



A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol

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ARTICLE INFO

Article history:

Received 5 August 2010

Received in revised form 28 October 2010

Accepted 29 October 2010

Available online 9 November 2010

Keywords:

Nanoparticulate zero-valent iron

Hydrogen peroxide

Fenton-like

4-Chloro-3-methyl phenol

Hydroxyl radicals

ABSTRACT

The removal of biocide 4-chloro-3-methyl phenol (CMP) was investigated by heterogeneous Fenton-like system using nanoparticulate zero-valent iron (nZVI) as catalyst. The properties of nZVI before and after reaction were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effects of pH value, initial concentration of CMP, nZVI dose and hydrogen peroxide (H_2O_2) concentration were determined. The experimental results showed that lower pH value and CMP concentration brought faster degradation rate. With the initial pH value of 6.1 and initial CMP concentration of 0.7 mM, the optimal dosage of reagents were 0.5 g nZVI/L and 3.0 mM H_2O_2 . At pH 6.1, the degradation of CMP followed two-stage first-order kinetic that composed of an induction period (first-stage) and a followed rapid degradation stage (second-stage). According to the effects of scavengers *n*-butanol and KI, hydroxyl radicals ($\bullet OH$), especially the surface-bounded $\bullet OH$, had a dominant role in the oxidation of CMP. The degradation intermediates, carboxylic acids and chloride ion produced during the reaction process were monitored by high performance liquid chromatography (HPLC), liquid chromatography/mass spectrometry (LC/MS) and ion chromatography (IC). On the basis of these findings, the possible mechanistic steps of CMP degradation were proposed.

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1. Introduction

Over the past few decades, Fenton technology has been extensively studied as one of the best options for the destruction of various recalcitrant organic pollutants in water. A solution of Fe^{2+}/Fe^{3+} and hydrogen peroxide (H_2O_2), known as Fenton reagent, underlines the generation of highly reactive hydroxyl radicals ($\bullet OH$) which can oxidize many organic contaminants rapidly [1,2]. However, it is well known that the homogeneous Fenton process has many disadvantages, such as the requirement of further treatments for the iron ions and sludge, the acidification of effluents before decontamination, and the neutralization of treated solutions before disposal [3–5].

Heterogeneous Fenton-like systems using iron supported catalysts, e.g., zero valent iron (Fe^0) [6,7], goethite ($\alpha-FeOOH$) [8,9], Fe_3O_4 [1,10,11] and Fe^0/Fe_3O_4 [12], have recently been developed. Many of these systems are slow and need additional assistants such as UV or visible light irradiation and ultrasound that increase the cost of equipment and operation [13–16]. Recently, it is noticed that nanoparticles are potentially useful for the remediation of polluted

sites because they have large specific surface area and high surface reactivity, and they can reach or penetrate into zones that are inaccessible to microsize solid catalysts [10,12,17,18]. The application of nanoparticles in heterogeneous Fenton-like systems has been summarized by Garrido-Ramírez et al. [18].

The oxidation kinetic and mechanisms of heterogeneous Fenton-like reactions have been extensively investigated. Many studies have found that the first-order linear relationship is obtained in the degradation of organic pollutants [4,11,12,19]. However, Zhou et al. [6] have suggested that two-stage first-order degradation kinetic for the oxidation of 4-chlorophenol in zero valent iron/ H_2O_2 system is obviously observed. For the degradation mechanisms, there has been much debate as to whether oxidation of organic pollutants in heterogeneous Fenton-like systems involves the hydroxyl radicals mechanism or Fe(IV) based mechanism or both [20–26]. Keenan and Sedlak [21] indicated that the nature of the oxidants formed in the nanoparticulate zero-valent iron (nZVI) and oxygen (O_2) system changes with pH from $\bullet OH$ at low pH to another less reactive species (such as the ferryl ion) at neutral pH values. Lee et al. [23] have concluded that at neutral pH the active oxidant changes from Fe(IV) in the absence of polyoxometalate (POM) to $\bullet OH$ in the presence of POM for the oxidation of organic compounds by Fenton and Fenton-like systems. Nevertheless, there are many arguments about the dominated oxidant and the reactivity of Fe(IV) toward organics in various operating condi-

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tions [25,26]. Therefore, further work is required for more details of the degradation kinetic and mechanisms in various heterogeneous Fenton-like systems.

In the present study, 4-chloro-3-methyl phenol (CMP) was chosen as a model pollutant representative of chlorophenols widely used as biocide and preservative in cosmetics and medical products and in electrode paste [27]. We investigated the heterogeneous Fenton-like oxidation of CMP using nZVI and H₂O₂. The effect of initial parameters on the degradation of CMP in the nZVI/H₂O₂ system was investigated, and detailed reaction kinetic was studied. A CMP degradation pathway was also proposed according to the identification of reaction intermediates.

2. Materials and methods

2.1. Reagents

All chemicals used in this study were of analytical grade and were used without further purification. Commercial reductive iron powders were purchased from Tianjin Jinke Fine Chemical Industry Research Institute. Kalium borohydride (KBH₄) was purchased from Nankai Fine Chemical Factory. Ferrous sulfate (FeSO₄·7H₂O) was obtained from Shenyang Reagent Factory. CMP and methylhydroquinone were supplied by Aladdin Chemistry Co., Ltd. Methyl-*p*-benzoquinone was supplied by Shandong Weifang Tongrun Chemistry Co., Ltd. Carboxylic acids, H₂O₂ (30%, v/v), H₂SO₄, *n*-butanol and KI were obtained from Beijing Chemical Factory. Argon (Ar) gas was supplied by Beijing Aolin Gas Company. Deionized and doubly distilled water was used to prepare solutions in this study.

2.2. Preparation and characterization of nanoparticles

Nanoparticulate zero-valent iron used in this study was prepared according to the method of Cheng et al. [28]. A 100 mL 20 mM KBH₄ aqueous solution was added dropwise to a three-necked flask containing 100 mL 4 mM FeSO₄·7H₂O aqueous solution with violently stirring under Ar protecting at ambient temperature. After stirring for 1.5 h, ferrous iron was reduced by borohydrate forming zero-valent iron particles. The synthesized iron particles were deposited and then washed with deionized water for two times. Finally, nanoparticles were dried at room temperature under vacuum for instant usage.

The nanoparticles were characterized by X-ray diffraction (XRD, Bruker, D8-Advance, 40 kV and 40 mA, Cu K α) and scanning electronic microscopy (SEM, JSM-6301F, JEOL).

2.3. Experimental procedure

All experiments were conducted in a conical flask (25 mL) placed on a rotary shaker (TZ-2EH, Beijing Wode Company) under dark circumstance. The temperature and the rotate speed of rotary shaker were 30 °C and 150 rpm, respectively. The reaction suspension containing determined nZVI and 10 mL CMP solution was prepared, and its initial pH was adjusted by H₂SO₄. During the heterogeneous Fenton-like reaction the pH decreased slightly and the variation was kept within 0.1 pH. The experiments were initiated by adding a given amount of H₂O₂ to the solution. Samples were taken at a given time intervals during the reaction, and then 10 μ L 1 M *n*-butanol was immediately added into 1 mL sample as reaction inhibitor. Samples were filtered through a 0.22 μ m filter film to remove catalyst particles before analyses of the solution. Each experiment was carried out in triplicate; all results were expressed as a mean value and standard deviations were presented.

2.4. Sample analysis

CMP and its intermediates were quantified by means of a high performance liquid chromatography (Agilent 1200 Series, Agilent, USA) equipped with a diode array detector (DAD) and a C18, 5- μ m (4.6 mm \times 150 mm) reversed-phase column (ZORBAX Eclipse XDB-C18, Agilent, USA). The temperature of column was maintained at 30 °C, and the sample loop volume was 20 μ L. The concentration of CMP was determined by HPLC with the detection set to 280 nm, using a mixture of methanol and water at a ratio of 70:30 (v/v) as the mobile phase at a flow rate of 0.8 mL/min. For intermediates analysis, samples were analyzed at a flow rate of 0.8 mL/min and UV absorbance wavelength of 254 nm with a mobile phase of methanol and water at a ratio of 60:40 (v/v).

Attempts to identify degradation intermediates of CMP were made using liquid chromatography and mass spectrometry (LCMS-2010EV, Shimadzu, Japan), equipped with a photo diode array (PDA) using a deuterium lamp and a tungsten lamp, and a mass spectrum (MS) using an atmospheric pressure chemical ionization (APCI) source. Separation of the compounds was performed on the same column used in the HPLC above at 32 °C using a mixture of methanol and water at a ratio of 60:40 (v/v) and a flow rate of 0.8 mL/min. The scan range of PDA was from 190 to 800 nm with a slit width of 1.2 nm. The MS was operated in positive-ion (ES⁺) and negative-ion (ES⁻) electrospray modes with a mass range of 10–400 *m/z*. The other experimental conditions were: nitrogen flow rate 1.5 L/min, cell temperature 40 °C, curved desolvation line (CDL) temperature 250 °C, heat block temperature 250 °C, injection volume 50 μ L.

Chloride ions (Cl⁻) and carboxylic acids produced during the oxidation of CMP were analyzed using an ion chromatography (DX-100, Dionex, Germany) with a Dionex RFICTM IonPac® AS 14 analytical column (4 mm \times 250 mm) and a Dionex RFICTM IonPac® AG 14 guard column (4 mm \times 50 mm). The eluent was 3.5 mM Na₂CO₃ and 1.0 mM NaHCO₃ at a flow rate of 1.0 mL/min, and the sample loop volume was 25 μ L.

The concentration of total organic carbon (TOC) was measured by a Shimadzu TOC-V CPH TOC analyzer with an OTC-18-port sampler (Shimadzu, Japan). The solution pH was measured with a microprocessor pH meter (HI 223, HANNA, Italy).

3. Results and discussion

3.1. Characterization of nanoparticulate zero-valent iron

The representative XRD patterns before and after heterogeneous Fenton-like reaction are shown in Fig. 1. As seen in Fig. 1a, the diffraction peaks indicate that the prepared iron catalyst is mainly in its Fe⁰ state, in agreement with JCPDS (65-4899). The spectroscopy (Fig. 1b) shows the evidence of formation of iron oxides after 1 h heterogeneous Fenton-like reaction, possibly associated with lepidocrocite (JCPDS No. 44-1415), which is consistent with the iron corrosion phenomenon observed in water. According to previous studies [6,29,30], lepidocrocite (γ -FeOOH) has been identified as the first iron corrosion product in the presence of oxygen, and the main reaction is described in Eq. (1).

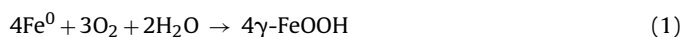


Fig. 2 shows typical SEM images of the synthesized nZVI before and after heterogeneous Fenton-like reaction, which corroborate the XRD results. The iron particles are composed of spherical particles with grain sizes of 80–150 nm (Fig. 2a). According to XRD, after reaction the iron corrosion product is lepidocrocite that has a flake-like structure as seen in Fig. 2b.

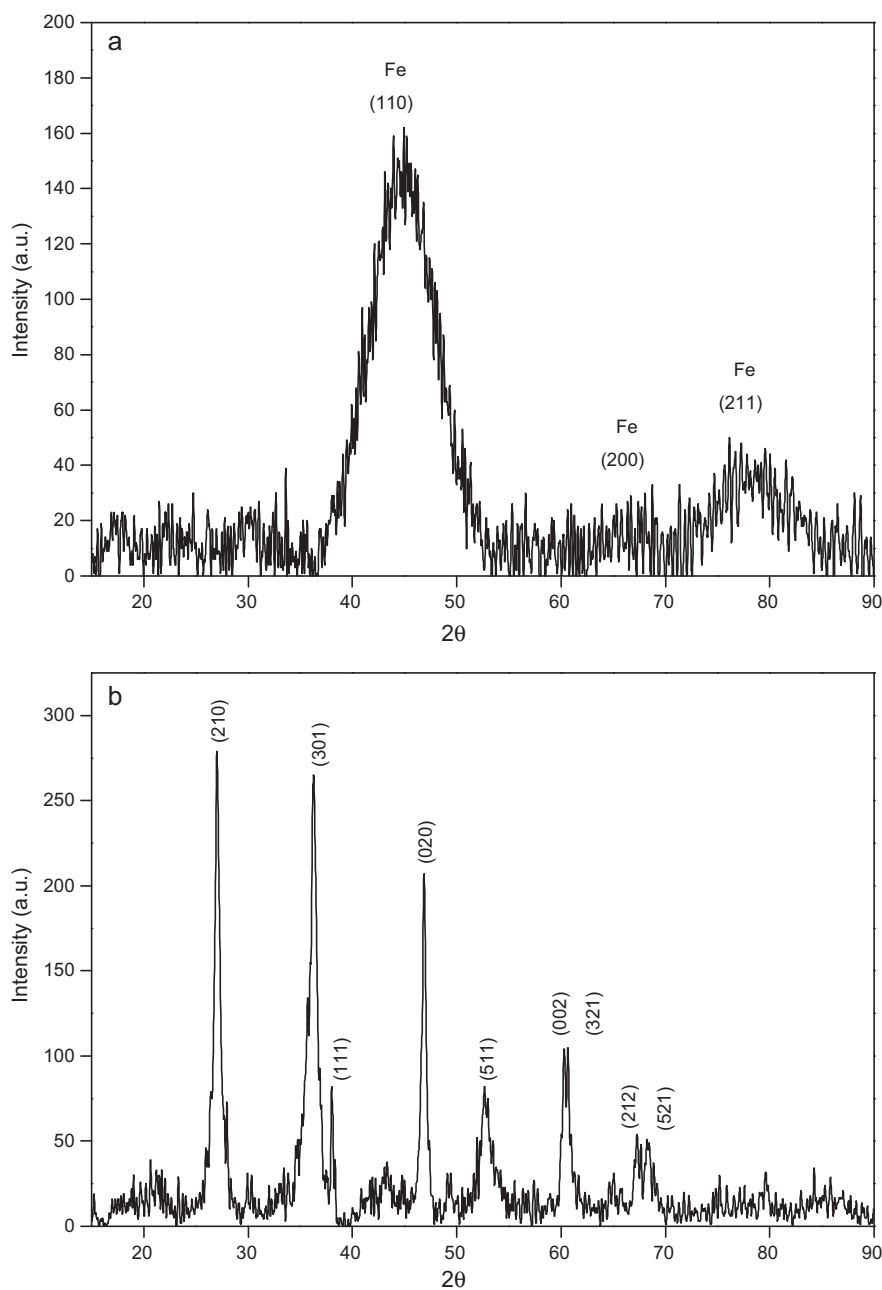


Fig. 1. XRD patterns of nZVI: (a) before reaction and (b) after reaction.

The result illustrates that after reaction noticeable corrosion and aggregation of nanoparticles occurred, forming larger dendritic structures.

3.2. Comparison experiments

It has been reported that nZVI can be used in the reduction of organic contaminants [28,31]. Therefore, batch experiments were conducted in anoxic bottles with 0.7 mM CMP and 1.0 g/L nZVI at initial pH 6.1 (solution original pH, not adjusted) to investigate the reductive dechlorination effect of CMP by nZVI. As shown in Fig. 3, after 60 min reaction little change in CMP concentration was observed, and even throughout 24 h reaction only 9% removal of CMP was observed (the inset of Fig. 3). About 0.034 mM free chloride was detected in the solution after 24 h reaction, indicat-

ing that the removal of CMP was probably expected to both nZVI surface adsorption and reductive dechlorination [28]. Thus, it can be neglected compared to the removal of CMP by oxidation in the nZVI/H₂O₂ system.

We also did the same experiment only with 60 mM H₂O₂ at pH 6.1 and found that CMP was hardly degraded (Fig. 3). However, the simultaneous presence of 0.5 g/L nZVI and 3 mM H₂O₂ could completely remove CMP within 15 min, indicating the high catalytic ability of nZVI to the H₂O₂ activation. As confirmed by the TOC measurement, 63% of TOC was removed within 60 min in the nZVI/H₂O₂ system. The comparison of nZVI with commercial reductive iron powders was investigated under similar reaction conditions: 0.7 mM CMP, 0.5 g/L catalyst, 3 mM H₂O₂ and pH 6.1. The average diameter of commercial reductive iron powders was 62 μm which was previously measured by our laboratory [28].

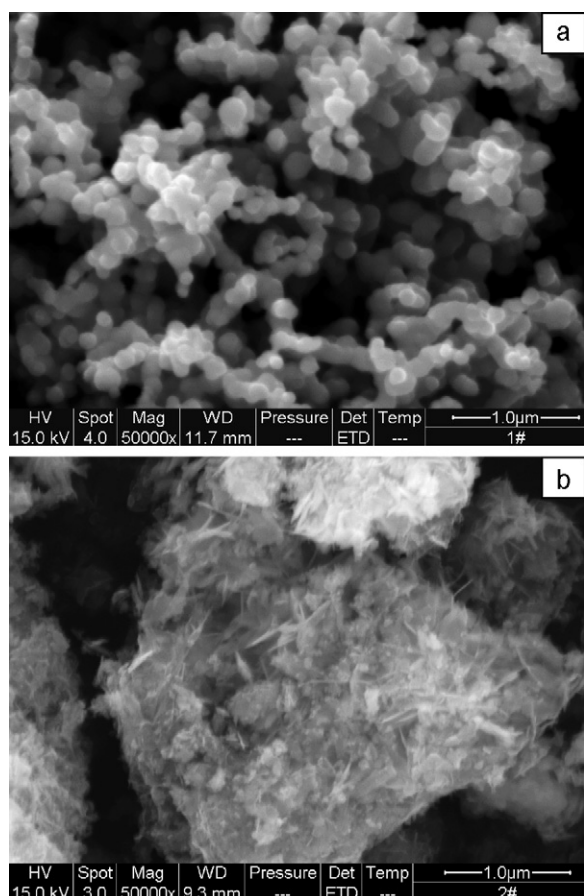


Fig. 2. SEM micrographs of nZVI: (a) before reaction and (b) after reaction.

The result (Fig. 3) shows that the catalytic ability of nZVI is much stronger than commercial reductive iron powders.

3.3. Effect of operational parameters on the degradation of CMP

3.3.1. Effect of pH

Besides enhancing catalytic activity, another motive to develop new heterogeneous Fenton-like catalyst is to extend the pH range.

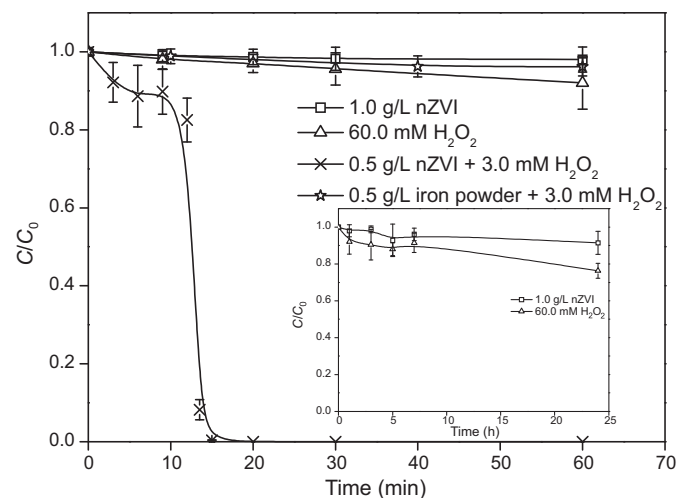
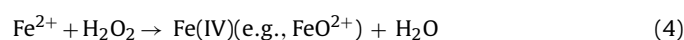
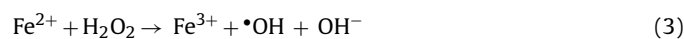
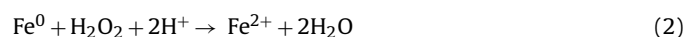


Fig. 3. Comparison of CMP degradation in nZVI (1.0 g/L) alone, H₂O₂ (60.0 mM) alone, nZVI (0.5 g/L) and H₂O₂ (3.0 mM), and reductive iron powder (0.5 g/L) and H₂O₂ (3.0 mM) experiments at pH 6.1 with initial CMP concentration 0.70 mM. Inset graph is the result of CMP degradation conducted in nZVI (1.0 g/L) alone and H₂O₂ (60.0 mM) alone throughout 24 h reaction time.

It has been proved that pH is one of the decisive factors influencing the performance of the Fenton-like process in the removal of pollutants due to its role in controlling the catalytic activity, the activity of the oxidant and the substrate, the dominant iron species, and the stability of hydrogen peroxide [10,20,32,33]. The influence of initial pH value of solutions on the degradation of CMP by the nZVI/H₂O₂ oxidation process was investigated at four different pH values of 3.0, 4.0, 5.0 and 6.1, as shown in Fig. 4a. With the decrease of solution pH, CMP degradation increased, and the best pH value achieved at pH 3.0 with 99% degradation within 1 min reaction.

The mechanism through which the nZVI/H₂O₂ system produces oxidants involves the two-electron oxidation of Fe⁰ followed by the Fenton reaction [21,23,24]. Initially, Fe⁰ is oxidized via a two-electron transfer from the particle surface to H₂O₂ (reaction (2)) [23,24]. Oxidants responsible for the oxidation of organic pollutants (mainly •OH) are generated by Fenton reaction (Eq. (3)) [23,24]. At pH values above 5, a weaker oxidant such as ferryl ion (e.g., FeO²⁺) that is more selective than •OH may be formed by reaction (4) [21,34,35].



In the experiment, the decreased oxidation efficiency at higher pH values can be ascribed to the decomposition of H₂O₂, the lower oxidation potential of hydroxyl radicals, and the deactivation of catalyst with the formation of ferric hydroxide complexes leading to a reduction of •OH [7,36,37]. An important observation here revealed that at solution original pH of 6.1, the complete degradation of CMP was obtained within 15 min of reaction. The activity of nZVI in the neutral pH range is higher than that of many reported heterogeneous Fenton-like catalysts [4,10,12,38,39]. Thus, no or less pH adjustment of the medium is needed for effective oxidation over the wider pH range, which is an important advantage for application.

3.3.2. Effect of initial concentration of CMP

Fig. 4b shows the effect of CMP initial concentration on the CMP degradation with pH 6.1, nZVI dose 0.5 g/L and H₂O₂ concentration 3.0 mM. The results showed that the reaction time for complete degradation of CMP extended when the initial concentrations of CMP increased from 0.35 to 1.05 mM. From previous study [11], more CMP molecules may adsorb on the nZVI surface occupying a greater number of iron active sites which become unavailable for H₂O₂, resulting in less hydroxyl radicals formed at the surface.

3.3.3. Effect of nZVI dose

The obtained results for CMP degradation as a function of the nZVI dose at various reaction times with pH 6.1, initial CMP concentration 0.7 mM and H₂O₂ concentration 3.0 mM are displayed in Fig. 4c. When the nZVI dose increased from 0.1 g/L to 0.5 g/L, the oxidation of CMP was moderately accelerated, mainly due to the increasing amount of active sites for H₂O₂ decomposition producing more reactive oxidants such as •OH [19,36,40]. Nevertheless, the degradation degree was not enhanced but a little decreased when the nZVI dose was increased to 0.6 g/L, attributed to the agglomeration of nZVI particles and the scavenging of hydroxyl radicals through undesirable reaction (5) [6,40]. Thus, the optimum nZVI dose was 0.5 g/L in our experiment.



3.3.4. Effect of H₂O₂ concentration

The effect of H₂O₂ concentration on CMP degradation was investigated over a range of 0.6–6.0 mM at pH 6.1, initial CMP

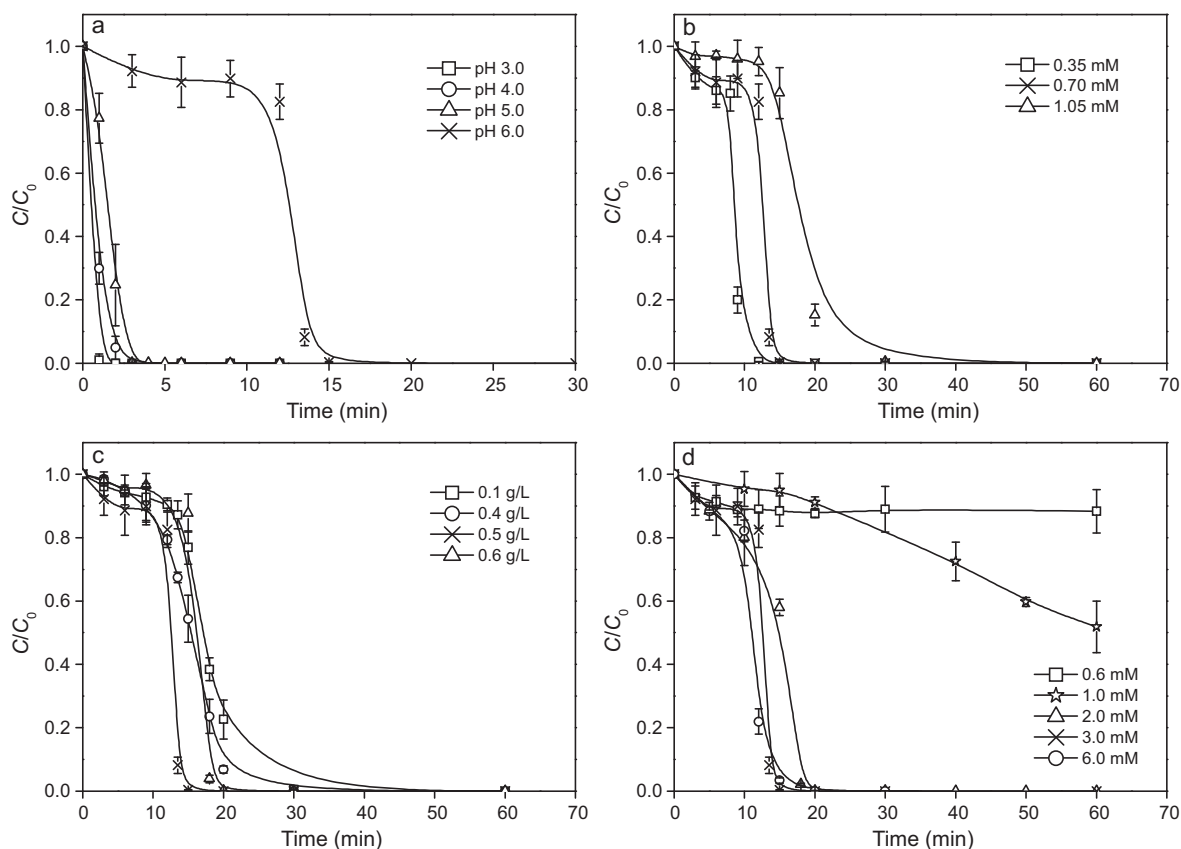
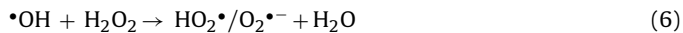


Fig. 4. Effect of operating parameters on CMP degradation in the nZVI/H₂O₂ heterogeneous system: (a) pH; (b) initial CMP concentration; (c) nZVI addition; (d) H₂O₂ dosage. Except for the investigated parameter, other parameters fixed on pH 6.1, CMP 0.70 mM, nZVI 0.5 g/L and H₂O₂ 3.0 mM.

concentration 0.7 mM and nZVI dose 0.5 g/L. At low H₂O₂ concentrations of 0.6 and 1.0 mM, the CMP oxidation rates were very slow because of the insufficient •OH in aqueous solution. As the H₂O₂ concentration increased to 3.0 mM, the CMP degradation was obviously enhanced, because more radicals were formed [36]. However, for a higher concentration (6.0 mM), no significant additional improvement was observed due to the scavenging effect of hydroxyl radicals and the inhibition of iron corrosion by hydrogen peroxide [6,11]. As expressed by reaction (6), although other radicals (HO₂• and O₂•⁻) are generated, they are much less reactive that may be neglected [40]. Hence, we obtained the maximum H₂O₂ concentration of 3.0 mM for the effective degradation of CMP.



3.4. Two-stage first-order degradation kinetic at pH 6.1

The heterogeneous Fenton-like reaction observed here shows the two-stage first-order degradation kinetic at pH 6.1 which is composed of an induction period (first-stage) and a followed rapid degradation stage (second-stage) as shown in Fig. 5. The induction period, defined as a period of time during which no measurable reaction occurs or a time before a reaction suddenly increases in rate [41], is a function of initial CMP concentration, nZVI dose and H₂O₂ dosage. As seen in Fig. 5a, higher initial CMP concentration seemed to prolong the induction period and decrease the kinetic rate (*k*) of second-stage. Fig. 5b illustrates the effect of nZVI addition on the two-stage degradation kinetic. When nZVI dose increased from 0.1 to 0.5 g/L, the induction period was shortened from 15 to 12 min, and *k* of second-stage was increased from 0.35 to 1.79 min⁻¹. Excessive iron addition (0.6 g/L) inhibited the heterogeneous Fenton-like reaction with the induction

period of 15 min and *k* (second-stage) of 1.23 min⁻¹. As shown in Fig. 5c, from 0.6 to 3.0 mM H₂O₂ dosage, the first-stage was shortened and *k* of second-stage was increased, and much higher H₂O₂ dosage could not significantly enhance the oxidation of CMP. The trend described in Fig. 5 corroborated the effect of operational parameters on the degradation of CMP discussed in the above section.

The lower reaction rate in the first stage can be mostly ascribed to heterogeneous reactions occurred on the iron surface as seen in Eqs. (2) and (6). It is suggested that the induction period is an activation process of the surface iron species, and iron dissolution occurs on the nZVI surface, which may also caused by the gradual oxidation of the surface iron-CMP complexes by H₂O₂ [6,41]. Simultaneously, due to the presence of large activated area of iron and high concentration of H₂O₂ in the initial stage, most •OH produced on the nZVI surface could be scavenged quickly resulting in the slow oxidation of CMP [6]. As reported earlier, the rapid degradation of CMP in the second-stage could be mainly ascribed to the Fenton reaction on or near the nZVI surface [6]. To verify these conclusions, some experiments were carried out and the results were presented in Fig. 6. As an oxide layer was formed on the nZVI surface, catalyst particles were pretreated using 0.05 M H₂SO₄, and then washed twice by deionized water which was purged with the Ar gas. Although the induction period was shortened and the degradation of CMP was enhanced compared to that using the fresh particles, two-stage first-order degradation kinetic was obviously observed using the pretreated nZVI, indicating that the low reaction rate of first stage could not be attributed to the formation of surface oxide layer. First-order degradation kinetic could be applied very well on the degradation of CMP in the homogeneous Fenton system even though the dosage of reagent (Fe²⁺/H₂O₂) was decreased, which was consistent with the results reported by Lopez et al. [42].

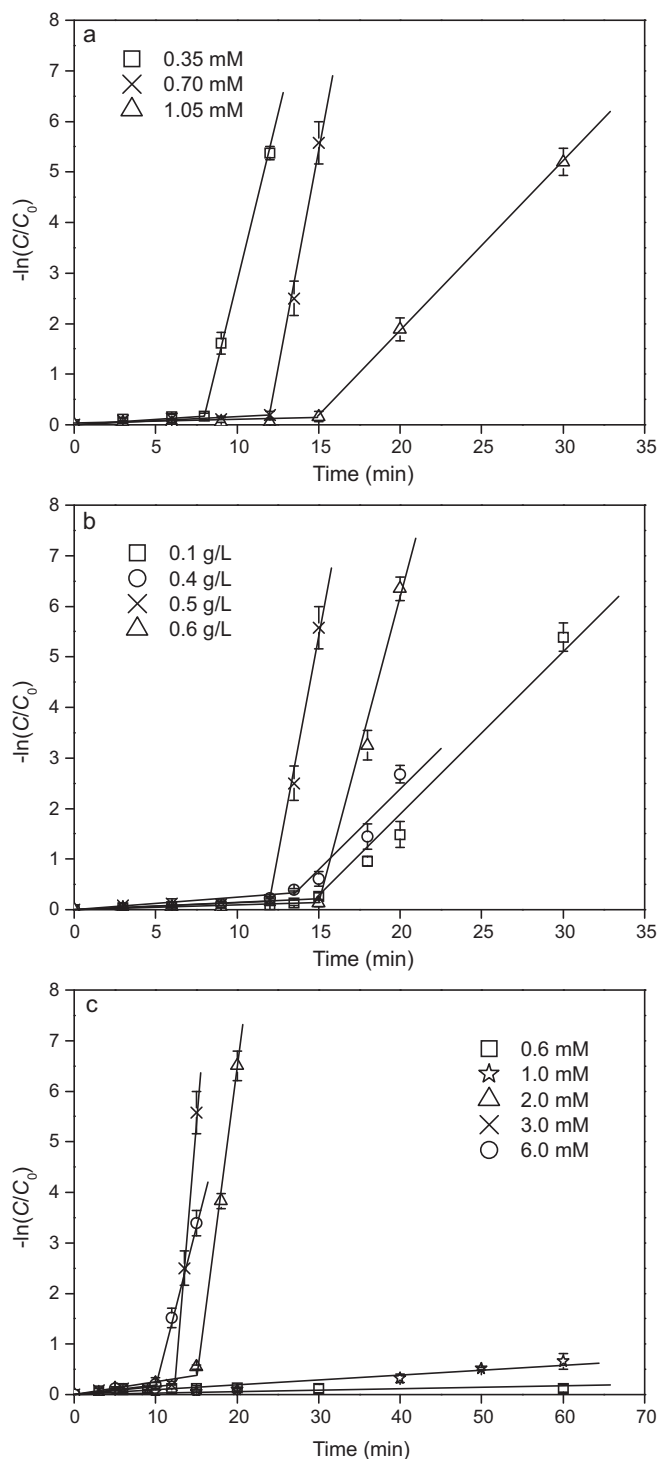


Fig. 5. Pseudo-first-order plots for CMP degradation in the nZVI/H₂O₂ heterogeneous system: (a) effect of initial CMP concentration; (b) effect of nZVI addition; (c) effect of H₂O₂ dosage. Except for the investigated parameter, other parameters fixed on pH 6.1, CMP 0.70 mM, nZVI 0.5 g/L and H₂O₂ 3.0 mM.

A k of 1.46 min^{-1} was achieved in the homogeneous Fenton system, which had the similar magnitude with the k of the second-stage (1.79 min^{-1}) in nZVI/H₂O₂ system. Although the possible heterogeneous catalysis effect of iron oxides on the nZVI surface could not be excluded, degradation of CMP in the second-stage could be mainly attributed to homogeneous dissolved Fe²⁺/H₂O₂ Fenton reaction on or near the nZVI surface.

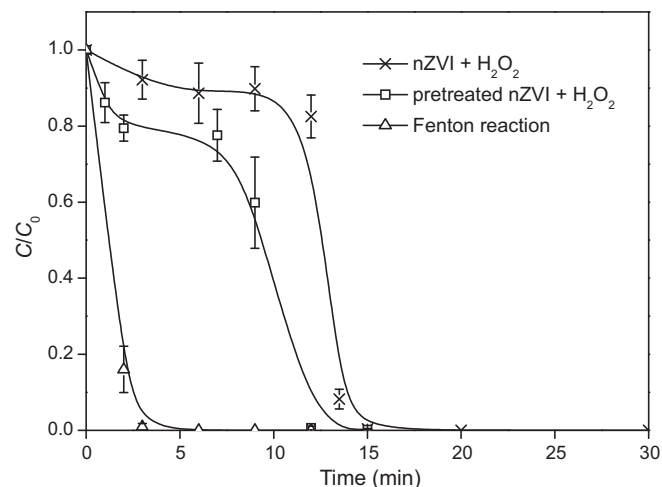


Fig. 6. Degradation of CMP in nZVI (0.5 g/L) and H₂O₂ (3.0 mM) system, pretreated nZVI (0.5 g/L) and H₂O₂ (3.0 mM) system, and homogeneous Fenton reaction (0.9 mM Fe²⁺, 0.3 mM H₂O₂) at pH 6.1 with initial CMP concentration 0.70 mM.

3.5. Reactive oxidizing species in the nZVI/H₂O₂ system

To investigate the reactive oxidizing species mediated in the process, the influence of different scavengers on the degradation of CMP at pH 6.1 was determined (Fig. 7). Excess *n*-butanol (350.0 mM) was added to the solution to scavenge all the hydroxyl radicals produced in the system [43,44]. As it can be seen, the degradation of CMP is strongly inhibited in the presence of *n*-butanol, indicating that CMP is mainly decomposed by the attack of •OH radicals (including surface-bound •OH and free •OH). However, 21% of degradation was still reached with the addition of *n*-butanol, suggesting that some minor degradation of CMP could also take place in the solution. Earlier studies have suggested that an alternate oxidant, such as Fe(IV), may be formed in the Fenton reactions at neutral pH values as seen in Eq. (4), which can react with many organic compounds [21,45]. It could be deduced that the minor degradation of CMP may be attributed to the action of Fe(IV).

Iodide ion is used to scavenge hydroxyl radicals produced at the surface of nZVI particles as Eqs. (7)–(9) [46,47]. As shown in Fig. 7, addition of excess KI (7.0 mM) resulted in a considerable decrease in the extent of CMP degradation from 100% (in 60 min in absence of KI) to 43%, indicating that surface-bound •OH played a significant

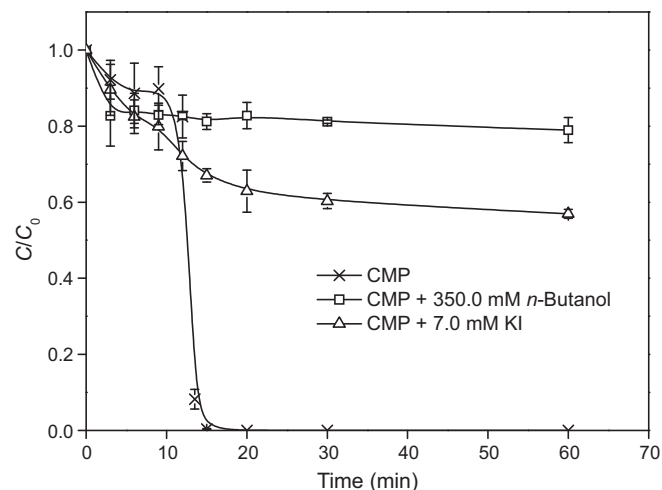
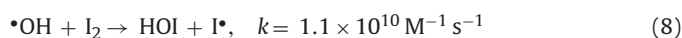
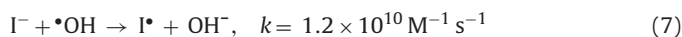


Fig. 7. Effect of radical scavengers on the degradation of CMP with nZVI 0.5 g/L, H₂O₂ 3.0 mM and initial CMP concentration 0.70 mM at pH 6.1.

Table 1
Intermediates identified by LC/MS and IC: nZVI 0.5 g/L; H₂O₂ 3.0 mM; initial CMP concentration 0.70 mM; pH 6.1.

Compounds	Structural formula	Sample time (min)					
		3	9	12	15	30	60
4-Chloro-3-methyl phenol		✓	✓	✓	✓		
Methylhydroquinone		✓	✓	✓	✓		
Methyl- <i>p</i> -benzoquinone			✓	✓	✓		
(2 <i>Z</i>)-But-2-enedioic acid			✓	✓	✓	✓	
Malonic acid	HOOCCH ₂ COOH		✓	✓	✓	✓	
Oxalic acid	HOOC-COOH		✓	✓	✓	✓	✓
Acetic acid	CH ₃ COOH		✓	✓	✓	✓	✓
Formic acid	HCOOH		✓	✓	✓	✓	✓

role in the degradation of CMP. Thus, the degradation of CMP was primarily attributed to the action of •OH, especially the surface-bound •OH.



3.6. Degradation pathway

To elucidate the possible mechanistic steps in the oxidation of CMP by nZVI/H₂O₂ at pH 6.1, the evolution of the main intermediate methyl-*p*-benzoquinone and chloride ion during CMP degradation was detected by HPLC and IC (Fig. 8), and the existence of some intermediates was measured by LC/MS and IC (Table 1). From Fig. 8, it can be seen that about 93% of the chlorine was released from the aromatic ring to form chloride ion, which was the first step in the oxidation of CMP. As reported by previous researches, the dechlorination was predominantly assigned to the hydroxyl substitution on the phenolic ring structure (*ipso*-substitution), which transformed the chloro-phenolics to phenolics or quinones [42,47]. After dechlorination, benzene derivatives such as methylhydroquinone were formed which could react with •OH yielding the aromatic byproduct methyl-*p*-benzoquinone. As shown in Fig. 8, the concentration of methyl-*p*-benzoquinone reached a peak value at about 15 min and then began to decrease. Combined to the data presented in Table 1, smaller organic acid molecules were generated afterward. The C–C bonds of methyl-*p*-benzoquinone were cleaved mainly by the action of •OH to form carboxylic acids such as (2*Z*)-but-2-enedioic acid and malonic acid. Eventually, some smaller molecular organic acids such as oxalic acid, acetic acid and

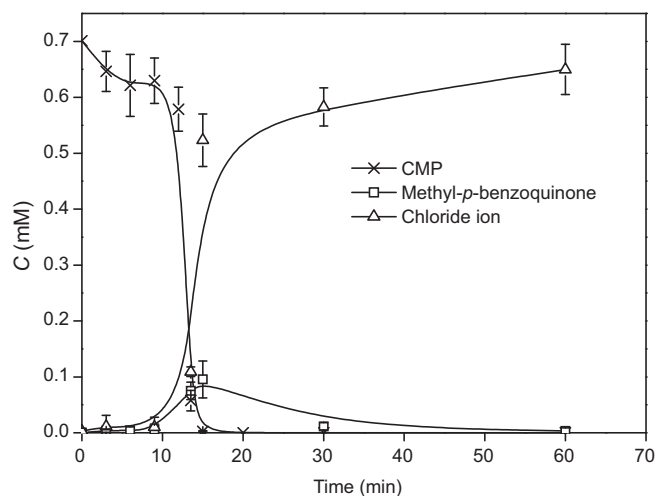


Fig. 8. Variation of the concentration of CMP, methyl-*p*-benzoquinone and chloride ion during CMP degradation detected by HPLC and IC.

formic acid remained in solution after a reaction time of 60 min which could be associated with the residual TOC value (37% after 60 min reaction).

4. Conclusions

Heterogeneous nZVI/H₂O₂ system has proven to be an efficient and rapid process for oxidation of CMP under neutral pH conditions, which is superior to alone nZVI, alone H₂O₂ and commercial reductive iron/H₂O₂ systems. In this study, experiments were done to investigate the influence of operational param-

ters on the degradation of CMP. Complete degradation could be achieved within 15 min with nZVI 0.5 g/L, H₂O₂ 3.0 mM and initial CMP concentration 0.70 mM at pH 6.1, while 63% of TOC was removed after 60 min reaction. At initial pH 6.1, two-stage first-order degradation kinetic was observed, which was composed of an initial slow degradation stage (first-stage) mostly ascribed to heterogeneous reactions occurred on the iron surface and a followed rapid degradation stage (second-stage) mainly ascribed to the Fenton reaction on or near the nZVI surface. The effect of scavengers indicated that •OH, especially the surface-bounded •OH, was the main oxidants responsible for the degradation of CMP. Furthermore, according to the intermediates and chloride ion determined by HPLC, LC/MS and IC, the possible degradation pathway was proposed.

The heterogeneous Fenton-like reaction may be applied as an attractive alternative for removing other organic compounds in wastewater. More work is needed to handle the eventual loss of catalytic activity and the recovery of catalyst for reuse, which may form the basis of effective application for environmental treatment.

Acknowledgements

The authors are grateful for the financial support provided by the National Natural Science Foundation of China (Grant Nos. 50978145; 50928802).

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