Superparamagnetic Fe₃O₄ nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds

Shengxiao Zhang, Xiaoli Zhao, Hongyun Niu, Yali Shi, Yaqi Cai*, Guibin Jiang

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

ABSTRACT

Fe₃O₄ magnetic nanoparticles (MNPs) with diameters about 10 nm were synthesized successfully and used to remove phenol and aniline from aqueous solution. The results showed that phenol and aniline could be eliminated easily from solution under acidic and neutral conditions in the presence of MNPs and H_2O_2. When the concentrations of Fe₃O₄ MNPs and H_2O_2 were 5 g L^{-1} and 1.2 M, respectively, phenol and aniline could be removed completely after 6 h of reaction at 308 K, and the total organic carbon (TOC) abatement efficiency for phenol and aniline were 42.79% and 40.38%. Some intermediates such as formic acid, acetic acid, fumaric acid and hydroquinone were detected during reaction. Fe₃O₄ MNPs exhibited good stability and reusability, also showed excellent catalysis ability to eliminate some substituted phenolic and aniline compounds from solution. Fe₃O₄ MNPs had good superparamagnetism and was readily separated from solution by applying an external magnetic field. Finally we proposed that phenol and aniline might be degraded by the hydroxyl free radicals (·OH) released from H_2O_2 in the presence of Fe₃O₄ MNPs as catalysts.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Many factories, such as coal conversion, petroleum refining, iron and steel, textiles, dyes, resins, plastics and agrochemicals, discharge wastewater containing phenolic or aniline compounds [1,2]. These compounds are harmful to human health, and suspected to be carcinogens. Many techniques including physical adsorption [3–8], electrochemical oxidation [9–11], biodegradation [12–14], catalytic wet oxidation [15–17], and Fenton reagent oxidation [18–20] have been adopted for the removal of phenolic and aniline pollutants. Though practicable and effective these methods are, they also have some drawbacks, such as high cost, incomplete removal, more toxic byproducts than original pollutants.

In recent years enzymes have been widely studied to remove phenolic and aniline compounds [21–25]. Horseradish peroxidase (HRP) and laccases are proved to be effective to eliminate phenols, biphenols, anilines by catalyzing oxidation in the present of H_2O_2 to form phenol- or aniline-derived oligomers [26]. In order to reduce the cost, enhance the stability, catalytic activity and reusability of enzyme, immobilization of enzyme on various natural or synthetic supports has been introduced to remove phenol and aniline [27–29]. Gao et al. have found that the Fe₃O₄ magnetic nanoparticles (MNPs) can catalyze the reactions of the substrate 3,3,5,5-tetramethlbenzidine (TMB), di-azo-aminobenzene (DAB) and o-phenylenediamine (OPD) in the presence of H_2O_2, correspondingly, the colors of their solutions change into blue, brown and orange respectively, indicating that the Fe₃O₄ MNPs have peroxidase-like activity towards typical peroxidase substrates [30]. Based on the peroxidase-like activity of Fe₃O₄ MNPs, Wei et al. have established an easy-to-make analytical approach to determine H_2O_2 and glucose concentration through the colorimetric method [31]. Since peroxidase has the ability to catalyze the oxidation of organic substrates, Fe₃O₄ MNPs, as a kind of peroxidase mimetic substance, may have the potential to be used in wastewater treatment.

Heterogeneous Fenton-like systems, consisting of catalysts and hydrogen peroxide, are effective for the degradation of organic compounds [32,33]. Han et al. have proved that Au/hydroxyapatite (Au/HAp) catalyst exhibits high activity and great potential for the complete oxidation of organic pollutants in aqueous media by peroxidation. They have proposed that a redox process Au(0) ↔ Au(&+) likely takes place during the wet peroxidation to produce hydroxyl (·OH) and perhydroxyl radicals (·HO₂) through catalytic decomposition of H_2O_2. The hydroxyl radicals are robust oxidants to oxidize organic substances into H_2O and CO_2 [34]. Zelmanov et al. have used Iron (3+) oxide-based nanoparticles as catalysts in advanced organic aqueous oxidation and gained high efficiency in the oxidation of ethylene glycol and phenol [35].

* Corresponding author. Chinese Academy of Sciences, Research Center for Eco-Environmental Sciences, P. O. Box 2871, Beijing 100085, China. Tel.: +86 10 62849239; fax: +86 10 62849182.

E-mail address: caiyaqi@rcees.ac.cn (Y. Cai).

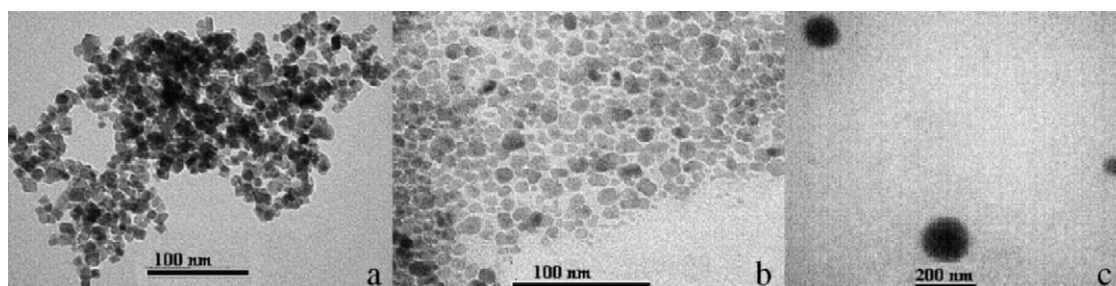**Fig. 1.** TEM image of Fe$_3$O$_4$ MNPs before (a) and after (b, c) reaction with phenol.

Peroxidase activity of Fe$_3$O$_4$ nanoparticles combined with its unique characteristic, such as easy preparation, high stability and convenient separation from solution by external magnetic field, provides a promising method to remove phenolic and aniline compounds from wastewater. The objective of our research is to degrade and mineralize organic pollutants in aqueous solution using the catalytic property of iron oxide nanoparticles. Fe$_3$O$_4$ MNPs were synthesized and used to degrade phenol and aniline in solution. The effects of Fe$_3$O$_4$ MNPs and H$_2$O$_2$ concentration, pH and temperature on the removal efficiency and total organic carbon (TOC) abatement efficiency of phenol and aniline were investigated. In addition, the stability, reusability of Fe$_3$O$_4$ MNPs and its potential to degrade some substituted phenolic and aniline compounds were also evaluated. Finally, the possible pathway for the degradation of phenol was discussed.

2. Experimental

2.1. Chemicals and materials

All reagents used in the experiment were of analytical reagent grade and used without further purification. 30% (w/w) hydrogen peroxide, phenol, *o*-chlorophenol, *p*-chlorophenol, aniline, 2-toluidine, *m*-toluidine and *p*-toluidine were obtained from Beijing Chemicals Corporation (Beijing, China). The stock solutions for phenolic and aniline compounds (10 mM) were prepared by dissolving suitable amount solid reagents in deionized water. Ferric chloride (FeCl$_3$·6H$_2$O) and ferrous chloride (FeCl$_2$·4H$_2$O) were purchased from Tianjin Jinke Chemical Reagent Corporation (Tianjin, China). HPLC-grade methanol and acetonitrile were obtained from Fisher Scientific Corporation (Fair Lawn, NJ, USA). Ultrapure water was prepared by using Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Preparation and characterization of Fe$_3$O$_4$ MNPs

Fe$_3$O$_4$ MNPs were prepared by the chemical coprecipitation method. FeCl$_2$·4H$_2$O (2 g) and FeCl$_3$·6H$_2$O (5.2 g) were dissolved into 25 mL deoxygenated water followed by adding 0.85 mL of concentrated hydrochloric acid. The resulting solution was dropped into 250 mL of 1.5 M NaOH solution under vigorous stirring and N$_2$ protection at 353 K. The obtained magnetic nanoparticles were separated from solution by a powerful magnet and rinsed with 50 mL deoxygenated water for two times. Finally the products were dispersed into 55 mL deoxygenated water to get 40 mg mL^{-1} suspension of Fe$_3$O$_4$ MNPs.

The morphology and size distribution of Fe$_3$O$_4$ MNPs were studied by using a transmission electron microscope (TEM) of H-7500 (Hitachi, Japan) operating at 80 kV accelerated voltage. Magnetic property of Fe$_3$O$_4$ MNPs was analyzed using a vibrating sample magnetometer (VSM, LDJ9600). The crystal phase was investigated by a Rigaku Dmax-RB X-ray diffraction (XRD) system.

2.3. Catalytic reaction experiment procedure

Batch tests were carried out in NaH$_2$PO$_4$–Na$_2$HPO$_4$ buffer solution. Fe$_3$O$_4$ MNPs and phenol or aniline solution were added into the buffer solution in sequence, the final solution volumes were 20 mL. The suspensions were vibrated at a speed of 200 rpm at 308 K. The reaction was initiated with the addition of H$_2$O$_2$, and 0.5 mL H$_2$O$_2$ were added every 5 min until to the preconcerted concentration. After 6 h of reaction MNPs were separated by applying an external magnetic field. The supernatants were filtered through 0.22 μm nylon membranes.

The concentrations of phenol and aniline compounds in supernatants were analyzed by using DIONEX Ultimate 3000 high-performance liquid chromatography (HPLC) equipped with Ultimate 3000 variable wavelength UV detector. An acclaim 120 C$_{16}$ column (5 μm, 120 Å; 4.6 mm × 150 mm) was used as separation column. Samples were injected into a 20 μL loop, and mobile phase for phenolic and aniline compounds were water–acetonitrile (25:75) and water–methanol (30:70), respectively, with a flow rate of 1 mL min^{-1}. The wavelengths were set at 270 nm for phenolic compounds and 280 nm for aniline compounds.

### 2.4. Degradation intermediates and TOC

The degradation intermediates of phenol were also determined with HPLC via a method previously described with slight modification [33,36,37]. The chromatographic conditions were as follows: acclaim 120 C$_{16}$ column (5 μm, 120 Å; 4.6 mm × 150 mm); samples were injected into a 20 μL loop; mobile phase was methanol–water containing 5% H$_3$PO$_4$ (10:90) with a flow rate of 1 mL min^{-1}. UV detector wavelength was set at 215 nm.

A Shimadzu TOC-5000 Total Organic Carbon Analyzer was used to test TOC of supernatant after reaction. Total carbon (TC) and inorganic carbon (IC) were determined using the standard curve. TOC value was calculated by subtracting IC from TC value.

3. Results and discussion

3.1. Characterization of Fe$_3$O$_4$ MNPs

Fig. 1 showed the TEM images of Fe$_3$O$_4$ MNPs before and after use in catalytic degradation of phenol. It could be seen in Fig. 1(a) that Fe$_3$O$_4$ MNPs before use were quasi-spherical in shape, and had nearly uniform distribution of particle size with an average diameter of about 10 nm. After use, there was no great change in particle size for most Fe$_3$O$_4$ MNPs as shown in Fig. 1(b). But a few Fe$_3$O$_4$ MNPs with diameters much larger than 10 nm were also observed as shown in Fig. 1(c). The same phenomenon was observed as Fe$_3$O$_4$ MNPs were used for aniline removal. The change of particle size suggested that a small part of Fe$_3$O$_4$ MNPs agglomerated during the reaction process, which might cause the decrease of particle amount and surface area, and lead to the decrease of catalytic activity.
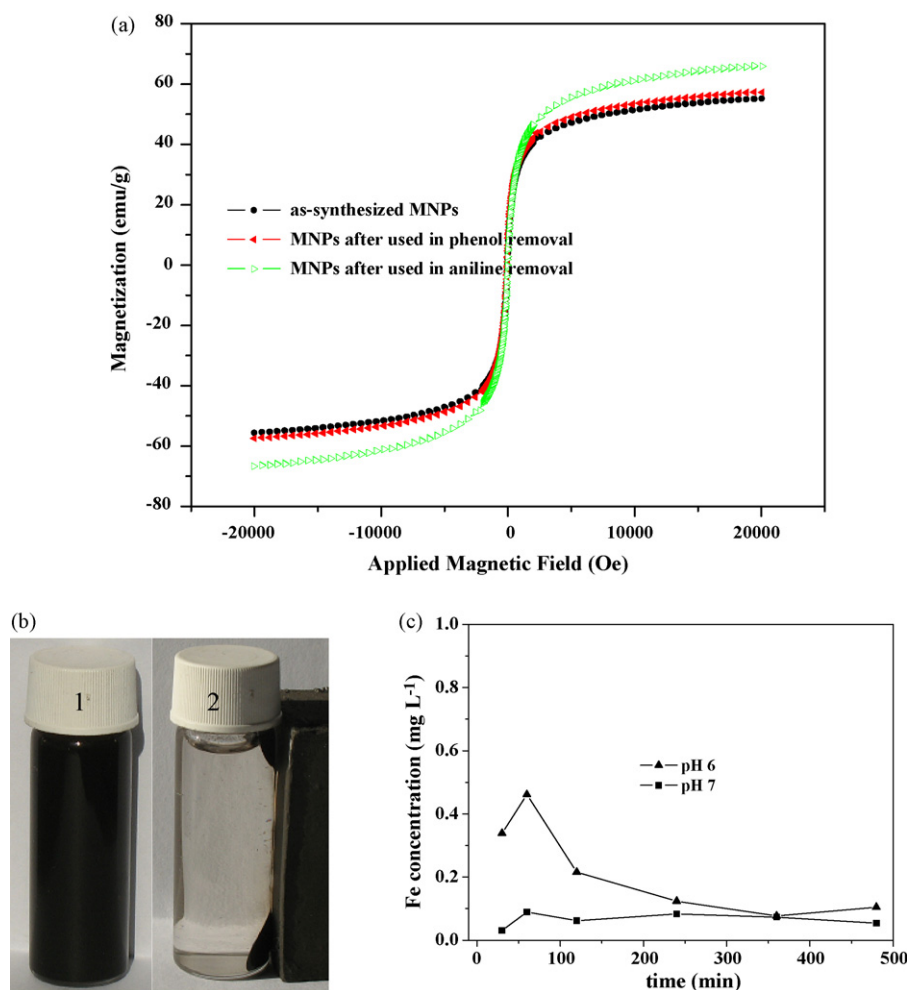
Fig. 2. VSM magnetization curves of as-synthesized Fe$_3$O$_4$ MNPs and Fe$_3$O$_4$ MNPs after reaction with phenol and aniline (a), reaction solution of phenol removal at pH 6 (b 1), reaction solution put in a magnetic field for 2 min (b 2), and iron concentration in the supernatants of reaction solution at pH 6 and pH 7 with reaction time (c).

The hysteresis loops of MNPs were investigated to check for their superparamagnetic behavior. Fig. 2(a) showed that there was no hysteresis in the hysteresis loop, and remanence and coercivity were zero, illustrating that MNPs were superparamagnetic. The maximal saturation magnetization of as-prepared MNPs, MNPs after use in catalytic degradation of phenol and aniline were 55.41, 57.28 and 66.19 emu g^{-1}, respectively. For saturation magnetization of 16.3 emu g^{-1} is enough for magnetic separation from solution with a magnet [38], the large saturation magnetization made MNPs easily separated from solution by applying an external magnetic field. Fig. 2(b) showed that when the reaction solution was placed adjacent to a magnet it became limpid within a few seconds. To test the leaching of iron from magnetic nanoparticles into aqueous solution during reaction process, the supernatants of reaction solutions both at pH 6 and pH 7 were acidized with nitric acid, and iron concentrations were investigated using ICP-MS. As can be seen from Fig. 2(c) the iron concentrations leaching into the reaction solutions at pH 7 were always below 0.1 mg L^{-1} with reaction time increasing from 0.5 h to 8 h. At pH 6 the maximum iron concentrations was 0.46 mg L^{-1} when contact time is 1 h, and with time increasing the iron concentrations decrease until below 0.1 mg L^{-1} at 6 h. The iron concentrations leaching into solutions are below the maximum acceptable drinking water concentration for iron (0.3 mg L^{-1}) set by the World Health Organization [39], so leaching of iron in this system might not cause metal pollution in the water.

The crystal phase of MNPs was investigated by XRD. The results showed (date not shown) that there was no obvious difference between as-prepared MNPs and MNPs after use in catalytic degradation of phenol. Their patterns were found to match well with that of cubic crystalline bulk magnetite.

3.2. Effect of Fe$_3$O$_4$ MNPs and H$_2$O$_2$ concentration

As shown in Fig. 3, with the increase of MNPs concentration, the removal efficiency of phenol and aniline increased slowly, and TOC abatement efficiency also increased. When the concentration of MNPs reached to 5 g L^{-1}, phenol and aniline could be removed completely, but only about 35% TOC was abated.

In the treatment of water containing phenol and aniline with HRP, the highest proportion of the cost is from the enzyme. In order to reduce the treatment cost, some techniques, for example, addition of polyethylene glycol (PEG) to avoid inactivation of enzyme, immobilization HRP on certain support, had been used to reduce the amount of enzyme required. Compared with HRP, MNPs could be easily prepared, hardly inactivated, and endure badly ambient environment conditions. Gao et al. found that MNPs required a H$_2$O$_2$ concentration two orders of magnitude higher than HRP to reach the maximal level of peroxidase activity [30]. This phenomenon was confirmed in our study. Fig. 4 showed that the removal efficiency of phenol and aniline increased rapidly with the addition of H$_2$O$_2$, and slowed down gradually as the H$_2$O$_2$ concentration was higher
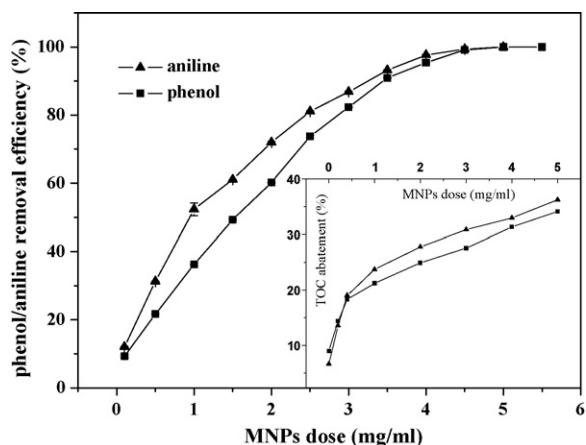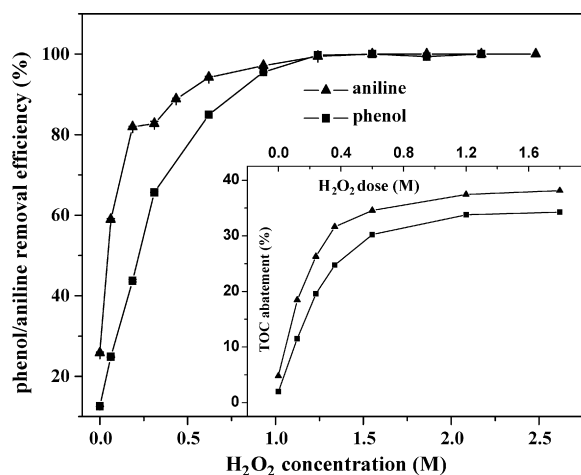
Fig. 3. Effect of MNPs concentration on removal efficiency and TOC abatement efficiency of phenol and aniline. Control: [phenol/aniline]$_0$ = 1 mM; [H$_2$O$_2$] = 1.2 M; pH = 6–7; temperature = 308 K; reaction time = 6 h. Error bars represent the range of 2 independent experiments.

than 0.5 M. The slowing down of the reaction rate may be caused by the decrease of reactant concentration. When the concentration of H$_2$O$_2$ was in the range of 1.0–1.5 M, complete removal of phenol and aniline was gained. The TOC abatement efficiency showed similar trend, but it was lower than phenol/aniline removal efficiency.

3.3. Effect of pH

In batch experiments the effect of pH on removal efficiency of phenol and aniline was also examined in series of buffer solution (pH = 3–6: Na$_2$HPO$_4$–citric acid buffer; pH = 6–8: Na$_2$HPO$_4$–NaH$_2$PO$_4$ buffer; pH = 9–11: Na$_2$CO$_3$–NaHCO$_3$ buffer). It was shown in Fig. 5 that most of the phenol and aniline were removed under acidic and neutral conditions, and the removal efficiency was low at alkaline conditions. The TOC abatement efficiency was about 35% under acidic and neutral conditions, and when pH above 7, the TOC abatement decreased sharply until to about 5% at pH 11. This might be caused by two reasons: Firstly, H$_2$O$_2$ is not stable in alkaline solution [40], and can be decomposed immediately to produce H$_2$O and O$_2$ as shown in Eq. (1):

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{1}$$

Fig. 4. Effect of H$_2$O$_2$ concentration on removal efficiency and TOC abatement efficiency of phenol and aniline. Control: [phenol/aniline]$_0$ = 1 mM; [MNPs] = 5 g/L; pH = 6–7; temperature = 308 K; reaction time = 6 h. Error bars represent the range of 2 independent experiments.
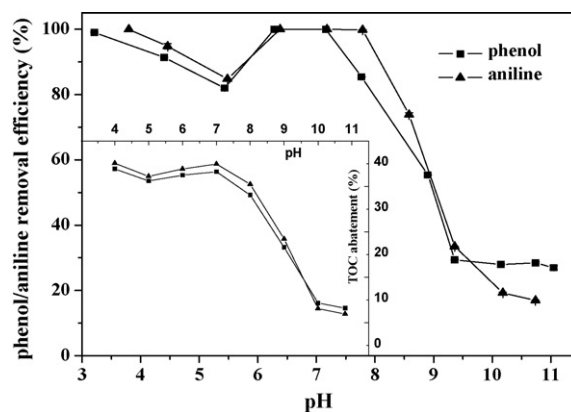
Fig. 5. Effect of pH on removal efficiency and TOC abatement efficiency of phenol and aniline. Control: [phenol/aniline]$_0$ = 1 mM; [MNPs] = 5 g/L; [H$_2$O$_2$] = 1.2 M; temperature = 308 K; reaction time = 6 h. Error bars represent the range of 2 independent experiments.

Secondly, under acid or neutral condition protonated surface of iron oxide was beneficial to the formation of metal oxide–phenol/aniline inner-sphere complexes, which would promote reaction, while under basic condition the combination of OH$^-$ with Fe^{3+} and Fe^{2+} on the surface of the MNPs might separate the reactants from surface metal centers. So the decrease in activity of the oxide, as pH increases, could be caused by less favorable conditions for the formation of the protonated inner-sphere complex [32].
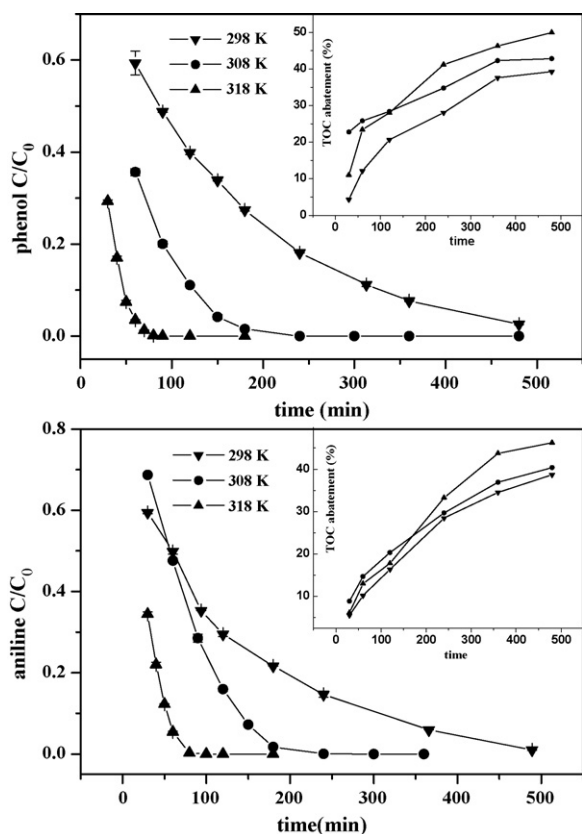
3.4. Effect of temperature

To check the effect of temperature on the removal efficiency and TOC abatement efficiency of phenol and aniline, the reaction kinetics experiments of the two compounds were conducted at 298 K, 308 K, and 318 K, separately. The kinetic curve in Fig. 6 showed that with the temperature increasing from 298 K to 318 K, the time for complete removal of phenol and aniline was decreased from 8 h to 1.5 h, and TOC abatement efficiency increased from 35% to 45% after 8 h reaction. However, the removal efficiency of phenol was reduced with the increase of temperature because of the thermal inactivation of enzyme in the HRP technique [26]. The reactivity of Fe$_3$O$_4$ MNPs would not be affect under high temperature. Furthermore, the thermal mobility of reactant could be accelerated at high temperature, resulting in enhancement of reaction rate. So in the treatment of wastewater containing phenol and aniline with MNPs, high temperature could be taken to accelerate the removal of these compounds. In this experiment, a temperature of 308 K was selected for all the experiment.

3.5. Stability, reusability of MNPs and removal of some substituted phenolic and aniline compounds

Fe$_3$O$_4$ MNPs stored for 40 days in sealing vessel under ambient conditions were used to remove phenol and aniline, and no obvious decrease of the removal efficiency was observed, meaning the excellent stability of MNPs. The reusability of MNPs was also examined under the above optimized conditions. The MNPs separated from the reactions solution were rinsed with 20 mL deioned water and used in the next batch. The results showed that after eight times of recycle, over 80% of phenol could be degraded, and TOC abatement efficiency decreased from 39.56% to 28.83%, which suggested that the reused MNPs still remained good activity. The reduced removal efficiency might be caused by two reasons: firstly, conglomeration of MNPs led to decrease of activation; secondly, part of MNPs might be rinsed during discarding of supernatants.

Fig. 6. Effect of temperature on removal efficiency and TOC abatement efficiency of phenol and aniline. Control: [phenol/aniline]$_0$ = 1 mM; [MNPs] = 5 g/L; [H$_2$O$_2$] = 1.2 M; pH = 6–7; reaction time = 6 h. Error bars represent the range of 2 independent experiments.

The removal efficiency of several substituted phenolic and aniline compounds by this system, including *o*-chlorophenol, *p*-chlorophenol, 2-toluidine, *m*-toluidine, *p*-toluidine, was investigated. The results (data were not shown) showed that these compounds could be eliminated completely, indicating that not only phenol and aniline but also their derivatives could be removed from solution by catalytic oxidation of MNPs.

3.6. Possible reaction mechanism

Comparative study showed that there was no obvious loss of phenol in the absence of both Fe$_3$O$_4$ MNPs and H$_2$O$_2$ after incuba-
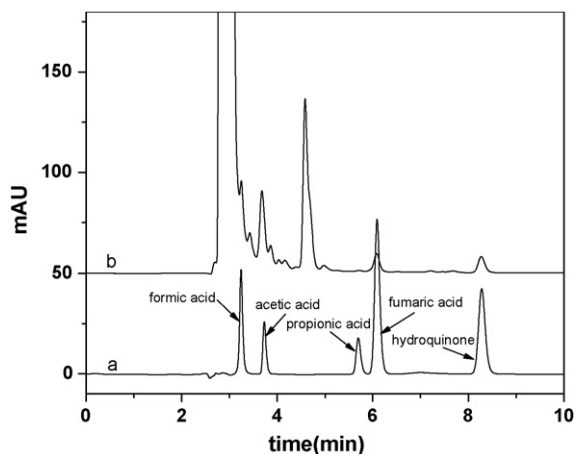
Fig. 7. Chromatograms of (a) standard solution containing some short chain acids and hydroquinone and (b) degradation solution of phenol.
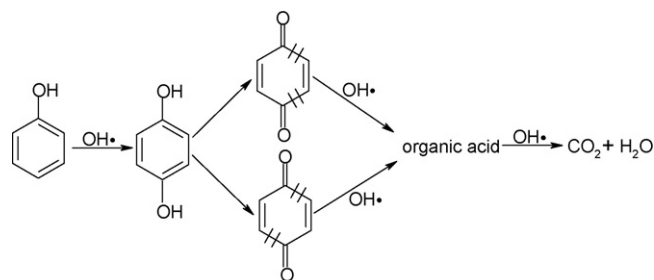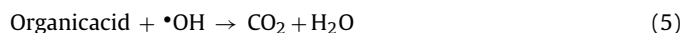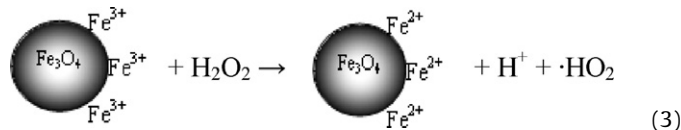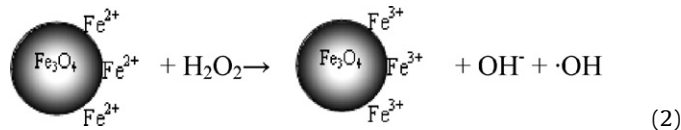

Scheme 1. Possible pathway for phenol mineralization.

tion for 6 h at 308 K. Without Fe$_3$O$_4$ MNPs or H$_2$O$_2$ in the reaction solution, only 3.31% or 12.6% of phenol was removed. In order to rule out the possibility that the loss of phenol was caused by the so-called Fenton reactions, MNPs were soaked into buffer solution (pH 4) for 4 h, then separated by external magnetic field, and the supernatants were used as reaction medium to degrade phenol. The results showed that only 13.1% phenol was removed. These results suggested that the removal of phenol was not mainly based on adsorption by Fe$_3$O$_4$ MNPs, direct oxidation by H$_2$O$_2$ or Fenton reaction, furthermore the oxidation of phenol by molecular oxygen was not operative which took place only under high pressure and temperature [41]. So the loss of phenol was caused mainly by catalytic oxidation of Fe$_3$O$_4$ MNPs in the presence of H$_2$O$_2$.

In order to investigate degradation intermediates of phenol, the reaction solution was analyzed by HPLC after 4 h of reaction. The chromatogram was compared with chromatograms of some short chain acids and hydroquinone. As shown in Fig. 7, intermediates including formic acid, acetic acid, fumaric acid and hydroquinone were detected.

For the existence of mineralization and intermediates detected, the degradation of phenol and aniline should be divided into two stages: breakage of benzene ring and oxidation of chain organic compound. When excessive H$_2$O$_2$ were added into the reaction solution, as shown in Eqs. (2) and (3) a redox process Fe (2+) ↔ Fe (3+) on MNPs surface took place to produce hydroxyl (·OH) and perhydroxyl radicals (·HO$_2$) [42,43]. The hydroxyl radicals could destroy benzene ring and finally convert them into H$_2$O and CO$_2$. Based on these results, we proposed degradation process of phenol as follows:

$$\text{Fe}_3\text{O}_4 \overset{\text{Fe}^{2+}}{\underset{\text{Fe}^{2+}}{\text{Fe}^{2+}}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \overset{\text{Fe}^{3+}}{\underset{\text{Fe}^{3+}}{\text{Fe}^{3+}}} + \text{OH}^- + \cdot\text{OH} \tag{2}$$

$$\text{Fe}_3\text{O}_4 \overset{\text{Fe}^{3+}}{\underset{\text{Fe}^{3+}}{\text{Fe}^{3+}}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \overset{\text{Fe}^{2+}}{\underset{\text{Fe}^{2+}}{\text{Fe}^{2+}}} + \text{H}^+ + \cdot\text{HO}_2 \tag{3}$$

$$\text{Ph} + {}^\bullet\text{OH} \rightarrow \text{organic acid} \tag{4}$$

$$\text{Organic acid} + {}^\bullet\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{5}$$

Here Ph represented for phenol. Based on the intermediates detected and the literature about ·OH breaking benzene ring [34], the breakage of benzene ring could be illustrated as Scheme 1.

To confirm the existence of hydroxyl free radical, tert-butanol, a strong radical scavenger [44], was added into the solution just before reaction. Fig. 8 showed that the presence of tert-butanol remarkably decreased the reactive rate and removal efficiency of phenol and aniline, indicating that the hydroxyl free radicals were mainly responsible for the removal of the two compounds. The
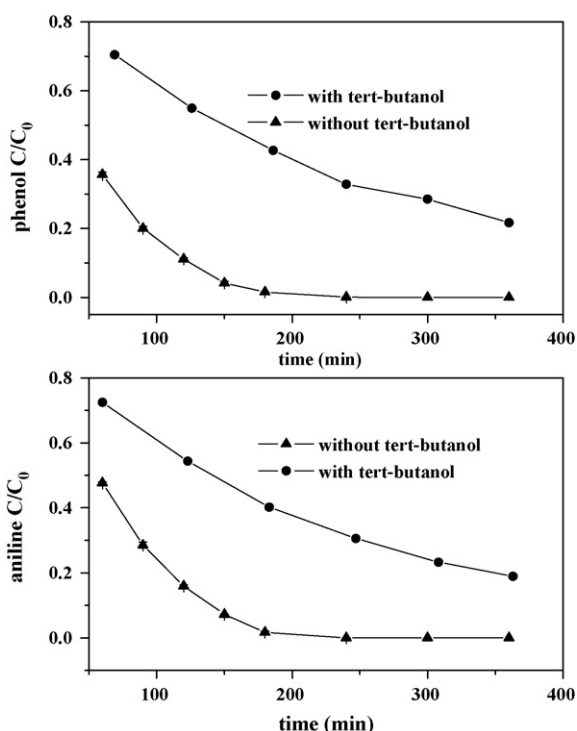
Fig. 8. Effect of addition of tert-butanol on removal efficiency of phenol and aniline. Control: [phenol/aniline]$_0$ = 1 mM; [MNPs] = 5 g/L; mole ratio of [tert-butanol]/[H$_2$O$_2$] = 0.5; pH = 6–7; temperature = 308 K. Error bars represent the range of 2 independent experiments.

results suggested that MNPs could catalyze H$_2$O$_2$ to form ·OH radicals.

4. Conclusions

In this study Fe$_3$O$_4$ MNPs had been successfully synthesized and used as catalysts to remove phenol and aniline from aqueous solution. The results showed that both phenol and aniline could be eliminated completely under optimized conditions. Fe$_3$O$_4$ MNPs had good stability and reusability, and could be separated from solution by applying an external magnetic field for their superparamagnetism. Based on the experiment results, a reasonable mechanism had been proposed to interpret the degradation process of phenol.

Acknowledgments

References

[1] G. Emtiazi, M. Satar, F. Mazaherion, The utilization of aniline, chlorinated aniline, and aniline blue as the only source of nitrogen by fungi in water, Water Res. 35 (2001) 1219–1224.
[2] Q.G. Huang, J.X. Tang, J.W.J. Walter, Precipitation for enzyme-catalyzed phenol oxidative coupling products: background ion and pH effects, Water Res. 39 (2005) 3021–3027.
[3] C.H. Ko, C. Fan, P.N. Chiang, M.K. Wang, K.C. Lin, p-Nitrophenol, phenol and aniline sorption by organo-clays, J. Hazard. Mater. 149 (2007) 275–282.
[4] J.Q. Jiang, C. Cooper, S. Ouki, Comparison of modified montmorillonite adsorbents. Part 1: preparation, characterization and phenol adsorption, Chemosprere 47 (2002) 711–716.
[5] F. Amiri, H. Börnick, E. Worch, Sorption of phenols onto sandy aquifer material: the effect of dissolved organic matter (DOM), Water Res. 39 (2005) 933–941.
[6] K.P. Singh, A. Malik, S. Sinha, P. Ojha, Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material, J. Hazard. Mater. 150 (2008) 626–641.
[7] W.M. Zhang, Z.W. Xu, B.C. Pan, Adsorption enhancement of laterally interacting phenol/aniline mixtures onto nonpolar adsorbents, Chemosphere 66 (2007) 2044–2049.
[8] G.G. Stavropoulos, P. Samaras, G.P. Sakellaropoulos, Effect of activated carbons modification on porosity, surface structure and phenol adsorption, J. Hazard. Mater. 151 (2008) 414–421.
[9] Y.J. Li, F. Wang, G.D. Zhou, Aniline degradation by electrocatalytic oxidation, Chemosphere 53 (2003) 1229–1234.
[10] Y. Yavuz, A.S. Koparal, Electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide electrode, J. Hazard. Mater. 136 (2006) 296–302.
[11] P. Thepsithar, P.L.R. Edward, Removal of phenol from contaminated kaolin using electrokinetically enhanced in situ chemical oxidation, Environ. Sci. Technol. 40 (2006) 6098–6103.
[12] E.M. Contreras, M.E. Albertario, N.C. Bertola, N.E. Zaritzky, Modelling phenol biodegradation by activated sludges evaluated through respirometric techniques, J. Hazard. Mater. 158 (2008) 366–374.
[13] L. Amor, M. Eiroa, C. Kennes, Phenol biodegradation and its effect on the nitrification process, Water Res. 39 (2005) 2915–2920.
[14] P. Bergauer, P.A. Fonteyne, N. Nolard, Biodegradation of phenol and phenol-related compounds by psychrophilic and cold-tolerant alpine yeasts, Chemosphere 59 (2005) 909–918.
[15] A. Santos, P. Yustos, B. Durban, Catalytic wet oxidation of phenol: kinetics of phenol uptake, Environ. Sci. Technol. 35 (2001) 2828–2835.
[16] J. Carriazo, E. Guélou, J. Barrault, Catalytic wet peroxide oxidation of phenol by pillared clays containing Al–Ce–Fe, Water Res. 39 (2005) 3891–3899.
[17] A.F.J. Santiage, J.F. Sousa, R.C. Guedes, C.E.M. Jerônimo, M. Benachour, Kinetic and wet oxidation of phenol catalyzed by non-promoted and potassium-promoted manganese/cerium oxide, J. Hazard. Mater. 138 (2006) 325–330.
[18] J. Sajiki, J. Yonekubo, Inhibition of seawater on bisphenol A (BPA) degradation by Fenton reagents, Environ. Int. 30 (2004) 145–150.
[19] R. Maciel Jr., G.L. Sant'Anna, M. Dezotti, Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions, Chemosphere 57 (2004) 711–719.
[20] F. Mijangos, F. Varona, N. Villota, Changes in solution color during phenol oxidation by Fenton reagent, Environ. Sci. Technol. 40 (2006) 5538–5543.
[21] M. Tonegawa, J. Dec, J.M. Bollag, Use of additives to enhance the removal of phenols from water treated with horseradish and hydrogen peroxide, J. Environ. Qual. 32 (2003) 1222–1227.
[22] Q.G. Huang, J. Walter, Weber Jr., Peroxidase-catalyzed coupling of phenol in the presence of model inorganic and organic solid phases, Environ. Sci. Technol. 38 (2004) 5238–5245.
[23] P.S. González, E. Agostini, S.R. Milrad, Comparison of the removal of 2,4-dichlorophenol and phenol from polluted water, by peroxidases from tomato hairy roots, and protective effect of polyethylene glycol, Chemosphere 70 (2008) 982–989.
[24] K.E. Simmons, R.D. Minard, J.M. Bollag, Oligomerization of 4-chloroaniline by oxidoreductases, Environ. Sci. Technol. 21 (1987) 999–1003.
[25] H.E. Mohammad, P.A. Christian, Combination of ultrasound and oxidative enzyme: sono-biodegradation of phenol, Appl. Catal. B-Environ. 53 (2004) 257–263.
[26] D. Nelson, E. Elisa, Potential applications of oxidative enzymes and phenoloxidase-like compounds in wastewater and soil treatment: a review, Appl. Catal. B-Environ. 28 (2000) 83–99.
[27] A. Fishman, I. Levy, U. Cogan, Stabilization of horseradish peroxidase in aqueous-organic media by immobilization onto cellulose using a cellulose-binding-domain, J. Mol. Catal. B-Enzym. 18 (2002) 121–131.
[28] J. Cheng, S.M. Yu, P. Zuo, Horseradish peroxidase immobilized on aluminum-pillared interlayered clay for the catalytic oxidation of phenolic wastewater, Water Res. 40 (2006) 283–290.
[29] S. Dalal, M.N. Gupta, Treatment of phenolic wastewater by horseradish peroxidase immobilized by bioaffinity layering, Chemosphere 67 (2007) 741–747.
[30] L.Z. Gao, L. Zhuang, L. Nie, Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, Nat. Nanotechnol. 2 (2007) 577–583.
[31] 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.
[32] M.D.R. Pizzigallo, P. Ruggiero, C. Crecchio, Oxidation of chloroanilines at metal oxidae surfaces, J. Agric. Food Chem. 46 (1998) 2049–2054.
[33] H.P. Nguyen, T.K.H. Tran, V.T. Nguyen, Characterization and activity of Fe-ZSM-5 catalysts for the total oxidation of phenol in aqueous solutions, Appl. Catal. B-Environ. 34 (2001) 267–275.
[34] Y.F. Han, N. Phonthammachai, K. Ramesh, Removing organic compounds from aqueous medium via wet peroxidation by gold catalysts, Environ. Sci. Technol. 42 (2008) 908–912.
[35] G. Zelmanov, R. Semiat, Iron (3) oxide-based nanoparticles as catalysts in advanced organic aqueous oxidation, Water Res. 42 (2008) 492–498.
[36] M.E. Suarez-Ojeda, F. Stüber, A. Fortuny, Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst, Appl. Catal. B-Environ. 58 (2005) 105–114.
[37] 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. 136 (2006) 859–865.

[38] Z.Y. Ma, Y.P. Guan, H.Z. Liu, Synthesis and characterization of micron-sized monodisperse superparamagnetic polymer particles with amino groups, J. Polym. Sci. Polym. Chem. 43 (2005) 3433–3439.

[39] WHO, Guidelines for Drinking Water Quality, third ed., vol. I, Geneva, Italy, 2004.

[40] C.L. Hsueh, Y.H. Huang, C.C. Wang, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere 58 (2005) 1409–1414.

[41] F. Forty, C. Ferry, C. Bengoa, Catalytic removal of phenol from aqueous phase using oxygen or air as oxidant, Catal. Today 24 (1995) 79–83.

[42] W.J. Song, M.M. Cheng, J.H. Ma, W.H. Ma, C.C. Chen, J.C. Zhao, Decomposition of hydrogen peroxide driven by photochemical cycling of iron species in clay, Environ. Sci. Technol. 40 (2006) 4782–4787.

[43] W.J. Song, W.H. Ma, J.H. Ma, C.C. Chen, J.C. Zhao, Photochemical oscillation of Fe (II)/Fe (III) ratio induced by periodic flux of dissolved organic matter, Environ. Sci. Technol. 39 (2005) 3121–3127.

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