Ascorbic Acid/Fe@Fe₂O₃: A Highly Efficient Combined Fenton Reagent to Remove Organic Contaminants

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Abstract

In this study, we demonstrate that the combination of ascorbic acid and Fe@Fe₂O₃ core-shell nanowires (AA/Fe@Fe₂O₃) offers a highly efficient Fenton reagent. This combined Fenton reagent exhibited extremely high activity on the decomposition of H₂O₂ to produce •OH for the degradation of various organic contaminants, including rhodamine B, methylene blue, alachlor, atrazine, siduron, lincomycin, and chloroamphenicol. The contaminant degradation constants in the AA/Fe@Fe₂O₃/H₂O₂ Fenton systems were 38 – 53 times higher than those in the conventional homogeneous Fenton system (Fe(II)/H₂O₂) at pH 3.8. Moreover, the •OH generation rate constant in the AA/Fe@Fe₂O₃/H₂O₂ Fenton system was 1 – 3 orders of

magnitudes greater than those of heterogeneous Fenton systems developed with other iron-containing materials (α -FeOOH, α -Fe₂O₃, FeOCl, and so on). The high activity of AA/Fe@Fe₂O₃ was attributed to the effective Fe(III)/Fe(II) cycle and the iron-ascorbate complex formation to stabilize ferrous ions with desirable and steady concentrations. During the AA/Fe@Fe₂O₃/H₂O₂ Fenton process, ascorbic acid served as a reducing and complexing reagent, enabling the reuse of Fe@Fe₂O₃ nanowires. We systematically investigated the alachlor and ascorbic acid degradation and found that they could be effectively degraded in the AA/Fe@Fe₂O₃/H₂O₂ system, accompanying with 100% of dechlorination and 92% of denitrification. This study sheds light on the importance of Fe(III)/Fe(II) cycle for the design of high efficient Fenton system and provides an alternative pathway for the organic contaminants removal.

Keywords: Fe@Fe₂O₃ Core-Shell Nanowires; Ascorbic Acid; Alachlor; Degradation; Fenton Reaction

1. Introduction

Hydroxyl radical ($\bullet$ OH), one of the most powerful oxidizing agents, could oxidize and even mineralize a wide range of organic contaminants [1-3]. As one of the most used AOPs, traditional homogeneous Fenton process can produce $\bullet$ OH via the reactions of hydrogen peroxide with soluble Fe(II) or Fe(III) salts (Eqs. 1-3).

Although traditional homogeneous Fenton reaction is able to degrade different kinds of recalcitrant organic contaminants [4-6], it suffers from the narrow working pH range of 2.0 – 3.5 and the generation of iron sludge [7-9]. These drawbacks could be overcome by the development of heterogeneous Fenton systems with a broad working pH range of 3.0 – 9.0 and an advantage of easy separation of Fenton reagents. Unfortunately, most iron based heterogeneous Fenton reagents exhibited much lower activity to catalyze the decomposition of hydrogen peroxide than their homogeneous counterparts. For instance, Voelker and his coworkers reported goethite, hematite and ferrihydrite as heterogeneous Fenton reagents could decompose hydrogen peroxide to produce $\bullet\text{OH}$ with low rate constants of 4.00×10^{-7} , 4.25×10^{-5} and 2.00×10^{-5} , respectively [10]. Such poor reactivity of heterogeneous Fenton reagents was attributed to the slow Fe(III)/Fe(II) cycle during the heterogeneous Fenton process. Recently, Han et al. reported FeOCl nanosheets with high activity and durability for the H_2O_2 decomposition [11]. However, the preparation of FeOCl nanosheets involved the utilization of argon atmosphere and 40 h of high temperature (653 K) calcination, limiting their wide application. Therefore, it is of great importance, but still a challenge to develop easily available, reusable and high efficient heterogeneous Fenton catalysts.

Recently, we found that Fe@Fe₂O₃ core-shell nanowires could greatly enhance Fenton (Fe(II)/H₂O₂) oxidation of RhB at pH > 4. The $\bullet\text{OH}$ generation rate of Fe(II)/Fe@Fe₂O₃/H₂O₂ reached as high as $4.27 \times 10^{-3} \text{ s}^{-1}$, about 1.5 times that (2.93

$\times 10^{-3} \text{ s}^{-1}$) of $\text{FeOCl}/\text{H}_2\text{O}_2$ Fenton system [11-15]. Unfortunately, only 80% of $\text{Fe}@\text{Fe}_2\text{O}_3$ nanowires' reactivity could be maintained after five cycles of use. In this study, we demonstrate that the combination of ascorbic acid and $\text{Fe}@\text{Fe}_2\text{O}_3$ nanowires ($\text{AA}/\text{Fe}@\text{Fe}_2\text{O}_3$) offers a highly efficient Fenton reagent to degrade various organic contaminants, including rhodamine B, methylene blue, alachlor, atrazine, siduron, lincomycin, and chloroamphenicol. In this system, the combined Fenton reagent ($\text{AA}/\text{Fe}@\text{Fe}_2\text{O}_3$) exhibits extremely high activity on the decomposition of H_2O_2 to produce hydroxyl radical. The roles of ascorbic acid on the reusability of $\text{Fe}@\text{Fe}_2\text{O}_3$ nanowires and the $\text{Fe(III)}/\text{Fe(II)}$ cycle during Fenton oxidation of organic contaminants are discussed in detail.

2. Experiments Section

2.1 Chemicals and Materials

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaBH_4 (96%), ascorbic acid (AA), hydrogen peroxide (H_2O_2 , 30% in water), acetic acid, hydroxylamine hydrochloride, sodium acetate (NaAc), tert-butyl alcohol (TBA), 1, 10-phenanthroline, HCl and NaOH were all of analytical grade and purchased from National Medicines Corporation Ltd. China. Alachlor was obtained from Sigma-Aldrich. Acetonitrile, acetone, and dichloromethane were of HPLC grade and obtained from Merck KGaA. All the chemicals were used as received without further purification. Deionized water was used throughout the experiments. 0.2 mol/L of H_2O_2 stock solutions were prepared by diluting 30% H_2O_2 . 0.25 mol/L of AA stock solution was prepared by directly dissolving AA in deoxygenized and deionized water.

The concentration of alachlor stock solution was 20 mg/L. All the stock solutions were freshly prepared before use. NaOH and HCl solutions were used to adjust the pH value of the solutions.

2.2 Sample Preparation

Core-shell Fe@Fe₂O₃ nanowires were synthesized with the method described in our previous report [16]. Nano-Fe@Fe₂O₃ was synthesized with previously reported hydrothermal and solvothermal method [17].

2.4 Analysis Method

The concentration of alachlor was analyzed by high performance liquid chromatography (HPLC, LC-20AT, Shimadzu, Japan) equipped with UV detector and an Agilent TC-C18 reverse phase column. The mobile phase was 0.75% acetic acid/acetonitrile (40:60, v/v) at a flow rate of 1 mL/min and the effluent was monitored by the UV detector at a wavelength of 225 nm. The injection volume was 10 µL, and the temperature of column was maintained at 35 °C.

The possible alachlor degradation intermediates were analyzed using gas chromatography-mass spectrometry (GC-MS) (Thermo Fisher Scientific, Trace 1300 equipped with ISQ) with a DB-5 column (30 m × 0.25 mm). The methods of the samples pre-treatment and the subsequence injections were same with that described in our previous work.[18]

The concentrations of Fe(II) and total dissolved irons were measured by a 1,10-phenanthroline method [19]. Samples were analyzed by measuring the characteristic absorption of Fe(II)-1,10-phenanthroline complex at $\lambda = 510$ nm with a

UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). Hydroxylamine hydrochloride was utilized as the reducing agent for the total iron concentration measurement.

A (p-hydroxyphenyl) acetic acid (POHPAA) method was used to detect the amount of generated H_2O_2 [20]. The fluorescence intensity measurement was performed on a Fluoro Max-P spectrophotometer (FL1008M018, Cary, USA). ESR spectra of $\text{DMPO}\cdot\text{OH}$ was obtained by using a JES FA 200 X-band spectrometer (JEOL, Japan) employing 9.50 GHz field modulation with 100 ms of sampling time, 2×10^5 of field modulation amplitude, 9.05×10^9 Hz of microwave frequency, 0.998 mW of microwave power, 60 of receiver gain, and 30 ms of receiver time constant. An ion chromatograph (IC, Dionex ICS-900, Thermo, USA) equipped with an AS23 column was used to detect anions. The injection volume was 10 μL , the flow rate was 1.0 mL/min. A mixture containing 0.8 mmol/L NaHCO_3 and 4.5 mmol/L Na_2CO_3 was used as the mobile phase. The pH was measured using a pH meter (Thermo Orion 720A+) equipped with a Mettler Toledo Inlab 437 pH combination electrode.

AA concentration was measured by a modified previously described method: 700 μL sample, 150 μL 85% H_3PO_4 , 150 μL 3% ferric ammonium sulfate were mixed and then 3 mL 0.4% 2, 2'-bipyridine was mixed to make the final volume of 4 mL at different intervals [21]. After 30 min reaction, samples were analyzed by a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan), and the characteristic absorption of $\text{Fe(II)}\text{-}2, 2'\text{-bipyridine}$ complex at $\lambda = 525$ nm was measured.

The possible intermediates of AA were identified by liquid chromatography-mass

spectrometry (LC-MS, TSQ Quantum MAX, Thermo) with a Hypersil Gold C18 column of 150 mm $\times$ 2.1mm and 2 μ m particle size, 300 Å. The column was maintained at 30°C. The injected sample volume was 10 μ L, while the mobile phase was composed of water and acetonitrile (95:5, v/v) at a flow rate of 0.2 mL/min. The mass spectral analysis was performed on a AB Sciex 4000 QTRAP triple quadrupole mass spectrometer from Thermo equipped with an ESI interface operating in positive ion mode, with the following set of operation parameters: capillary voltage, 3000 V; nebulizer pressure, 40 psi; drying gas flow, 8 l/min; drying gas temperature, 80°C. LC-MS accurate mass spectra were recorded across the range 50–250 m/z.

The surface electronic states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000), and all binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon.

2.6 Quantification of •OH

We measured the generation rates of •OH ($V_{\bullet OH}$) by employing the oxidation of benzoic acid (BA) as the probe reaction according to the following modified method described [10, 11]. In this case, BA can react with •OH in a well-defined manner and obey the pseudo-first-order kinetics. Due to the high probe concentration ($[BA]/[H_2O_2] > 1000$), the scavenging effect of other scavengers (Si) can be ruled out (Eq. 6). Then the consumption of •OH rate can be described by following equations (Eqs. 4 – 6).

$$-\frac{d[probe]}{dt} = k_{probe}[probe] \quad (4)$$

$$V_{\bullet OH} = k_{\bullet OH, P}[BA][\bullet OH] + \sum k_{\bullet OH, i}[Si][\bullet OH] \quad (5)$$

$$V_{\bullet\text{OH}} = k_{\bullet\text{OH}, \text{P}}[\text{BA}][\bullet\text{OH}] = k_{\text{BA}}[\text{BA}] \quad (6)$$

Based on Eqs 4 and 6, the generation rate of $\bullet\text{OH}$ vs. the concentration of H_2O_2 can be plotted. The rate constant of $\bullet\text{OH}$ generation can be regarded as the slope of the fitting line (Eq. 7).

$$V_{\bullet\text{OH}} = k_{\bullet\text{OH}}[\text{H}_2\text{O}_2] \quad (7)$$

2.7 Fenton Degradation Experiments

All the experiments were performed in 100 mL conical flasks under air bubbling with a rate of 1.5 L/min at room temperature (25 ± 5 °C). Typically, 250 μL of 0.2 mol/L H_2O_2 solution and 200 μL of 0.25 mol/L AA solution were added into 50 mL of the alachlor solutions (20 mg/L). Then 5 mg of $\text{Fe@Fe}_2\text{O}_3$ catalyst was added to trigger the alachlor degradation under air bubbling with a rate of 1.5 L/min. The pH of alachlor solution decreased from 6.7 to 3.5 when 200 μL of 0.25 mol/L AA solution was added to the alachlor solution either in the presence or the absence of $\text{Fe@Fe}_2\text{O}_3$. During the degradation, the pH of alachlor solution increased from 3.6 to 4.25 in the presence of $\text{Fe@Fe}_2\text{O}_3$, while the pH of the solution kept at 3.6 in the absence of $\text{Fe@Fe}_2\text{O}_3$. At predetermined time intervals, 900 μL of the reaction solution was sampled, followed with the filtration by 0.22 μm nylon membrane. And then 100 μL of ethanol was added immediately to the sampled solution to quench the reaction for the subsequent high pressure liquid chromatography (HPLC) measurement. For comparison, anaerobic alachlor degradation was conducted by bubbling high-purity argon gas for 30 min prior to the initiation of the reaction and during the entire degradation experiment with a flow rate of 1.5 L/min. The alachlor degradation with

Fe@Fe₂O₃ nanowires in the presence of both ascorbic acid and H₂O₂ was denoted as AA/Fe@Fe₂O₃/H₂O₂. The initial pH values of the AA/Fe@Fe₂O₃/H₂O₂ system was 3.8. For comparison, 100 μ L of 1.0 mmol/L Fe(II) stock solution was added to H₂O₂ solution to obtain Fe(II)/H₂O₂ and AA/Fe(II)/H₂O₂ systems with other conditions identical to those of the AA/Fe@Fe₂O₃/H₂O₂ system. To clarify the reaction between AA and Fe(III) directly, 200 μ L of 1.0 mmol/L Fe(III) stock solution was added to 50 ml of 1 mmol/L AA solution to obtain AA/Fe(III) system with the same initial pH as that of the AA/Fe@Fe₂O₃/H₂O₂ system. To evaluate the stability of Fe@Fe₂O₃ nanowires, the used catalyst was removed from the suspension, and then washed with deionized water and ethanol, finally vacuum dried for the next cycle of use.

2.8 TOC Measurement

The degradation of 20 mg/L alachlor was chosen to study the mineralization of organic molecules in the AA/Fe@Fe₂O₃/H₂O₂ system. The concentrations of AA, H₂O₂ and Fe@Fe₂O₃ were all same as degradation experiments described above. 4 mL of the degradation solutions were sampled every 20 min and analyzed immediately after filtration through a 0.22 μ m membrane. For comparison, the TOC (total organic carbon analysis) change in the AA/Fe@Fe₂O₃/H₂O₂ system without adding alachlor was measured. The total organic carbon (TOC) content was determined by a Shimadzu TOC-V CPH analyzer.

3. Results and Discussion

Alachlor was chosen as a model contaminant to systematically investigate its degradation mechanism and the generation of reactive oxygen species in the

AA/Fe@Fe₂O₃/H₂O₂ system. First, we investigated the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system in the presence of 0.5, 1.0 and 1.5 mmol L⁻¹ of AA and found the degradation rate of alachlor first increased along with increasing the AA concentration and then kept steady (Figure S1 in the SM). The alachlor degradation rate in case of 1.0 mmol L⁻¹ AA was close to that of 1.5 mmol L⁻¹ AA. Thus, 1.0 mmol L⁻¹ was chosen as the optimal concentration of AA in this study. As shown in Figure 1a, alachlor could not be removed in the presence of Fe@Fe₂O₃, or AA, or H₂O₂ within 60 min. Meanwhile, the combination of AA/Fe@Fe₂O₃, or Fe@Fe₂O₃/H₂O₂, or AA/H₂O₂ could not induce the obvious degradation of alachlor in 60 min. Interestingly, more than 80% of alachlor was degraded within 10 min in the AA/Fe@Fe₂O₃/H₂O₂ system, while its complete degradation was finished in 50 min. All the alachlor degradation curves obeyed pseudo-first-order kinetics (Figure 1b). The alachlor degradation rate constant was found to be 0.21 min⁻¹ in the AA/Fe@Fe₂O₃/H₂O₂ system, which was 48 times that (0.0043 min⁻¹) of the conventional homogeneous Fenton system at pH 3.8. Subsequently, we attempted to clarify the intrinsic reasons for the high efficiency of AA/Fe@Fe₂O₃/H₂O₂ system by designing a series of experiments.

Since the pH value is crucial for the Fenton oxidation of organic contaminants, we first studied the pH influence and found that the degradation of alachlor was dependent on the pH value of AA/Fe@Fe₂O₃/H₂O₂ system. Along with the pH increasing from 3.8 to 6.7, the alachlor degradation percentage within 4 hours decreased from 100% to 25% (Figure S2 in the SM), suggesting that the increase in

the pH value is bad for alachlor degradation in the system.

As the addition of ascorbic acid decreased the pH value of alachlor solution from 6.5 to 3.8, we monitored the pH changes during the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system and found the pH value increased slightly from 3.8 to 4.2 (Figure S3 in the SM), indicative of the consumption of H⁺ during the alachlor degradation. Therefore, we conducted the alachlor degradation by adjusting the initial pH value to 3.8 with 1.0 mol/L of H₂SO₄ instead of ascorbic acid, and found that alachlor was not degraded (Figure S4 in the SM). This result suggested that the superior performance of AA/Fe@Fe₂O₃ was not attributed to the acidity effect of ascorbic acid, but to other factors.

Besides its acidity, AA can also serve as a reductant. The reduction potential of dehydroascorbic acid (DHA)/AA is -0.06 V (NHE) (Eq. 8) [22-23], while the reduction potential of Fe(III)/Fe(II) is +0.771 V (Eq. 9). Thus, AA is able to reduce Fe(III) to produce Fe(II) theoretically [22-24]. In addition, Hsieh group reported that the reaction rate constant was found to be $1.464 \pm 0.44 \text{ mM}^{-0.811} \text{ min}^{-1}$ for 1:1 of AA/Fe(III) at pH 5.0 and room temperature [25].

To confirm this opinion, we mixed AA and Fe(III) in the water (AA/Fe(III)) and then monitored the concentration changes of Fe(III) and Fe(II) in the AA/Fe(III) system (Figure 2a). The Fe(III) concentration sharply decreased from 80 to 14.9 $\mu\text{mol/L}$ within 2 min, and then slightly decreased to 10 $\mu\text{mol/L}$ in the later 58 min. Simultaneously, the Fe(II) concentration increased from 0 to 65.1 $\mu\text{mol/L}$ in the first 2

min, and then kept at about 70 $\mu\text{mol/L}$ in the later reaction time. These results confirmed that Fe(III) could be reduced to Fe(II) by AA in the aqueous solution. Subsequently, we compared the change of iron species concentrations in the $\text{H}_2\text{SO}_4/\text{Fe@Fe}_2\text{O}_3$ and $\text{AA}/\text{Fe@Fe}_2\text{O}_3$ systems at the same initial pH value to check the reductive effect of AA on the surface Fe(III) of $\text{Fe@Fe}_2\text{O}_3$ (Figure 2b). Within 60 min, only 2.8 $\mu\text{mol/L}$ of Fe(III) was generated in the $\text{H}_2\text{SO}_4/\text{Fe@Fe}_2\text{O}_3$ system at pH 3.8, while the Fe(III) and Fe(II) concentrations in the $\text{AA}/\text{Fe@Fe}_2\text{O}_3$ system respectively increased to 65 and 3.1 $\mu\text{mol/L}$, further confirming the pronounced reductive effect of AA on the Fe(III)/Fe(II) cycle. This was because Fe(III) could coordinate with AA to form Fe(III)–AA complex both in solution or on the surface of iron based materials (Figure 2c). The electron transfer from AA to both surface and dissolved Fe(III) thus resulted in the effective Fe(III)/Fe(II) cycle [22, 24-28]. As expected, the reductive effect of AA also promoted the Fe(III)/Fe(II) cycle during the alachlor degradation in the $\text{AA}/\text{Fe@Fe}_2\text{O}_3/\text{H}_2\text{O}_2$ system. At the reaction time of 60 min, the dissolved Fe(II) concentration in the $\text{AA}/\text{Fe@Fe}_2\text{O}_3/\text{H}_2\text{O}_2$ system gradually increased to 38.6 $\mu\text{mol/L}$ (Figure 2d). This value was much higher than those values of the systems in the absence of AA (0.69 $\mu\text{mol/L}$) or in the absence of AA and H_2O_2 (0.086 $\mu\text{mol/L}$), confirming that the presence of AA could promote the generation of soluble Fe(II) in the $\text{AA}/\text{Fe@Fe}_2\text{O}_3/\text{H}_2\text{O}_2$ system. Meanwhile, the Fe(III) concentration first increased and then slightly decreased in the $\text{AA}/\text{Fe@Fe}_2\text{O}_3/\text{H}_2\text{O}_2$ system, accordingly the total iron ion concentration first increased and then kept steady (Figure S5 in the SM). The variation trend of iron species concentration

validated that the Fe(III)/Fe(II) cycle could be effectively realized in the AA/Fe@Fe₂O₃/H₂O₂ system owing to the reducibility of AA.

We subsequently compared the alachlor degradation efficiencies in the AA/Fe(II)/H₂O₂ and Fe(II)/H₂O₂ systems with initial ferrous ions concentration of 38.6 μ mol/L (Figure 3). In the Fe(II)/H₂O₂ system, 5% of alachlor was removed within 5 min and the concentration of alachlor did not change in the later 55 min. Interestingly, the addition of AA could increase the alachlor degradation percentage from 5% to 30% within 60 min, confirming that AA could promote the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system via accelerating the Fe(III)/Fe(II) cycle in soluble form. Regarding their same soluble ferrous ions concentration of 38.6 μ mol/L, the much higher alachlor removal efficiency (100%) of the AA/Fe@Fe₂O₃/H₂O₂ system than that (30%) of the AA/Fe(II)/H₂O₂ system in 50 min suggested the indispensable contribution of surface Fe(II) on Fe@Fe₂O₃ to the alachlor degradation, as revealed by the XPS analysis of the surface Fe(II) and Fe(III) of the freshly prepared and used Fe@Fe₂O₃ nanowires (Figure S6 in the SM). It was found that the value of Fe(II)/Fe_{total} increased from 0.421 for the freshly prepared Fe@Fe₂O₃ nanowires to 0.535 for the used ones (Table S1 in the SM), confirming that the surface Fe(II) content of Fe@Fe₂O₃ increased because of the promoted Fe(III)/Fe(II) cycle in the presence of AA. Therefore, we conclude the addition of AA can promote the Fe(III)/Fe(II) cycle in both soluble and surface bound forms. Interestingly, ascorbate free radical (AscH $\cdot$) [29-30] was detected in AA/Fe@Fe₂O₃/H₂O₂ system in the absence of DMPO (Figure S7 in the SM). As

AscH• was able to reduce Fe(III) to Fe(II) [26,31], it might also promote the Fe(III)/Fe(II) cycle in the AA/Fe@Fe₂O₃/H₂O₂ system.

To figure out the contribution of the iron core of Fe@Fe₂O₃ on the alachlor degradation, we prepared Fe₂O₃ nanoparticles (nano-Fe₂O₃) and compared the alachlor degradation in AA/Fe@Fe₂O₃/H₂O₂ and AA/nano-Fe₂O₃/H₂O₂ systems (Figure S8 in the SM). It was found that the degradation efficiency of alachlor in the AA/nano-Fe₂O₃/H₂O₂ system was about 60% that in the AA/Fe@Fe₂O₃/H₂O₂ system, revealing the major contribution of AA to the Fe(III)/Fe(II) cycle and the alachlor degradation.

Besides the Fe(III)/Fe(II) cycle, the decomposition of H₂O₂ is also crucial for the generation of •OH to oxidize organic pollutants during the Fenton process. We therefore monitored the concentration change of H₂O₂ in the AA/Fe@Fe₂O₃/H₂O₂ system (Figure S9 in the SM). It was interesting to found that the trend of the H₂O₂ concentration changed along with Fe(II) concentrations, illustrating that the complete decomposition of H₂O₂ was attributed to the steady supply of ferrous irons in the AA/Fe@Fe₂O₃/H₂O₂ system, accompanying with the generation of abundant •OH to degrade organic contaminants.

Apart from •OH, there might be other reactive oxygen species accounting for the alachlor degradation because of molecular oxygen activation induced by Fe@Fe₂O₃ nanowires [31-32]. Therefore, we investigated the contribution of different reactive oxygen species to the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system by adding *iso*-propanol (TBA) and superoxide dismutase (SOD) as the •OH and O₂•⁻

scavengers, respectively (Figure S10 in the SM). The addition of SOD did not affect the alachlor degradation, indicating the negligible contribution of $O_2^{\cdot-}$ to the alachlor degradation. The dramatic alachlor removal efficiency decrease induced by the addition of TBA suggested that $\cdot OH$ was the major reactive species for the alachlor degradation. We also studied the alachlor degradation under anaerobic conditions by bubbling ultrahigh pure argon gas through the solutions during the entire degradation and found that the alachlor degradation was independent of molecular oxygen. These results revealed that $\cdot OH$ was the major reactive oxygen species for the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system, and the $\cdot OH$ production was not from the dissolved oxygen in the solution.

Subsequently, the generation of $\cdot OH$ in the different systems was investigated with DMPO-trapped ESR spectra (Figure 4). The ESR signal of DMPO- $\cdot OH$ was split into four single lines of intensity ratio 1 : 2 : 2 : 1. Obviously, the steady-state concentration of $\cdot OH$ in the AA/Fe@Fe₂O₃/H₂O₂ system was much higher than that of the homogeneous Fenton systems (AA/Fe(II)/H₂O₂ and Fe(II)/H₂O₂), in good accordance with their alachlor degradation results. We subsequently evaluated the $\cdot OH$ generation rate ($V_{\cdot OH}$) in the AA/Fe@Fe₂O₃/H₂O₂ system by employing the oxidation of benzoic acid (BA) as the probe reaction according to the method reported by Voelker and his coworkers [10]. The reaction between BA and $\cdot OH$ obeyed the pseudo-first-order kinetics. The oxidation rate constant of BA in the AA/Fe@Fe₂O₃/H₂O₂ system was as high as $2.12 \times 10^{-2} \text{ s}^{-1}$ (Figure S11a in the SM), and therefore the $\cdot OH$ generation rate constant in this Fenton system was calculated to

be $6.82 \times 10^{-3} \text{ s}^{-1}$ (Figure S11b in the SM), which was 1 – 3 orders of magnitudes greater than those of heterogeneous Fenton systems developed with other iron-containing materials, such as α -FeOOH, α -Fe₂O₃, FeOCl, and so on (Table 2) [10, 11]. These comparison results further confirmed the superior ability of AA/Fe@Fe₂O₃ as a combined Fenton reagent.

The stability and reusability of Fe@Fe₂O₃ nanowires was thus investigated. The activity of Fe@Fe₂O₃ nanowires after six cycles of reaction was almost the same as that of the freshly prepared ones in the AA/Fe@Fe₂O₃/H₂O₂ system (Figure 5a), suggesting their remarkable durability. SEM analysis revealed that the wire like morphology could be well kept for the used Fe@Fe₂O₃ (Figure 5b). Meanwhile, XRD pattern of the used Fe@Fe₂O₃ nanowires could be ascribed to metallic iron phase (JCPDS file No. 85-1410), the same as that of the fresh ones (Figure S12 in the SM). These results revealed Fe@Fe₂O₃ nanowires were reusable for the Fenton oxidation of organic pollutants in the presence of AA.

On the basis of the above results, we could explain the high efficient alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system as follows. Owing to the reducibility of AA and the iron core of Fe@Fe₂O₃, the Fe(II)/Fe(III) cycle could be promoted both on the surface of Fe@Fe₂O₃ and in the solution, steadily supplying both soluble and surface bound Fe(II) to completely decompose H₂O₂ for the generation of abundant •OH. These •OH would oxidize and finally mineralize alachlor in the solution, as revealed by Scheme 1. Obviously, the presence of AA is crucial for the stability and reusability of Fe@Fe₂O₃ nanowires for the Fenton oxidation of alachlor.

Gas chromatograph-mass spectrometry analysis was further employed to investigate the degradation pathway of alachlor (Figure S13 in the SM). Among them, twelve intermediates were identified by comparing the obtained fragments in the mass spectra with the previous data reported in the literatures (Table S2 in the SM) [33-34]. These identified intermediates included the dealkylation products (Figure S14 in the SM). Moreover, IC analysis revealed the generation of NO_3^- and Cl^- during the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system (Figure 6a). The dechlorination and denitrification efficiencies were as high as 98% and 100% respectively, confirming the effective alachlor degradation and detoxification in the AA/Fe@Fe₂O₃/H₂O₂ system. Besides that, the mineralization of alachlor was measured by total organic carbon (TOC) analysis. Because AA was also an organic matter, we investigated the TOC change in the AA/Fe@Fe₂O₃/H₂O₂ system in presence or absence of alachlor. Obviously, the TOC changes in the AA/Fe@Fe₂O₃/H₂O₂ system in the absence of alachlor reflected the AA mineralization, and the differences of TOC in the AA/Fe@Fe₂O₃/H₂O₂ system in the presence or absence of alachlor could be regarded as the TOC removal of alachlor. The experiments were conducted in triplicate and averaged data and error range were presented. The initial TOC values of the AA/Fe@Fe₂O₃/H₂O₂ system in the presence or absence of alachlor were 84.7 and 72.1 mg/L, respectively. Therefore, the initial TOC value of alachlor was calculated to be 12.6 mg/L, consistent with the theoretical value (12.5 mg/L). As shown in the Figure 6b, 21.7% of alachlor and 31.2% of AA in the AA/Fe@Fe₂O₃/H₂O₂ system were mineralized in the first 1 h, but the TOC values

continued to decline over time. About 37.1% of alachlor and 44.8% of AA could be mineralized within 2 h, suggesting the simultaneous mineralization of alachlor and AA in the AA/Fe@Fe₂O₃/H₂O₂ system. On the basis of these results, we proposed a possible degradation mechanism of alachlor in the AA/Fe@Fe₂O₃/H₂O₂ system (Scheme 2).

The degradation of AA in the AA/Fe@Fe₂O₃/H₂O₂ system was also investigated. We first compared the concentration change of AA in the AA/Fe(III) and AA/Fe@Fe₂O₃/H₂O₂ systems and interestingly found AA was degraded more quickly in the AA/Fe@Fe₂O₃/H₂O₂ system than in the AA/Fe(III) system (Figure S15 in the SM), suggesting that AA could be oxidized by both Fe(III) and reactive oxygen species (ROS). Therefore, AA could be degraded along with alachlor in the AA/Fe@Fe₂O₃/H₂O₂ system, revealing the environmental friendliness of the AA/Fe@Fe₂O₃/H₂O₂ system. Liquid chromatograph-mass spectrometry analysis was then employed to investigate the intermediates of AA in the AA/Fe@Fe₂O₃/H₂O₂ system in the absence of alachlor. The identified intermediates included dehydroascorbic acid ($m/z = 173$), 2,3-diketogulonic acid ($m/z = 191$), 4,5,5,6-tetrahydroxy-2,3-diketoheptanoic acid ($m/z = 207$), threonic acid ($m/z = 135$), 3,4-dihydroxy-5-(hydroxymethyl)furan-2(5H)-one ($m/z = 145$), 3,4-dihydroxyfuran-2(5H)-one ($m/z = 115$), furan-2,3,4(5H)-trione ($m/z = 113$), and oxalic acid ($m/z = 89$) (Figure S16 in the SM). On the basis of these results, we also proposed a possible degradation pathway of AA (Figure S17 in the SM).

The performance of the combined heterogeneous Fenton reagent AA/Fe@Fe₂O₃

was also evaluated by degrading typical organic contaminants, including dyes (rhodamine B and methylene blue), herbicides (atrazine, and siduron), and antibiotics (lincomycin and chloroamphenicol) at pH 3.8. As shown in Figure 7 and Table 2, all the organic compounds could be quickly degraded within 60 min in the AA/Fe@Fe₂O₃/H₂O₂ Fenton system. In contrast, the degradation of these contaminants in the conventional homogeneous Fenton (Fe(II)/H₂O₂) system at pH 3.8 was not obvious. All the contaminant degradation processes were found to obey pseudo-first-order kinetics (Figure 7). Their degradation rate constants (k_{obs}) in the AA/Fe@Fe₂O₃/H₂O₂ system were between 0.106 – 0.238 min⁻¹, which were about 38 – 53 times higher than those in the Fe(II)/H₂O₂ system, suggesting that AA/Fe@Fe₂O₃ is a superior combined Fenton reagent.

4. Conclusions

Heterogeneous Fenton reaction is very promising for the wastewater treatment and the groundwater remediation. However, its ineffective Fe(III)/Fe(II) cycle lowers the yield of reactive oxygen species and thus restricts its application. It is of great environmental significance to design high efficient heterogeneous Fenton system with effective Fe(III)/Fe(II) cycle. Ascorbic acid, widely existing in most fruits and vegetables, is consider to be an important eco-friendly reductant and antioxidant. The pronounced Fe(III)/Fe(II) cycle promotion effect of ascorbic acid offers us to a new pathway to design high efficient heterogeneous Fenton systems for the wastewater treatment and the groundwater remediation. Meanwhile, the ubiquitous coexistence of ascorbic acid with iron containing minerals in natural aquatic environments suggests

that ascorbic acid might play indispensable roles in the transformation and mineralization of organic contaminants in the environment. More importantly, this study also reveals that the combination of ascorbic acid and Fe@Fe₂O₃ nanowires offers a highly efficient Fenton reagent for potential wastewater treatment.

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References

- [1] E. Brillas, I. Sires, M. A. Oturan, Electron-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, *Chem. Rev.* 109 (2009) 6570–6631.
- [2] F. Pardo, J. M. Rosas, A. Santos, A. Romero, Remediation of a biodiesel blend contaminated soil by using a modified Fenton process, *Environ Sci. Pollut. Res.* 21 (2014) 12198–12207.
- [3] R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten, B. Wehrli, The challenge of micropollutants in aquatic systems, *Science*

313 (2006) 1072–1077.

[4] P. Bautista, A. F. Mehedano, J. A. Casas, J. J. Rodriguez, An overview of the application of Fenton oxidation to industrial wastewaters treatment, *J. Chem. Technol. Biotechnol.* 83 (2008) 1323–1338.

[5] M. Trapido, N. Kulik, A. Goi, Y. Veressinina, R. Munter, Fenton treatment efficacy for the purification of different kinds of wastewater, *Water Sci. Technol.* 60 (2009) 1795–1801.

[6] A. Dulov, N. Dulova, M. Trapido, Combined physicochemical treatment of textile and mixed industrial wastewater, *Ozone Sci. Eng.* 33 (2011) 285–293.

[7] F. Haber, J. Weiss, The catalytic decomposition of hydrogen peroxide by iron salts, *Proc. R. Soc. London, A.* 147 (1934) 332–351.

[8] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.

[9] J. H. Ma, W. J. Song, C. C. Chen, W. H. Ma, J. C. Zhao, Y. L. Tang, Fenton degradation of organic compounds promoted by dyes under visible irradiation, *Environ. Sci. Technol.* 39 (2005) 5810–5815.

[10] W. P. Kwan, B. M. Voelker, Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems, *Environ. Sci. Technol.* 37 (2003) 1150–1158.

[11] X. J. Yang, X. M. Xu, J. Xu, Y. F. Han, Iron oxychloride (FeOCl): An efficient Fenton-Like catalyst for producing hydroxyl radicals in degradation of organic contaminants, *J. Am. Chem. Soc.* 135 (2013) 16058–16061

- [12] Z. H. Ai, L. R. Lu, J. P. Li, L. Z. Zhang, J. R. Qiu, M. H. Wu, Fe@Fe₂O₃ core-shell nanowires as iron reagent. 1. Efficient degradation of rhodamine B by a novel sono-Fenton process, *J. Phys. Chem. C* 111 (2007) 4087–4093.
- [13] Z. H. Ai, L. R. Lu, J. P. Li, L. Z. Zhang, J. R. Qiu, M. H. Wu, Fe@Fe₂O₃ core-shell nanowires as the iron reagent. 2. An efficient and reusable sono-Fenton system working at neutral pH, *J. Phys. Chem. C* 111 (2007) 7430–7436.
- [14] T. Luo, Z. H. Ai, L. Z. Zhang, Fe@Fe₂O₃ core-shell nanowires as iron reagent. 4. Sono-Fenton degradation of pentachlorophenol and the mechanism analysis, *J. Phys. Chem. C* 112 (2008) 8675–8681.
- [15] J. G. Shi, Z. H. Ai, L. Z. Zhang, Fe@Fe₂O₃ core-shell nanowires enhanced Fenton oxidation by accelerating the Fe(III)/Fe(II) cycles, *Water Res.* 59 (2014) 145–153.
- [16] L. R. Lu, Z. H. Ai, J. P. Li, Z. Zheng, Q. Li, L. Z. Zhang, Synthesis and characterization of Fe-Fe₂O₃ core-shell nanowires and nanonecklaces, *Cryst. Growth Des.* 7 (2007) 459–464.
- [17] L. Chen, X. Yang, J. Chen, J. Liu, H. Wu, H. Zhan, C. Liang, M. Wu, Continuous shape- and spectroscopy-tuning of hematite nanocrystals, *Inorg. Chem.* 49 (2010) 8411–8420.
- [18] Y. X. Qin, F. H. Song, Z. H. Ai, P. P. Zhang, L. Z. Zhang, Protocatechuic Acid Promoted Alachlor Degradation in Fe(III)/H₂O₂ Fenton System, *Environ. Sci. Technol.* 49 (2015) 7948–7956.
- [19] A. E. Harvey, J. A. Smart, E. S. Amis, Simultaneous spectrophotometric

determination of iron(ii) and total iron with 1,10-phenanthroline, *Anal. Chem.* 27 (1955) 26–29.

[20] A. L. Lazrus, G. L. Kok, S. N. Gitlin, J. A. Lind, S. E. McLaren, Automated fluorimetric method for hydrogen peroxide in atmospheric precipitation, *Anal. Chem.* 57 (1985) 917–922.

[21] D. M. Burman, H. G. Shertzer, A. P. Senft, T. P. Dalton, M. B. Genter, Antioxidant perturbations in the olfactory mucosa of alachlor-treated rats, *Biochem. Pharmacol.* 66 (2003) 1707–1715

[22] M. B. Davies, J. Austin, D. A. Partridge, *Vitamin C: Its Chemistry and Biochemistry*, Royal Society of Chemistry (1991).

[23] H. Borsook, G. Keighley, Oxidation-reduction potential of ascorbic acid (Vitamin C), *Proc. Natl. Acad. Sci.* 19 (1933) 875–879.

[24] Y. Deng, Effect of pH on the reductive dissolution rates of iron (III) hydroxide by ascorbate, *Langmuir* 13 (1997) 1835–1839.

[25] Y. H. P. Hsieh, Y. P. Hsieh, Kinetics of Fe(III) reduction by ascorbic acid in aqueous solutions, *J. Agric. Food Chem.* 48 (2000) 1569–1573.

[26] D. Suter, S. Banwart, W. Stumm, Dissolution of hydrous iron (III) oxides by reductive mechanisms, *Langmuir* 7 (1991) 809–813.

[27] S. Fukuchi, R. Nishimoto, M. Fukushima, Q. Zhu,. Effects of reducing agents on the degradation of 2, 4, 6-tribromophenol in a heterogeneous Fenton-like system with an iron-loaded natural zeolite. *Appl. Cataly. B: Environm.* 147 (2014) 411–419.

[28] J. Bolobajev, M. Trapido, A. Goi, Improvement in iron activation ability of

- alachlor Fenton-like oxidation by ascorbic acid. *Chem. Eng. J.* 281 (2015) 566–574.
- [29] G. R. Buettner, B. A. Jurkiewicz, Ascorbate free radical as a marker of oxidative stress: an EPR study. *Free. Radical. Bio. Med.* 14 (1993) 49–55.
- [30] M. K. Sharma, G. R. Buettner, Interaction of vitamin C and vitamin E during free radical stress in plasma: an ESR study. *Free. Radical. Bio. Med.* 14 (1993) 649–653.
- [31] Z. H. Ai, Z. T. Gao, L. Z. Zhang, W. W. He, J. J. Yin, Core-shell structure dependent reactivity of Fe@Fe₂O₃ nanowires on aerobic degradation of 4-chlorophenol, *Environ. Sci. Technol.* 47 (2013) 5344–5352.
- [32] L. Wang, M. H. Cao, Z. H. Ai, L. Z. Zhang, Dramatically Enhanced Aerobic Atrazine Degradation with Fe@Fe₂O₃ Core-shell Nanowires by Tetrapolyphosphate, *Environ. Sci. Technol.* 48 (2014) 3354–3362.
- [33] P. N. Moza, K. Hustert, S. Pal, P. Sukul, Photocatalytic decomposition of pendimethalin and alachlor, *Chemosphere* 25 (1992) 1675–1682.
- [34] X. J. Wei, Y. J. Feng, X. J. Sun, J. F. Liu, L. M. Zhu, Effectiveness and pathways of electrochemical degradation of pretilachlor herbicides, *J. Hazard. Mater.* 189 (2011) 84–91.

Figure Captions

Figure 1. (a) Time profiles of the alachlor degradation in different systems. (b) Plots of $-\ln(C/C_0)$ versus time for the degradation of alachlor. The initial concentrations of alachlor, AA and H_2O_2 were 7.4×10^{-5} , 1×10^{-3} and 1×10^{-3} mol/L, respectively; the dosage of Fe@Fe₂O₃ was 0.1 g/L; the initial pH was 3.8.

Figure 2. (a) Variation of Fe(III) and Fe(II) concentrations in the AA/Fe(III) system. The initial concentrations of AA and Fe(III) were 1.0×10^{-3} and 0.08×10^{-3} mol/L, respectively. (b) Variation of iron concentrations in the H_2SO_4 /Fe@Fe₂O₃ system and

AA/Fe@Fe₂O₃ system. (c) The proposed models for the coordination of Fe(III)-AA: (left) in solution; (right) on the surface of Fe@Fe₂O₃. (d) Variation of ferrous concentrations in different systems during the alachlor degradation. The initial pH was 3.8.

Figure 3. (a) Time profiles of the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂, AA/Fe(II)/H₂O₂, and Fe(II)/H₂O₂ systems. (b) Plots of $-\ln(C/C_0)$ versus time for the degradation of alachlor in different systems. Initial concentrations of alachlor, AA, H₂O₂ and Fe(II) were 7.4×10^{-5} , 1×10^{-3} , 1×10^{-3} , and 0.386×10^{-4} mol/L, respectively; the dosage of Fe@Fe₂O₃ was 0.1 g/L; the initial pH was 3.8.

Figure 4. Electron spin resonance (ESR) spectra of DMPO-OH adduct at 30 s in the AA/Fe@Fe₂O₃/H₂O₂ system (a), AA/Fe(II)/H₂O₂ system (b) and traditional homogeneous Fenton Fe(II)/H₂O₂ (c) system.

Figure 5. (a) Reusability of Fe@Fe₂O₃ for the degradation of alachlor at pH 3.8 – 4.5.

(b) SEM images of the fresh and used Fe@Fe₂O₃ nanowires.

Figure 6. (a) Concentration change of NO_3^- and Cl^- during the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system. (b) Time profiles of the variation of the TOC in the AA/Fe@Fe₂O₃/H₂O₂ system in the presence or absence of alachlor.

Figure 7. (a) Time profiles of the contaminants degradation in the AA/Fe@Fe₂O₃/H₂O₂ systems. (b) Plots of $-\ln(C/C_0)$ versus time for the degradation of the contaminants. The initial concentrations of the contaminants were shown in Table 2; the initial concentrations of AA and H₂O₂ were 7.4×10^{-5} , 1×10^{-3} and 1×10^{-3} mol/L, respectively; the dosage of Fe@Fe₂O₃ was 0.1 g/L; the initial pH was 3.8.

Scheme 1. Schematic illustration for the possible hydroxyl radical generation mechanism during the alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system.

Scheme 2. Possible alachlor degradation pathway in the AA/Fe@Fe₂O₃/H₂O₂ system.

Table 1. Comparison of $\bullet\text{OH}$ formation rates by the H_2O_2 decomposition over different reagents.

Material	$[\text{H}_2\text{O}_2]$ mmol/L	Dosage of Catalyst (g/L)	K_p [s^{-1}]	$K_{\bullet\text{OH}}$ [s^{-1}]	Reference
$\alpha\text{-Fe}_2\text{O}_3$	12.0	2.0	-	4.00×10^{-7}	10
$\alpha\text{-FeOOH}$	5.0	0.6	-	4.25×10^{-5}	10
$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$	-	-	-	2.00×10^{-5}	10
FeOCl	15.6	0.2	-	2.93×10^{-4}	11
AA/Fe@Fe ₂ O ₃	1.0	0.1	2.12×10^{-2}	6.82×10^{-3}	This study

Table 2. The degradation efficiencies of different organic contaminants by the AA/Fe@Fe₂O₃/H₂O₂ and Fe(II)/H₂O₂ systems.

Entry	Contaminants	Initial Conc. (ppm)	$k^{\text{a}}_{\text{obs}}$ (min^{-1})	$k^{\text{b}}_{\text{obs}}$ (min^{-1})
1	RhB	20	0.22	0.0056
2	Methylene Blue	20	0.24	0.0058
3	Atrazine	20	0.20	0.0037
4	Siduron	30	0.11	0.0024
5	Lincomycin	30	0.32	0.0079
6	Chloroamphenicol	30	0.19	0.0042

^aAA/Fe@Fe₂O₃/H₂O₂ system: the initial concentrations of AA and H₂O₂ were 1×10^{-3}

and 1×10^{-3} mol/L, respectively; the dosage of Fe@Fe₂O₃ was 0.1 g/L; the initial pH was 3.8. ^b Fe(II)/H₂O₂ system: the initial concentrations of H₂O₂ and Fe(II) were 1×10^{-3} and 5×10^{-5} mol/L; the initial pH was 3.8.