the unadsorbed organic compounds near the interface region, in accordance with the E–R mechanism. Afterwards, other radicals, i.e., oxygen-centered radicals and carbon-centered radicals, were formed, as well as some intermediates and carboxyl acids. The parent compounds and the generated compounds could be adsorbed onto the catalyst, which may reduce the catalytic reactivity due to the loss of the surface reactive sites. In addition, the generated refractory compound like chlorinated organics probably hindered the further mineralization of the 4-chlorocatechol system. Catechol, on the other hand, achieved mineralization to a larger degree may be due to the formation of carbon-centered radicals.

4. Conclusion

The synthesized nano-magnetite quasi-spherical particles was used as heterogeneous catalyst to remove catechol and 4-chlorocatechol from aqueous solution. Prior to the addition of H_2O_2 , only about 10% of catechol or 4-chlorocatechol adsorbed onto nano- Fe_3O_4 possibly by forming inner-sphere complex. All the parent compounds were oxidized within 3 h after the addition of H_2O_2 , following a pseudo-second order kinetics. The (chloro-)catechols in solution were mainly attacked by the surface generated $\cdot\text{OH}$ and HO_2/O_2^- in accordance with the E–R mechanism, based on the results of in-situ ATR-FTIR and iron leaching analysis. Meanwhile, the generated carboxyl acids and some intermediates like ethers or dimers adsorbed on the magnetite surface. 4-Chlorocatechol was oxidized faster with the strong oxidant of $\cdot\text{OH}$ probably due to its active redox property and its relatively less adsorption, which led to the more generation of ROS. And because of the generated refractory chlorinated organics and the limited reactivity of oxygen-centered radicals, the DOC removal was only 40% for 4-chlorocatechol. Catechol, however, was mineralized to a larger degree, with the formation of carbon carbon-centered radicals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2014.07.063>.

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