Humic acid coated Fe$_3$O$_4$ magnetic nanoparticles as highly efficient Fenton-like catalyst for complete mineralization of sulfathiazole

Hongyun Niu[a], Di Zhang[a,b], Shengxiao Zhang[a,c], Xiaole Zhang[a,d], Zhaofu Meng[b], Yaqi Cai[a,*]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] College of Science, Northwest A & F University, Yangling, Shaanxi 712100, China
[c] School of Chemistry and Materials Science, Ludong University, Yantai 264025, China
[d] College of Chemical Engineering and Biological Technology, Hebei Polytechnic University, Tangshan 063000, Hebei, China

ARTICLE INFO

ABSTRACT

Humic acid coated Fe$_3$O$_4$ magnetic nanoparticles (Fe$_3$O$_4$/HA) were prepared for the removal of sulfathiazole from aqueous media. Fe$_3$O$_4$/HA exhibited high activity to produce hydroxyl ($^\bullet$OH) radicals through catalytic decomposition of H$_2$O$_2$. The degradation of sulfathiazole was strongly temperature-dependent and favored in acidic solution. The catalytic rate was increased with Fe$_3$O$_4$/HA dosage and H$_2$O$_2$ concentration. When 3 g L^{-1} of Fe$_3$O$_4$/HA and 0.39 M of H$_2$O$_2$ were introduced to the aqueous solution, most sulfathiazole was degraded within 1 h, and >90% of total organic carbon (TOC) were removed in the reaction period (6 h). The major final products were identified as environmentally friendly ions or inorganic molecules (SO$_4^{2-}$, CO$_2$, and N$_2$). The corresponding degradation rate (k) of sulfathiazole and TOC was 0.034 and 0.0048 min^{-1}, respectively. However, when 3 g L^{-1} of bare Fe$_3$O$_4$ were used as catalyst, only 54% of TOC was eliminated, and SO$_4^{2-}$ was not detected within 6 h. The corresponding degradation rate for sulfathiazole and TOC was 0.01 and 0.0016 min^{-1}, respectively. The high catalytic ability of Fe$_3$O$_4$/HA may be caused by the electron transfer among the complexed Fe(II)-HA or Fe(III)-HA, leading to rapid regeneration of Fe(II) species and production of $^\bullet$OH radicals.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Sulfonamides are among the most widely used antimicrobials in human and veterinary medicine [1,2]. This kind of antimicrobials shows high resistance to biological degradation, and has been detected in wastewater, surface water, and groundwater samples. Their presence may cause DNA damage to bacteria or eukaryotic cells and lead to the potential development of antimicrobial resistance among microorganisms in aqueous environment [1–4]. However, elimination of the sulfonamides in some sewage treatments plants has been incomplete, for example, sulfamethoxazole is hardly biodegraded within 3 days in the presence of excess of N-containing compounds (such as ammonium) [4]. In recent years, various chemical oxidation processes have been investigated to degrade sulfa drugs from aquatic environment, including using free chlorine (HOCl/OCl$^-$) [5], potassium ferrate Fe(VI) or Fenton's reagent [6,7], and UV-TiO$_2$ [8,9]. Although these methods are effective, they suffer from shortcomings, e.g. incomplete removal, more

toxic byproducts, and the use of additional processes such as coagulation, sedimentation or filtration to eliminate the reagents [10].

Fe$_3$O$_4$ magnetic nanoparticles (MNPs) have attracted significant interest in many fields due to their advantages such as facile recovery and recycling [11,12]. Recently, the potential application of Fe$_3$O$_4$ MNPs in heterogeneous Fenton system has been investigated. Fe$_3$O$_4$ MNPs can decompose H$_2$O$_2$ to produce hydroxyl radicals which are robust oxidants to oxidize organic pollutants into CO$_2$ and H$_2$O [11–16]. Yan [15] and Cai [16] reported that phenol and aniline compounds were removed completely from aqueous media by Fe$_3$O$_4$ MNPs in the presence of H$_2$O$_2$. However, the H$_2$O$_2$-activating ability of Fe$_3$O$_4$ MNPs is generally not strong, and the utilization efficiency of H$_2$O$_2$ and catalytic degradation rate of target substances is low [11,12]. It is a great challenge to improve the catalytic performance of Fe$_3$O$_4$ MNPs. Wang et al. [11] applied sonochemical technology in the preparation of Fe$_3$O$_4$ MNPs to improve the inherent properties of the nanoparticles. As a result, the degradation rate of Rhodamine B catalyzed by the new Fe$_3$O$_4$ MNPs was 12.6-folds of that by Fe$_3$O$_4$ MNPs synthesized via a conventional reverse co-precipitation method. Shin et al. [12] immobilized poly(3,4-ethylene-dioxythiophene) on the surface of Fe$_3$O$_4$. The produced Fe$_3$O$_4$ MNPs with core–shell structure exhibited high catalytic performance for the degradation of Reactive Black 5 and Orange II. Wang and Shin suggested that the improve-

ment of catalytic activity of Fe_3O_4 was attributed to smaller particle size, larger BET surface area and higher dispersibility in aqueous solution.

Humic acid (HA), ubiquitous in soil and aquatic environment, can form complexes with iron and iron oxide through various types of carboxylate, phenolic, and carbonyl functional groups in HA molecule [17,18]. The role of HA on the degradation of organic compounds by Fenton or Fenton-like reactions has been explored [18–22]. The complexed HA may passivate the iron surface and therefore prevent electron transfer from iron to substances. On the other hand, HA may act as an electron-transfer mediator in the chemical degradation of organic pollutants. Both the inhibitive [18,19] and promoting effect [20,21] of HA on degradation of organic pollutants on the iron or iron oxide (such as goethite) surface have been reported. However, there is no report about the mineralization of organic compounds on Fe_3O_4 MNPs surface in the presence of HA by far. In this study, HA coated Fe_3O_4 MNPs (Fe_3O_4/HA) is prepared and used to remove sulfathiazole from water. Compared with Fe_3O_4 MNPs, Fe_3O_4/HA can catalyze H_2O_2 efficiently to produce hydroxyl radicals to mineralize most sulfathiazole within 6 h.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent grade or better and used without further purification. Hydrogen peroxide (30%) and ammonium hydroxide (25%) were obtained from Beijing Chemicals Corporation (Beijing, China). Ferric chloride ($FeCl_3 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 4H_2O$) were purchased from Tianjin Jinke Chemical Reagent Corporation (Tianjin, China). Humic acid sodium salts (lignite, technical, 50–60% as humic acid), carboxymethyl cellulose (sodium salt), polyethylene glycol, and polyacrylic acid were supplied by Acros Organics (Morris Plains, NJ). The 5-tertiary butyl-formyl-5-methyl-1-pyrroline-oxynitride (BMPO) was used as spin-trapping agent and kindly donated by Institute of Chemistry, Chinese Academy of Sciences. Sulfathiazole (98%) were supplied by Tokyo Kasei Kogyo Corporation (Tokyo, Japan), and the stock solutions for sulfathiazole compounds ($1000\,mg\,L^{-1}$) were prepared by dissolving suitable amount solid reagents with deionized water. HPLC-grade methanol and acetonitrile were obtained from Fisher Scientific Corporation (Fair Lawn, NJ). Ultrapure water was prepared in the lab using a Milli-Q SP reagent water system from Millipore (Milford, MA, USA).

2.2. Preparation and characterization of catalysts

Fe_3O_4/HA was prepared by the chemical coprecipitation method [18]. Briefly, $FeCl_2 \cdot 4H_2O$ (2 g) and $FeCl_3 \cdot 6H_2O$ (5.2 g) were dissolved into 100 mL deoxygenated water at 90 °C under vigorous stirring and N_2 protection. Then 10 mL of ammonium hydroxide (25%) and 50 mL of $2\,mg\,mL^{-1}$ HA were added rapidly and sequentially into the reaction solution. The mixture was aged for 30 min at 90 °C, and then cooled to room temperature with ice water. The obtained magnetic nanoparticles were separated from solution by a powerful magnet and washed with 50 mL water three times. The particles were heated for 1 h at 330 °C in the Muffle Furnace under the N_2 protection to remove the water-soluble HA [23]. Finally the products were dispersed into 100 mL deoxygenated water to get $20\,mg\,mL^{-1}$ of Fe_3O_4/HA. The Fe_3O_4 MNPs and Fe_3O_4 coated with carboxymethyl cellulose (Fe_3O_4/CMC), polyethylene glycol (Fe_3O_4/PEG) and polyacrylic acid (Fe_3O_4/PAA) was prepared with similar method.

The morphology and size distribution of Fe_3O_4/HA, Fe_3O_4 MNPs, Fe_3O_4/CMC, Fe_3O_4/PEG, and Fe_3O_4/PAA were studied by using a transmission electron microscope (TEM) of H-7500 (Hitachi, Japan) working at 80 kV accelerated voltage. The crystal phase was investigated by a Rigaku Dmax-RB X-ray diffraction (XRD) system. Fourier transform infrared (FTIR) spectra were taken in KBr pressed pellets on a NEXUS 670 FT-IR Spectrometer (Nicolet Thermo, USA). The specific surface areas of catalysts were determined by the BET method with N_2 gas (ASAP2000V3.01A; Micromeritics, Norcross, GA).

2.3. Experimental procedures

Batch experiment was carried out in 250-mL lined, capped glass bottles at 40 °C. The tests were initiated by turning on an end-over-end rotator at 250 rpm immediately after the additions of reactants into the bottles. The initial concentration of target substance was $50\,mg\,L^{-1}$, and the total volume of reaction solution was 100 mL. A series of batch experiments were conducted to evaluate the effect of Fe_3O_4/HA amount ($0–5\,g\,L^{-1}$) and H_2O_2 concentration (0–0.8 M) on sulfathiazole degradation. The dependence of sulfathiazole elimination on solution pH was investigated by adjusting pH from 3.5 to 9.0 with the addition of HCl or NaOH. The reaction solutions were not buffered against pH change to prevent any potential interference. The effect of temperature (25–60 °C) on sulfathiazole oxidation was tested at pH 3.5 in the presence of $3\,g\,L^{-1}$ Fe_3O_4/HA and 0.58 M H_2O_2. At the given time interval, suitable volume of reaction solutions were sampled, and the liquid phase was separated by using an external magnetic field immediately, and then centrifuged at 10,000 rpm for 5 min to remove the residual Fe_3O_4/HA. The supernatant was subjected to the measurement of sulfathiazole, SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, $CH_3NH_4^+$, and total organic carbon (TOC).

2.4. Analysis

Sulfathiazole was analyzed by using Dionex SUMMIT® HPLC system (Dionex, Sunyvale, CA) with a PDA-100 photodiode array detector. The analytical column was Dikma C_{18} column (5 μm, 4.6 mm × 150 mm). The mobile phase was composed of acetonitrile/water (75:25) containing 0.05% acetic acid. The wavelength was set at 260 nm, and the flow rate was $1.0\,mL\,min^{-1}$.

TOC was analyzed in TOC/TN analyzer (liquic TOC II) (Elementar Corporation, Germany) with Mill-Q water and 0.8% HCl as the mobile phase. The possible intermediate ions of sulfathiazole (SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, $CH_3NH_4^+$ and so on) were quantified by ion chromatography on a Dionex ICS-2000 system equipped with a conductivity detector. The analytical column for anions was IonPac AS19 anion-exchange column (4 × 250 mm, 7.5 mm) and the mobile phase was 36 mM KOH at a flow rate of $1.0\,mL\,min^{-1}$. The separation of cations was conducted on IonPac CS12A cation-exchange column (4 × 250 mm, 7.5 mm), and the mobile phase was 20 mM methanesulfonic acid (MSA) at a flow rate of $1.0\,mL\,min^{-1}$. The samples were centrifuged, filtered through 0.2 μm nylon membrane, and pretreated with RP column to remove organic compounds in reaction solution before the measurement of ions. The leached Fe ions were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer).

The reactive $^\bullet OH$ radicals were identified by the electron spin resonance (ESR) technology, which was obtained on a JEOL JES-FA200 with a microwave bridge (receiver gain, 1×10^5; modulation amplitude, 2 gauss; microwave power, 0.998 mW; modulation frequency, 100 kHz). One hundred microlitre of samples were collected from the reaction solution (Fe_3O_4/HA-H_2O_2 system and Fe_3O_4–H_2O_2 system) after being reacted for 5 min, and immedi-

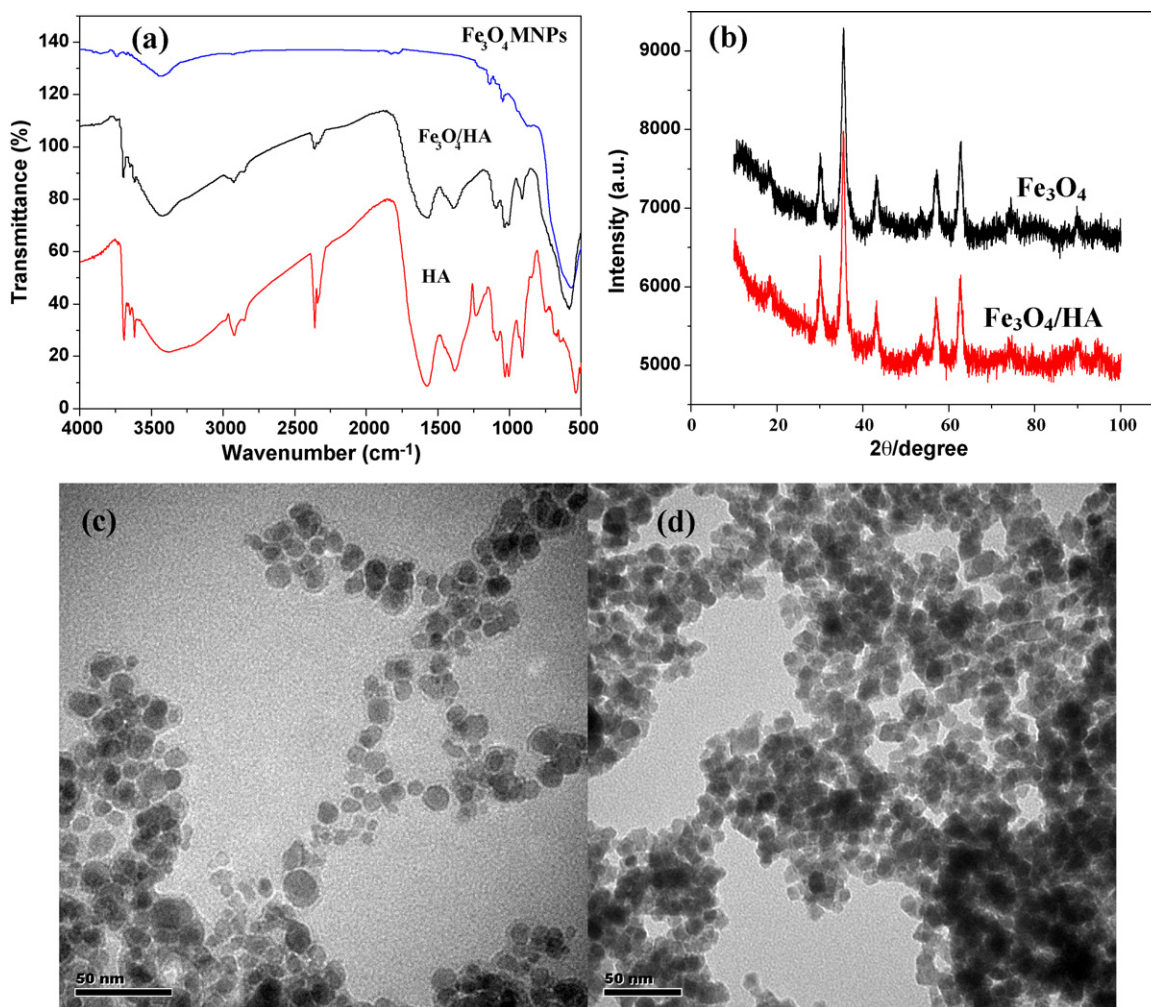**Fig. 1.** FTIR spectra (a) and X-ray powder diffraction pattern (b) of Fe_3O_4/HA and Fe_3O_4 MNPs; TEM image of Fe_3O_4/HA (c) and Fe_3O_4 MNPs (d).

ately mixed with 20 μL 0.2 mol L^{-1} BMPO to form BMPO-radicals adduct.

3. Results and discussion

3.1. Characterization of Fe_3O_4/HA

The surface chemistry of Fe_3O_4/HA and Fe_3O_4 MNPs was studied using FTIR spectrum. In Fig. 1a, the broad peaks centered at 574 cm^{-1} were ascribed to the stretching vibrations of Fe–O bond in the spectra of Fe_3O_4 and Fe_3O_4/HA. In the spectrum of pure HA, the peeks at ∼1600 cm^{-1} and 1400 cm^{-1}, ∼2920 and 2860 cm^{-1} were attributed to the stretching vibrations of –COO groups and –CH$_2$, –CH$_3$ species, respectively [24]. These peaks could also be observed in the spectrum of Fe_3O_4/HA, indicating the successful modification of HA on Fe_3O_4 surface. The XRD patterns of Fe_3O_4/HA and Fe_3O_4 MNPs are shown in Fig. 1b. The two materials had similar diffraction peaks at $2\theta = 30.2°$, 35.6°, 42.3°, 53.6°, 57.1° and 62.6°, which could be indexed to a cubic-phase of Fe_3O_4 [16]. This result indicated that the crystal structure of Fe_3O_4 MNPs was not changed after modification with HA. The surface areas for Fe_3O_4 and Fe_3O_4/HA were 127 and 109 m^2 g^{-1}, respectively. The TEM images demonstrated that Fe_3O_4/HA were quasi-spherical in shape, and had nearly uniform distribution of particle size (10–12 nm) (Fig. 1c). However, the Fe_3O_4 MNPs had no uniform size, and exhibited a high degree of aggregation (Fig. 1d).

3.2. Effect of Fe_3O_4/HA dosage and H_2O_2 concentration

In Fig. 2a, only 7% of sulfathiazole was removed with Fe_3O_4/HA alone in the absence of H_2O_2 within 6 h. The H_2O_2 had no reactivity without the presence of Fe_3O_4/HA (Fig. 2b). Similar phenomena also existed in the Fe_3O_4–H_2O_2 system. These observations ruled out the possibility of the remarkable complexation-mediated aggregation between sulfathiazole and Fe_3O_4/HA or Fe_3O_4 under the experimental condition.

Sulfathiazole was rapidly oxidized as soon as H_2O_2 was introduced into the reaction solution containing Fe_3O_4/HA and sulfathiazole. The removal efficiency of sulfathiazole at $t = 0$ min were generally enhanced with Fe_3O_4/HA dosage and H_2O_2 concentration and higher than 20% as H_2O_2 concentration was up to 0.10 M (Fig. 2). Under the tested conditions, sulfathiazole degradation approximately followed the pseudo-first-order kinetics, which may be expressed as $\ln(c_t/c_0) = kt + y$, where y is a constant, t is reaction time (min), k is the apparent rate constant (min^{-1}), and c_0 and c_t are sulfathiazole concentrations (mmol L^{-1}) at time of $t = 0$ and $t = t$, respectively [11,18]. With the dosage of Fe_3O_4/HA fixed at 3 g L^{-1} at pH 3.5, the degradation rate (k) of sulfathiazole was increased from 0.0014 to 0.0579 min^{-1} as the concentration of H_2O_2 ranged from 0.002 to 0.8 M (Fig. 2a and Table S1). Complete disappearance of sulfathiazole occurred in 240 min when the concentration of H_2O_2 was higher than 0.2 M. As the concentration of H_2O_2 was fixed at 0.39 M at pH 3.5, k value increased from 0.0073 to 0.0603 min^{-1} with the increase of Fe_3O_4/HA dosage from
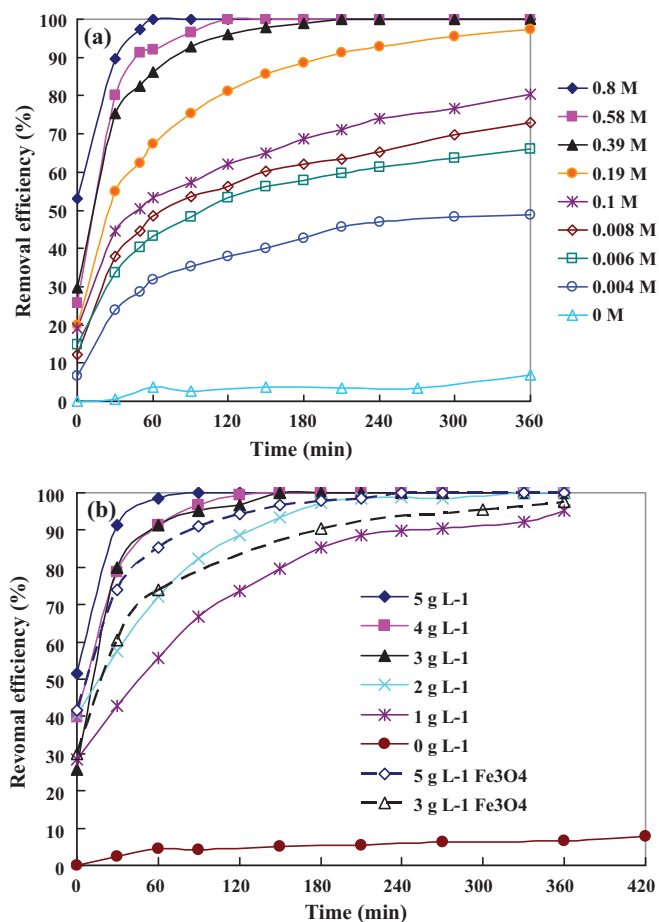
Fig. 2. Effect of H_2O_2 concentration (a) and Fe_3O_4/HA dosage (b) on the degradation of sulfathiazole in Fe_3O_4/HA-H_2O_2 system. $C_o = 50$ mg L^{-1}, pH = 3.5, $T = 40\,^{\circ}$C, (a) Fe_3O_4/HA = 3 g L^{-1}; (b) $H_2O_2 = 0.39$ mol L^{-1}.

1 to 5 g L^{-1} (Table S1). When the dosage of Fe_3O_4/HA was up to 3 g L^{-1}, 90% of sulfathiazole was removed within 60 min and total elimination was observed in 240 min. If the bare Fe_3O_4 MNPs were used as catalyst, however, at least 5 g L^{-1} of Fe_3O_4 were required to ultimately remove sulfathiazole within 240 min ($k = 0.0272$ min^{-1}) (Fig. 2b).

3.3. Effect of pH and temperature

The influence of pH on the degradation of sulfathiazole was explored by adjusting the solution pH to 3.5, 5.5, 7.0, and 9.0. Fig. 3 describes the disappearance of sulfathiazole at different pH levels in the presence of 3 g L^{-1} of Fe_3O_4/HA and 0.39 M H_2O_2. The sulfathiazole removal efficiency decreased with increasing pH, and the corresponding k value at pH 3.5, 5.5, 7.0, and 9.0 was 0.0341, 0.0169, 0.0069 and 0.004 min^{-1}, respectively. Though the degradation rate of sulfathiazole was low at neutral and alkali solution, more than 95% and 84% of sulfathiazole was removed at pH 7.0 and pH 9.0 at the end of the reaction period, respectively. When 3 g L^{-1} Fe_3O_4 and 0.39 M H_2O_2 were utilized to remove sulfathiazole, the k values for target compound degradation at pH 3.5 and 5.5 were 0.01 and 0.0035 min^{-1}, respectively, which implied that the degradation rate of sulfathiazole catalyzed by Fe_3O_4/HA at pH $\geq$ 7.0 was comparable or superior to that by Fe_3O_4 at pH 5.5. These observations suggested that sulfathiazole degradation could be conducted in a wide range of pH value in Fe_3O_4/HA-H_2O_2 system.

Degradation kinetics of sulfathiazole was also investigated at different temperatures (25, 30, 35, 40, 50 and 60 $^{\circ}$C, respectively).
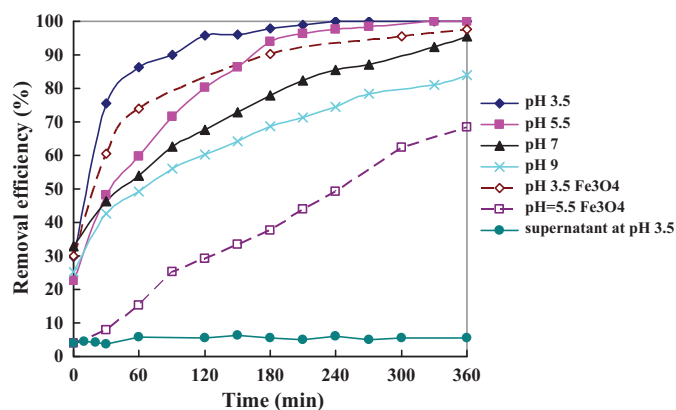

Fig. 3. Effect of solution pH on the disappearance of sulfathiazole in Fe_3O_4/HA-H_2O_2 and Fe_3O_4-H_2O_2 systems. $C_o = 50$ mg L^{-1}, $T = 40\,^{\circ}$C; $H_2O_2 = 0.39$ mol L^{-1}; dosage of catalyst = 3 g L^{-1}.

The k value was increased with the enhancement of temperature from 25 to 60 $^{\circ}$C ($k = 0.0061$, 0.0145, 0.0241, 0.0341, 0.0641 and 0.0777 min^{-1}, respectively) (Fig. 4), which was in agreement with the studies by Gao et al. [13].

3.4. Stability and reusability of Fe_3O_4/HA

Liu et al. [17] observed that Fe_3O_4 can be eroded after suspending Fe_3O_4/HA in 0.001 M HCl solution, though the immobilized HA could improve the stability of Fe_3O_4 in acid solution. In the present study, Fe_3O_4/HA (3 g L^{-1}) were immersed in acid solution (pH 3.5) for 6 h, then the supernatant was collected and analyzed with ICP-AES and TOC/TN analyzer to detect the leached Fe ions and HA, respectively. The concentration of Fe ions and HA was less than 0.1 mg L^{-1} and 5 mg L^{-1} (as TOC), respectively. Since the leached Fe^{2+}/Fe^{3+} ions in solution can catalyze the breakdown of H_2O_2 and lead to degradation of sulfathiazole, the supernatant was also used to oxidize sulfathiazole by adding H_2O_2. Sulfathiazole was hardly degraded in this solution (Fig. 3), thus the H_2O_2-activation effect was primarily attributed to the catalyst but not the dissolved iron ions and HA.

Wu et al. [25,20] reported that HA could be degraded in the presence of Fenton reagent. So we studied the stability of Fe_3O_4/HA in the Fenton runs by determining the concentration of leached Fe ions and HA (as TOC) in reaction solution (pH 3.5) containing 3 mg L^{-1} Fe_3O_4/HA and 0.39 M H_2O_2 without sulfathiazole. The concentration of iron ions and HA in reaction solution were also lower than 0.1 mg L^{-1} and 5 mg L^{-1}, respectively within the reac-
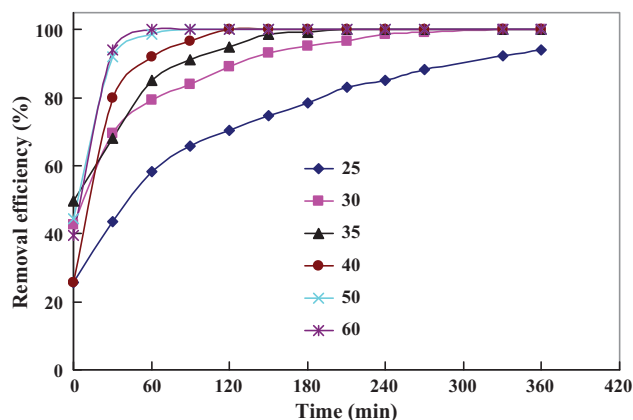

Fig. 4. Effect of temperature on the degradation of sulfathiazole in Fe_3O_4/HA-H_2O_2 system. $C_o = 50$ mg L^{-1}, pH = 3.5; Fe_3O_4/HA = 3 g L^{-1}, $H_2O_2 = 0.58$ mol L^{-1}.
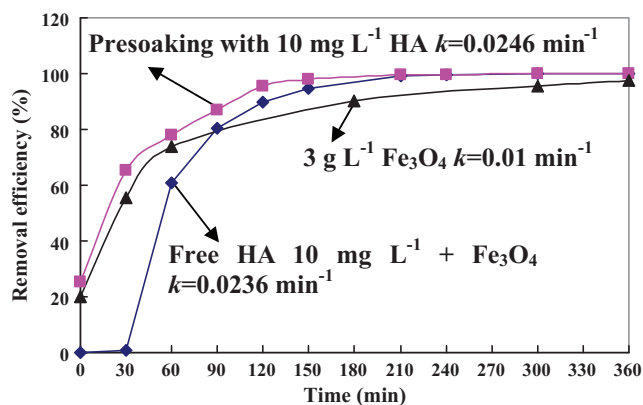
Fig. 5. Degradation of sulfathiazole in the presence of Fe_3O_4 ($3 \, g \, L^{-1}$) and $10 \, mg \, L^{-1}$ of free HA or Fe_3O_4 ($3 \, g \, L^{-1}$) presoaked with $10 \, mg \, L^{-1}$ of HA.

tion period (6 h) (Fig. S1). The excellent stability of Fe_3O_4/HA in the presence of H_2O_2 may result from the complexation of HA with Fe_3O_4 surface. The reusability of the catalyst was also evaluated. After each reaction, Fe_3O_4/HA was separated from reaction solution with a powerful magnet, and the separated Fe_3O_4/HA was reused in the next Fenton process without any treatment. The results showed that after three times of recycle, all the sulfathiazole was removed from solution in 6 h (Fig. S2), suggesting that the reused MNPs still remained good activity. These studies implied perfect stability of Fe_3O_4/HA in Fenton runs.

3.5. The importance of HA immobilization on Fe_3O_4 MNPs

The nature organic substance (such as HA and fulvic acid) in solution is reported to enhance the oxidation of organic compounds through Fenton reaction (zerovalent iron as catalyst) [20]. To check whether modification of HA improve the ability of HA to enhance the performance of Fe_3O_4 MNPs, experiments were conducted with $3 \, g \, L^{-1}$ Fe_3O_4 and $0.39 \, M$ H_2O_2 in the presence of free HA ($10 \, mg \, L^{-1}$, average concentration of HA in natural water) at pH 3.5. Sulfathiazole was not degraded in the first 30 min, but rapid oxidation happened in the next 30 min, and complete disappearance of sulfathiazole was observed after reaction for 6 h (Fig. 5). If Fe_3O_4 were presoaked in reaction solution with $10 \, mg \, L^{-1}$ HA for 5 h, 25% of target compound was degraded as soon as H_2O_2 was added. However, the two systems possessed similar degradation constant value ($k = 0.0236$ and $0.0246 \, min^{-1}$, respectively), and the catalytic efficiencies were higher than that of $3 \, g \, L^{-1}$ Fe_3O_4–$0.39 \, M$ H_2O_2 system ($k = 0.01 \, min^{-1}$). It could be inferred that the increased degradation of sulfathiazole in the former system was resulted from the gradual bonding of HA on Fe_3O_4 surface. Thus it was the complexed-HA on Fe_3O_4 surface that played an important role on the improved catalytic activity of Fe_3O_4. This study also indicated that HA was readily adsorbed on Fe_3O_4 MNPs surface, but the pretreatment of Fe_3O_4 in HA solution at 90 °C to form HA coat was necessary to maintain the stability of HA and enhance the performance of Fe_3O_4 catalyst in Fenton runs.

3.6. Mineralization of sulfathiazole

The mineralization of sulfathiazole was evaluated by determining the concentration of TOC and the possible inorganic products such as SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, and so on. TOC from decomposition of sulfathiazole was calculated by subtracting the referenced TOC in blank Fenton runs from the total TOC in Fenton process. In Fig. 6a, the initial value of TOC for reference was $4 \, mg \, L^{-1}$. About 28% of TOC from sulfathiazole decomposition were removed at ini-

tial time ($t = 0 \, h$) in Fe_3O_4/HA-H_2O_2 system. The relatively high TOC removal efficiency at $t = 0 \, h$ is consistent with the corresponding high degradation efficiency of sulfathiazole at 0 h of reaction time. After reaction for 6 h, 90% of TOC was removed and the rate constant was $k = 0.0048 \, min^{-1}$. The remaining 10% of TOC should result from traces of refractory organic acids such as oxalic acid from sulfathiazole decomposition. The concentration of SO_4^{2-} increased fast with time, and almost all the sulfur element in the molecule of sulfathiazole was transformed to SO_4^{2-} after 6 h of reaction (Fig. 6b). However, the possible intermediate products of nitrogen (NO_3^-, NO_2^-, NH_4^+, $CH_3NH_4^+$, or $(CH_3)_2NH_4^+$) were not found in the process of reaction. Deiber et al. [26] and Takahashi et al. [27] reported that Mn/Ce catalyst or precious metals (Pd, Pt, Ru, Rh, etc.) deposited on ceramic could transform organic nitrogen to N-NH_3 and then oxidized the initially produced NH_3 to molecular nitrogen in wet air oxidation process. Thereby, we inferred that the nitrogen element in sulfathiazole molecule was converted to molecular nitrogen, which was harmless to the environment. To detect the possible binding of degradation by-products to the catalyst through HA-coupling and ionic interactions, the IR spectra of Fe_3O_4/HA after reaction for 2 h and 6 h in Fenton runs were determined. The results showed that the used Fe_3O_4/HA possessed similar IR spectra with that of the as-prepared Fe_3O_4/HA, indicating that the degradation by-products remained mainly in solution (Fig. S3). Therefore, TOC removal was caused by Fenton oxidation with Fe_3O_4/HA catalyst but not through binding with the catalyst. In general, the organic sulfathiazole was mostly oxidized to inorganic substance, such as CO_2, sulfate and N_2 in the system of Fe_3O_4/HA and H_2O_2. In a comparison study, only 54% of TOC was degraded ($k = 0.0016 \, min^{-1}$), and nearly no sulfate element was transformed to SO_2^{4-} after reaction for 6 h when $3 \, g \, L^{-1}$ of bare Fe_3O_4 were used as catalyst (Fig. 6a and b).

3.7. Plausible mechanism

To investigate the effect of particle dispersibility in solution, the hydrodynamic size of Fe_3O_4 and Fe_3O_4/HA was determined with laser particle size analyzer. The average size of Fe_3O_4 MNPs and Fe_3O_4/HA was 4.4 and 2.8 μm, respectively, demonstrating that the aggregation of catalyst with HA coat in solution was still remarkable. Thus, we proposed that the high catalytic ability of Fe_3O_4/HA was not mainly resulted from the increased dispersibility in solution. In a comparison study, Fe_3O_4 coating with PEG, PAA, and CMC were also prepared. The TEM images of Fe_3O_4/CMC, Fe_3O_4/PEG, and Fe_3O_4/PAA were shown in Fig S4. The particle size of these materials followed the order of Fe_3O_4/PAA (less than 8 nm) < $Fe_3O_4 \approx Fe_3O_4$/CMC (8–10 nm) < Fe_3O_4/HA $\approx Fe_3O_4$/PEG (10–12 nm). The specific surface areas and average hydrodynamic size for Fe_3O_4/PEG, Fe_3O_4/CMC, and Fe_3O_4/PAA was $93.1 \, m^2 \, g^{-1}$, 4.1 μm; $96.8 \, m^2 \, g^{-1}$, 60 μm; and $114 \, m^2 \, g^{-1}$, 12 μm, respectively. The degradation rate constant of sulfathiazole catalyzed by Fe_3O_4/PEG, Fe_3O_4/CMC, and Fe_3O_4/PAA ($3 \, g \, L^{-1}$) was 0.0015, 0.0038 and $0.006 \, min^{-1}$, respectively, which was much lower than that obtained with Fe_3O_4. The reduced catalytic rate of these surface-modified Fe_3O_4 was probably caused by the fact that the surface coat obstructed the contact of target substance with the active site of the inner catalyst. Therefore, the surface properties and chemical compositions of Fe_3O_4 MNPs were very important to adsorb H_2O_2 in the Fenton-like catalysis for degradation the organic pollutants.

It has been confirmed that Fe_3O_4 MNPs can catalyze the breakdown of H_2O_2 and generate reactive oxygen species (ROS), such as $\bullet OH$, and perhydroxyl ($O_2^-\bullet/HO_2\bullet$) radicals [11–16]. ESR is used to identify these radicals by addition of the spin-trapping agent BMPO. In Fig. 7a, the fourfold characteristic peak with an intensity ratio of 1:2:2:1 is shown in the ESR spectra of Fe_3O_4 and Fe_3O_4/HA
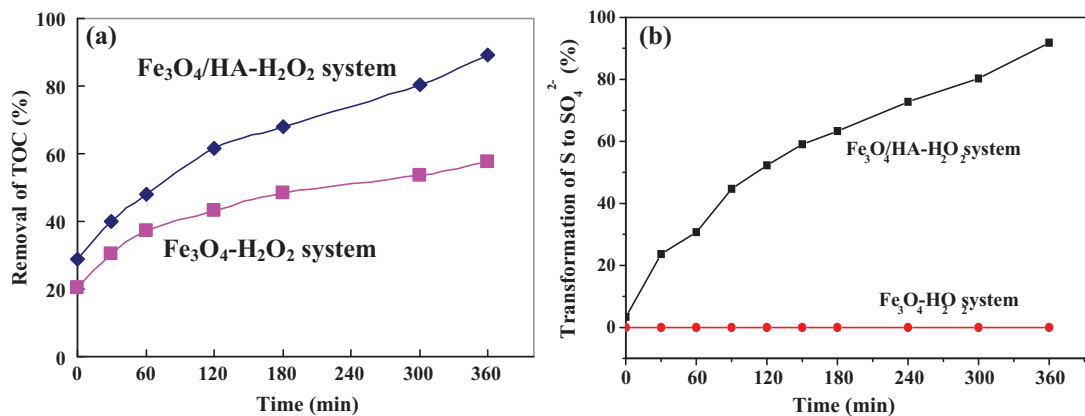
Fig. 6. Time evolution of the TOC (a) and SO_4^{2-} (b) during the process of sulfathiazole degradation in the system of Fe_3O_4/HA-H_2O_2 and Fe_3O_4–H_2O_2.

systems, which is consistent with the pattern of the typical BMPO-OH• adduct. The intensity of BMPO-OH• signal in Fe_3O_4/HA-H_2O_2 system was about three times of that in Fe_3O_4–H_2O_2 system. This ratio value was close to the ratio of sulfathiazole degradation rate between Fe_3O_4/HA-H_2O_2 and Fe_3O_4–H_2O_2 systems (3.4 times). After the addition of sulfathiazole, the intensity of BMPO-OH signal in Fe_3O_4/HA-H_2O_2 system decreased by 50%. These results indicated that the OH radicals were mainly responsible for the oxidation of sulfathiazole. To further confirm the existence of hydroxyl radicals, two strong hydroxyl radical scavengers PO_4/HPO_4/H_2PO_4 and tert-butanol [28,29] were added into the reaction solution, respectively. In the PO_4/HPO_4/H_2PO_4 buffer solution (pH 3.5) or with the addition of 2.5 mM of tert-butanol (five times of sulfathiazole concentration), the conversion of target compound catalyzed by Fe_3O_4/HA-H_2O_2 was only inhibited by 10–15% (Fig. 7b). The
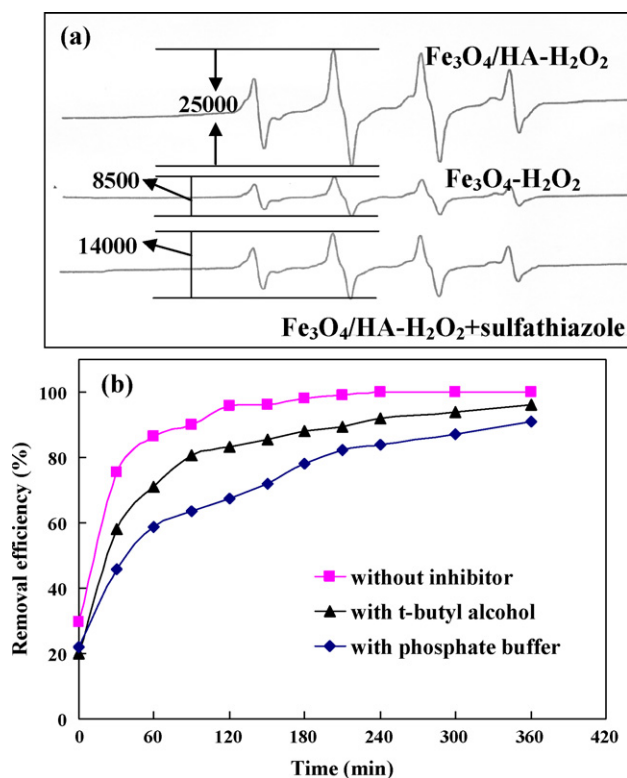

Fig. 7. BMPO spin-trapping ESR spectra of •OH in the system of Fe_3O_4/HA-H_2O_2 and Fe_3O_4–H_2O_2 during the degradation of sulfathiazole (a) and effect of radical inhibitors in Fe_3O_4/HA-H_2O_2 system (b).

low inhibitory effect of tert-butanol in Fenton-like reaction was also reported by Wang et al. [11] and Cai [16] with Fe_3O_4 MNPs as catalyst.

In Fenton (Fe^{2+}/H_2O_2) process, the generation of hydroxyl radicals and degradation of the contaminant were described in Eqs. (1) and (2), respectively:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{1}$$

$${}^\bullet OH + P \rightarrow intermediates \tag{2}$$

According to Eq. (1), Fe^{2+} was oxidized to Fe^{3+} and then regenerated through the reduction of Fe^{3+} by H_2O_2 (Eq. (3))

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot HO_2 + H^+ \tag{3}$$
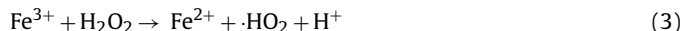
However, the reaction rate of Eq. (3) was much slower than that of Eq. (1), Fe^{2+} was quickly consumed, but slowly regenerated. The Fenton reaction slowed down due to the low concentration of Fe^{2+} [30]. The Fe^{2+} on Fe_3O_4 surface was reported to also be responsible for the initiation of Fenton-like reaction [13,31]. Therefore, the rapid generation of Fe^{2+} would accelerate the consumption of H_2O_2 and degradation of sulfathiazole. Scott et al. [32] suggested that iron would be strongly complexed within the structure of HA (as Fe(III) species), and the complexed Fe(III) could be rapidly reduced by HA. Strucyk and Sposito [33] found that an oxidant such as I_2 would preferentially transfer an electron from HA-complexed Fe(II), the resulting Fe(III) complex then being reduced by a HA semiquinone. Xie and Shang [18] determined the ESR spectra of Fe(III)-humic acid complexes and found that most Fe(III) was bound to phenolic and/or carboxylic groups at octahedral sites with little or no axial distortion from the cubic symmetry ligand field, where Fe(III) had been reported to be easily reduced. The ratio of Fe(III)/Fe(II) on the surface of Fe_3O_4 was about 2, so there were sufficient Fe(III)-HA complexes to regenerate Fe(II) to maintain Fe_3O_4 surface activation. On the other hand, NOM-Fe^{2+} was reported to have a higher reduction potential than aqueous-complexed ones (E(Fe(III)-NOM/Fe(II)-NOM = −0.2–0.3 V_{NHE} vs E^0 (Fe^{3+}/Fe^{2+}) = 0.77 V_{NHE})) [20]. Then the Fe(II)-HA complex would react more rapidly with H_2O_2 than Fe(II), which also contributed to the fast degradation rate of target substances and high-yield of •OH in the system of Fe_3O_4/HA-H_2O_2.

4. Conclusions

Humic acid coated Fe_3O_4 magnetic nanoparticles (Fe_3O_4/HA) were highly efficient to decompose H_2O_2 to produce large amount of hydroxyl radicals. In the presence of these radicals, high concentration of organic pollutant sulfathiazole could be mineralized to environmentally friendly ions or inorganic molecules (SO_4^{2-},

CO_2, and N_2) within 6 h. The degradation rate of sulfathiazole in Fe_3O_4/HA-H_2O_2 system was 3.4 times of that in Fe_3O_4–H_2O_2 system. The enhancement of catalytic performance of Fe_3O_4/HA had limited relationship with the particle size, surface area and dispersibility in water. It might result from the electron transfer among the complexed Fe(II)-HA or Fe(III)-HA, which led to the rapid regeneration of Fe(II) species and production $^{\bullet}$OH radicals. Hydroxyl radical scavengers (PO_4/HPO_4/H_2PO_4 and tert-butanol) exhibited low inhibitory effect on sulfathiazole degradation catalyzed by Fe_3O_4/HA-H_2O_2 system. The release of HA and Fe species to water was generally negligible under the reaction conditions. The studied system showed potential for the development of advanced oxidation processes based on a heterogeneous Fenton-like system with the aid of HA.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.086.

References

[1] A.K. Sarmah, M.T. Meyer, A.B.A. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere 65 (2006) 725–759.

[2] Y Kim, K. Choi, J. Jung, S. Park, P.G. Kim, J. Park, Aquatic toxicity of acetaminophen, carbamazepine, cimetidine, diltiazem and six major sulfonamides, and their potential ecological risks in Korea, Environ. Int. 33 (2007) 370–375.

[3] E.R. Campagnolo, K.R. Johnson, A. Karpati, C.S. Rubin, D.W. Kolpin, M.T. Meyer, J.E. Esteban, R.W. Currier, Antimicrobial residues in animal waste and water resources proximal to large-scale swine and poultry feeding operations, Sci. Total Environ. 299 (2002) 89–95.

[4] P. Drillia, S.N. Dokianakis, M.S. Fountoulakis, M. Kornaros, K. Stamatelatou, G. Lyberatos, On the occasional biodegradation of pharmaceuticals in the activated sludge process: the example of the antibiotic sulfamethoxazole, J. Hazard. Mater. 122 (2005) 259–265.

[5] M.C. Dodd, C.H. Huang, Transformation of the antibacterial agent sulfamethoxazole in reactions with chlorine: kinetics, mechanisms, and pathways, Environ. Sci. Technol. 38 (2004) 5607–5615.

[6] V.K. Sharma, S.K. Mishra, N. Nesnas, Oxidation of sulfonamide antimicrobials by Ferrate(VI)[FeVIO$_4^{2-}$]$^+$, Environ. Sci. Technol. 40 (2006) 7222–7227.

[7] W.W. Ben, Z.M. Qiang, X. Pan, M.X. Chen, Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent, Water Res. 43 (2009) 4392–4402.

[8] L.H. Hu, P.M. Flanders, P.L. Miller, T.J. Strathmanna, Oxidation of sulfamethoxazole and related antimicrobial agents by TiO$_2$ photocatalysis, Water Res. 41 (2007) 2612–2626.

[9] W. Baran, E. Adamek, A. Sobczak, A. Makowski, Photocatalytic degradation of sulfa drugs with TiO$_2$, Fe salts and TiO$_2$/FeCl$_3$ in aquatic environment—kinetics and degradation pathway, Appl. Catal. B: Environ. 90 (2009) 516–525.

[10] G. Zelmanov, R. Semiat, Iron(3) oxide-based nanoparticles as catalysts in advanced organic aqueous oxidation, Water Res. 42 (2008) 492–498.

[11] N. Wang, L.H. Zhu, D.L. Wang, M.Q. Wang, Z.F. Lin, H.Q. Tang, Sono-assisted preparation of highly-efficient peroxidase-like Fe$_3$O$_4$ magnetic nanoparticles for catalytic removal of organic pollutants with H$_2$O$_2$, Ultrason. Sonochem. 17 (2010) 526–533.

[12] S. Shin, H. Yoon, J. Jang, Polymer-encapsulated iron oxide nanoparticles as highly efficient Fenton catalysts, Catal. Commun. 10 (2008) 178–182.

[13] L.Z. Gao, J. Zhuang, L. Nie, J.B. Zhang, Y. Zhang, N. Gu, T.H. Wang, J. Feng, D.L. Yang, S. Perrett, X.Y. Yan, Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, Nat. Nanotechnol. 2 (2007) 577–583.

[14] H. Wei, E.K. Wang, Fe$_3$O$_4$ magnetic nanoparticles as peroxidase mimetics and their applications in H$_2$O$_2$ and glucose detection, Anal. Chem. 80 (2008) 2250–2254.

[15] J.B. Zhang, J. Zhuang, L.Z. Gao, Y. Zhang, N. Gu, J. Feng, D.L. Yang, J.D. Zhu, X.Y. Yan, Decomposing phenol by the hidden talent of ferromagnetic nanoparticles, Chemosphere 73 (2008) 1524–1528.

[16] S.X. Zhang, X.L. Zhao, H.Y. Niu, Y.L. Shi, Y.Q. Cai, G.B. Jiang, Superparamagnetic Fe$_3$O$_4$ nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds, J. Hazard. Mater. 167 (2009) 560–566.

[17] J.F. Liu, Z.S. Zhao, G.B. Jiang, Coating Fe$_3$O$_4$ magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water, Environ. Sci. Technol. 42 (2008) 6949–6954.

[18] L. Xie, C. Shang, Role of humic acid and quinine model compounds in bromate reduction by zerovalent iron, Environ. Sci. Technol. 39 (2005) 1092–1100.

[19] D. Colón, E.J. Weber, J.L. Anderson, Effect of natural organic matter on the reduction of nitroaromatics by Fe(II) species, Environ. Sci. Technol. 42 (2008) 6538–6543.

[20] S.H. Kang, W. Choi, Oxidative degradation of organic compounds using zerovalent iron in the presence of natural organic matter serving as an electron shuttle, Environ. Sci. Technol. 43 (2009) 878–883.

[21] A.L. Rose, T.D. Waite, Effect of dissolved natural organic matter on the kinetics of ferrous iron oxygenation in seawater, Environ. Sci. Technol. 37 (2003) 4877–4886.

[22] A. Georgi, A. Schierz, U. Trommler, C.P. Horwitz, T.J. Collins, F.-D. Kopinke, Humic acid modified Fenton reagent for enhancement of the working pH range, Appl. Catal. B: Environ. 72 (2007) 26–36.

[23] T. Weber, T. Allard, E. Tipping, M.F. Benedetti, Modeling iron binding to organic matter, Environ. Sci. Technol. 40 (2006) 7488–7493.

[24] H.B. Fu, Q. Xie, C. Shou, H.M. Zhao, Y.Z. Zhao, Interaction of humic substances and hematite: FTIR study, J. Environ. Sci. -China 17 (2005) 43–47.

[25] Y.Y. Wu, S.Q. Zhou, F.H. Qin, K. Zheng, X.Y. Ye, Modeling the oxidation kinetics of Fenton's process on the degradation of humic acid, J. Hazard. Mater. 179 (2010) 533–539.

[26] G. Deiber, J.N. Foussard, H. Debellefontaine, Removal of nitrogenous compounds by catalytic wet air oxidation kinetic study, Environ. Pollut. 96 (1997) 311–319.

[27] Y. Takahashi, K. Nitta, H. Ohya, M. Oguchi, The applicability of catalytic wet oxidation to CELSS, Adv. Space Res. 7 (1987) 81–84.

[28] G. Zelmanov, R. Semiat, Phenol oxidation kinetics in water solution using iron(3)-oxide-based nano-catalysts, Water Res. 42 (2008) 3848–3856.

[29] S.T. Xing, C. Hu, J.H. Qu, H. He, M. Yang, Characterization and reactivity of MnOx supported on mesoporous zirconia for herbicide 2 4-D mineralization with ozone, Environ. Sci. Technol. 42 (2008) 3363–3368.

[30] Y.X. Du, M.H. Zhou, L.C. Lei, Role of the intermediates in the degradation of phenolic compounds by Fenton-like process, J. Hazard. Mater. B 136 (2006) 859–865.

[31] R.C.C. Costa, M.F.F. Lelis, L.C.A. Oliveira, J.D. Fabris, J.D. Ardisson, R.R.V.A. Rios, C.N. Silva, R.M. Lago, Novel active heterogenous Fenton system based on Fe$_{3-x}$M$_x$O$_4$ (Fe, Co, Mn, Ni): the role of M^{2+} species on the reactivity towards H$_2$O$_2$ reaction, J. Hazard. Mater. B 129 (2006) 171–178.

[32] D.T. Scott, D.M. McKnight, E.L. Blunt-Harris, S.E. Kolesar, D.R. Lovley, Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms, Environ. Sci. Technol. 32 (1998) 2984–2989.

[33] Z. Struyk, G. Sposito, Redox properties of standard humic acids, Geoderma 102 (2001) 329–346.