



## Decomposing phenol by the hidden talent of ferromagnetic nanoparticles

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### ABSTRACT

Researches on modified Fenton reactions applied in phenol degradation have been focused on reducing secondary pollution and enhancing catalytic efficiency. Newly developed methods utilizing carriers, such as Resin and Nafion, to immobilize  $\text{Fe}^{2+}$  could avoid iron ion leakage. However, the requirement of high temperature and the limited reaction efficiency still restrained them from broad application. Based on a recently discovered "hidden talent" of ferromagnetic nanoparticles (MNPs), we established a MNP-catalyzed phenol removal assay, which could overcome these limitations. Our results showed that the MNPs removed over 85% phenol from aqueous solution within 3 h even at 16 °C. The catalytic condition was extensively optimized among a range of pH, temperature as well as initial concentration of phenol and  $\text{H}_2\text{O}_2$ . TOC and GC/MS analysis revealed that about 30% phenol was mineralized while the rest became small molecular organic acids. Moreover the MNPs were thermo-stable and could be regenerated for at least five rounds. Thus, our findings open up a wide spectrum of environmental friendly applications of MNPs showing several attractive features, such as easy preparation, low cost, thermo-stability and reusability.

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### 1. Introduction

Phenol and phenolic compounds are the most important representative of organic pollutants generated by various industrial processes. Since they are highly toxic and suspicious carcinogens, many processes such as physical adsorption (Nevskaia et al., 2004), chemical oxidation (Garcia-Molina et al., 2005) and biological degradation (Jiang et al., 2006) have been developed to remove phenol from wastewater. Among these methods, a solution of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ , known as Fenton reagent, is frequently used to drive the oxidation of organic contaminants (Tarr, 2003). However, the iron ions and the sludge generated by Fenton reagent required further treatments and rose up new disposal problems. To overcome the drawbacks, various modified Fenton systems have been developed. For example, immobilized Fenton reactions using  $\text{Fe}^{3+}$  loaded on resin, clay or Nafion have been developed (Sabhi and Kiwi, 2001; Catrinescu et al., 2003; Liou et al., 2004; Carriazo et al., 2005; Liou et al., 2005; Nikolopoulos et al., 2006). In addition, heterogeneous Fenton-like systems were made using goethite (Lu et al., 2002), hematite (Feng et al., 2004),  $\text{AFe}_2\text{O}_4$  ( $A = \text{Fe}, \text{Ni}, \text{Zn}$ )

(Guin et al., 2005) and  $\text{Fe}^0/\text{Fe}_3\text{O}_4$  (Moura et al., 2005), which are usually slow and need additional assistants such as UV and ultrasound. Compared with the chemical reagents, enzymatic catalysis is more active and environmental friendly. For instance, several commercial peroxidases were investigated for removing phenol from aqueous solutions (Bodalo et al., 2006). There were also attempts trying to immobilize them on clay and other vectors (Akhtar and Husain, 2006; Cheng et al., 2006). However, because of their protein nature, the instability and costliness of the enzyme made them not feasible in the treatment of wastewater although it has been reported for almost 30 year (Klibanov et al., 1980). Therefore, it is important and necessary to find new materials and establish new methods.

Recently we have found that the ferromagnetic nanoparticles (MNPs) are intrinsically active catalyst for oxidation reactions similar to that found in natural peroxidases (Gao et al., 2007). What is more, the MNPs have a definite advantage compared with their protein-based counterparts because they are considerably more stable over a wide range of temperatures and various levels of acidity. Based on this finding, we studied the potential application of MNPs in phenol removal and developed a MNP-catalyzed phenol degradation assay. Our data show that this assay is efficient and economical. Furthermore, the stability and reusability of MNPs promised broad applications in (but not restricted in) the treatment of phenolic wastewater.

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## 2. Materials and methods

### 2.1. Materials

Horseradish Peroxidase (HRP), 3,3',5,5'-tetramethyl benzidine, catalase, 5,5'-dimethyl-1-pyrroline-*N*-oxide (DMPO) and BSTFA (*N,O*-Bis (trimethylsilyl) trifluoro acetamide) + TMCS (Trimethylchlorosilane) were purchased from Sigma–Aldrich Inc (USA). H<sub>2</sub>O<sub>2</sub> (30% v/v), 4-AAP (4-aminoantipyrine), K<sub>3</sub>Fe(CN)<sub>6</sub>, Phenol, FeSO<sub>4</sub>, FeCl<sub>3</sub> · 6 H<sub>2</sub>O and NH<sub>3</sub> · H<sub>2</sub>O were from Beijing Chemical Reagents Company (China). All chemicals and reagents used were of analytical grade.

### 2.2. Methods

#### 2.2.1. MNP synthesis

MNPs with a diameter of 13 nm were prepared according to the method of Molday (1984). Briefly, a solution of 10 mM FeCl<sub>3</sub> and 6 mM FeSO<sub>4</sub> were mixed at pH 1.7 under N<sub>2</sub> protecting. Then, ammonia aqueous solution (1.5 M) was dropped into the mixture solution with violently stirring until the pH of the solution raised up to 9. The MNPs were washed immediately with water for 5 times and then ethanol for 2 times. Finally, MNPs were either dissolved in ethanol (for long time storage) or dried at room temperature under vacuum (for instant usage).

#### 2.2.2. Phenol removal reaction and detection

Unless otherwise stated, the experiments for MNP catalysis were carried out in a tube with 125 μl H<sub>2</sub>O (pH 3.0) containing 12 μg MNPs and 3 mM phenol. For HRP catalysis, the experiments were performed with 1.5 μg HRP and 3 M phenol in 125 μl 0.1 M Tris-HCl buffer (pH 8.0). The reactions were initiated by adding H<sub>2</sub>O<sub>2</sub> to a final concentration of 60 mM (for MNPs) or 6 mM (for HRP) for 3 h at room temperature. Then, 125 U ml<sup>-1</sup> (final concentration) Catalase was added to stop the reaction and decompose excessive H<sub>2</sub>O<sub>2</sub>. Finally, the reaction was centrifuged at 13000g for 3 min, and 2 μl supernatant from each reaction was taken for analysis.

Two microliter sample was mixed in a 96-well plate with 50 μl reaction buffer A (16.7 mM K<sub>3</sub>Fe(CN)<sub>6</sub> in 0.25 M NaHCO<sub>3</sub>) and 50 μl reaction buffer B (4.18 mM 4-AAP in 0.25 M NaHCO<sub>3</sub>). After incubation for 5 min, the phenol concentration was measured at 490 nm using a Bio-Rad Microplate Reader 550.

#### 2.2.3. Recycle of MNPs

A phenol removal experiment was performed using 24 μg MNPs. After each reaction, the MNPs were collected using a

magnet, washed with 200 μl deionized water and sonicated for 2 min. The regenerated MNPs were applied for the next reaction.

#### 2.2.4. Analysis of MNP-catalyzed products

For TOC assay, the MNP-catalyzed products were first diluted 15 times with H<sub>2</sub>O and then filtrated with a 0.45 μm Millipore filter before submitted into an analyzer (Analytika AG, Germany).

For GC/MS assay, the sample were first freeze-dried and dissolved in 1 ml methylene dichloride, followed by 0.1 ml BSTFA/TMCS (99:1) for derivatization. After incubating at 60 °C for 30 min, the sample were dehydrated by Na<sub>2</sub>SO<sub>4</sub> and filtrated with 0.45 μm Millipore filter before submitted to an analyzer (Agilent 7890GC/5975MSD, USA).

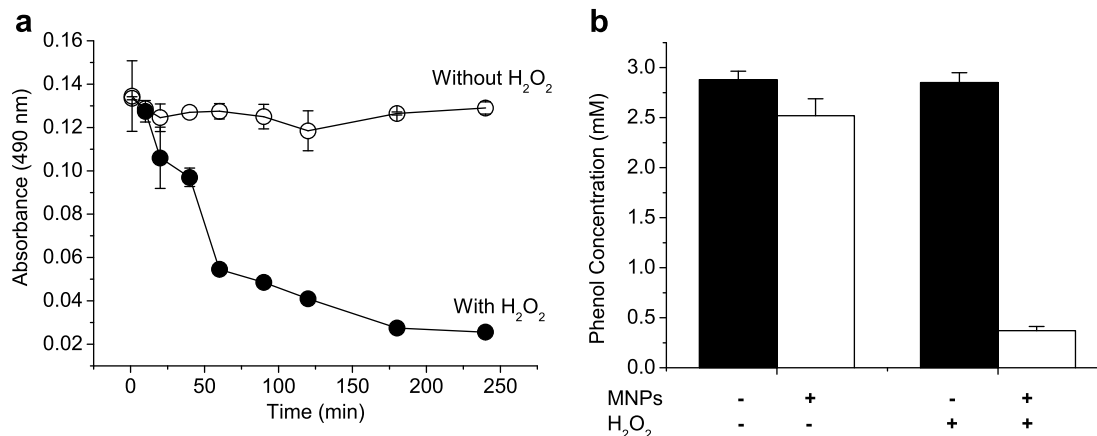
For electron spin resonance (ESR) assay, 40 μl samples were taken instantaneously at different time point from phenol removal reaction and mixed with 10 μl 500 mM DMPO to form DMPO-OH adduct. The amount of hydroxyl radicals was indicated by ESR signals using a Bruker model ER 200D spectrometer.

## 3. Results and discussion

### 3.1. MNPs catalyze phenol degradation

First, we prepared MNPs using the method of Molday (1984). The character of the MNPs was studied using TEM and ED photography, showing that the MNPs appeared approximately spherical with an average diameter of 13 nm (Supplemental Figs. 1 and 2). Their saturation magnetization value was 65.45 emu g<sup>-1</sup> and coercivity value was 20.89 Oe as determined by hysteresis loops (Supplemental Fig. 3) indicating the MNPs with good magnetism character. The detailed characterization of the MNPs has been presented elsewhere (Ma et al., 2004).

Next, we mixed these MNPs with hydrogen peroxide and phenol together in water solution to find out whether the peroxidase-like activity of MNPs could catalyze the decomposing of phenol. As shown in Fig. 1a, the MNPs dramatically degraded phenol in the reaction and about 60% phenol was removed within the first 60 min. The maximal phenol removal efficiency of MNPs was higher than 85% after 180 min. In contrast, little change in phenol concentration was observed in control reactions without H<sub>2</sub>O<sub>2</sub>. In addition, the absorption of phenol by MNPs was neglectable even with double dose (Fig. 1b). These data demonstrate that it is MNP catalysis but not unspecific absorption that results in phenol removal.



**Fig. 1.** The MNPs catalyzed phenol removal with little non-specific absorption. (a) Phenol concentration decreased as MNP catalysis went on and (b) absorption of phenol by MNPs was neglectable.

### 3.2. MNP-catalyzed phenol removal depend on $H_2O_2$ and phenol concentration

To test whether the catalytic activity of the MNPs is, like the conventional enzyme-HRP, dependent on the concentration of  $H_2O_2$ , we performed phenol removal experiments using a range of  $H_2O_2$  concentrations from 0.3 to 240 mM. Reactions were initiated by adding either 12  $\mu\text{g}$  MNPs or 1.5  $\mu\text{g}$  HRP. The results showed that both MNPs and HRP removed phenol effectively, but their dependence on  $H_2O_2$  was largely different. To reach the maximal level of phenol removal, the MNPs required 60 mM  $H_2O_2$ , which is one order of magnitude higher than HRP (6 mM). We believe that is because of their different catalyzing mechanism. As essentially iron oxides, MNPs might catalyze phenol removal through a chemical catalysis mechanism in which the  $Fe^{2+}/Fe^{3+}$  on the surface of  $Fe_3O_4$  particles might play as a Fenton-like reagent whereas HRP catalyzed the reaction in an enzymatic way. In addition, we found that further increasing of  $H_2O_2$  concentration would result in inhibition of both HRP and MNP catalysis. The HRP catalysis was sharply suppressed when  $H_2O_2$  concentration was more than 10 mM (Fig. 2a), while the MNP catalysis was inhibited when  $H_2O_2$  increased to 480 mM (Supplemental Fig. 4).

To detect whether the phenol concentration also affects the MNP catalysis, we used a range of initial phenol concentrations from 0.038 to 13.76 mM. As shown in Fig. 2b, MNP and HRP catal-

ysis were both decreasing with the increase of phenol concentration. More than 90% phenol was removed by either MNPs or HRP when the initial phenol concentration was around 2 mM. However, when phenol concentration increased to 12 mM, the MNPs showed 80% efficiency while the HRP remained less than 30%. Moreover, further study showed that the optimal  $H_2O_2$ /phenol ratio for HRP catalysis varied from 0.5 to 2.0 which is consistent with the previous report (Klibanov et al., 1983; Liu et al., 2002). However, the optimal  $H_2O_2$ /phenol ratio for MNPs ranged from 2 to 160, which is much broader than HRP. This indicates that the MNPs are better than HRP in handling large amount of pollutants.

### 3.3. MNP-catalyzed phenol removal depend on pH but not temperature

In order to find optimal condition of MNPs in phenol removal, we set up a range of values of pH from 1 to 9.5 and temperatures from 4 to 90 °C. The results showed that the MNP-catalyzed phenol removal was dependent on pH but not temperature. The optimal pH for MNP catalysis was restricted around 3. When the pH was lower than 2 or higher than 4, the MNP catalysis was sharply decreased (Fig. 3a). This observation is consistent with the typical Fenton process which is carried on at pH 3.0 (Edwards et al., 1992). It might be due to the catalytic hydration shell forms different complexes according to the pH range. In more acidic solutions,

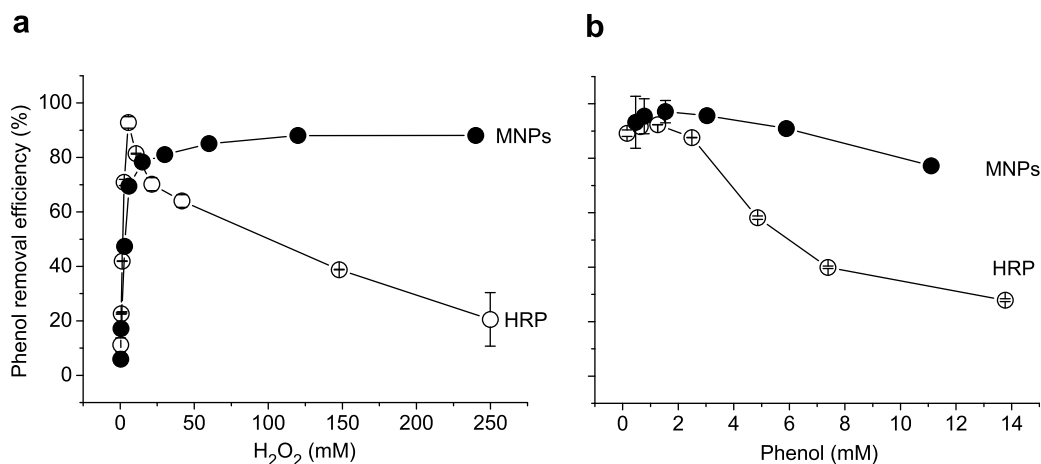


Fig. 2. Phenol removal efficiency of HRP and MNPs depend on the initial concentrations of both  $H_2O_2$  (a) and phenol (b). The reactions were taken at pH 3 for MNPs and pH 8 for HRP.

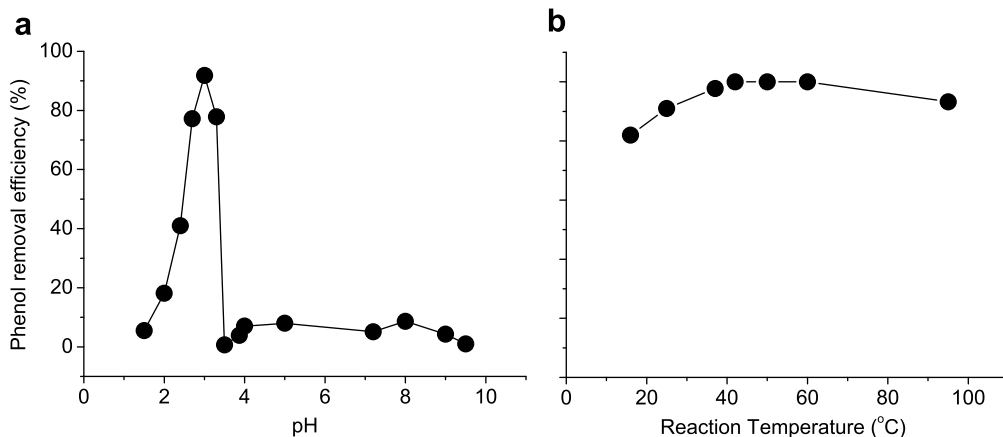
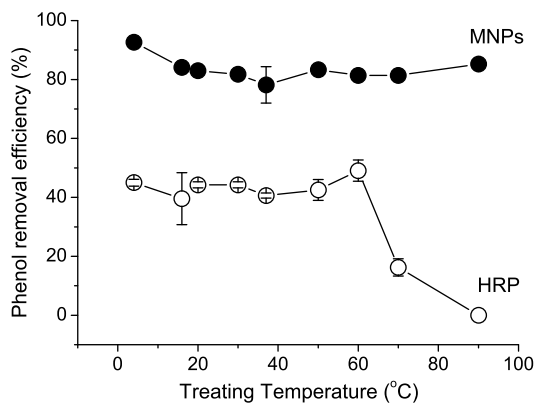
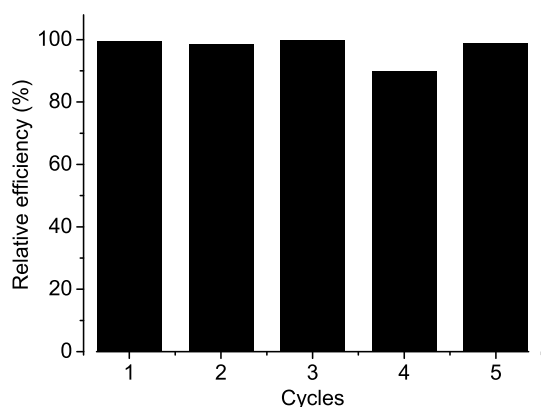


Fig. 3. Phenol removal efficiency of MNPs depends on pH (a) rather than temperature (b).



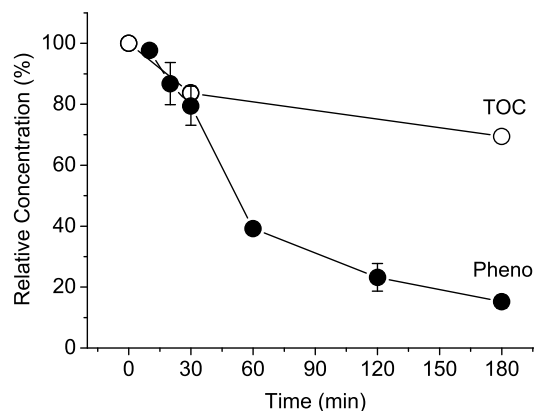
**Fig. 4.** Comparing the thermo-stability of MNPs and HRP. Both catalysts were first treated at temperatures indicated in the figure for 3 h and then applied for phenol removal experiment at the optimal condition.



**Fig. 5.** Reusability of the MNPs in phenol removals.

the  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  shell protonation will result in releasing hydration shell water; at more basic pH-values, the OH groups might replace the  $\text{H}_2\text{O}$  groups. Both of the effects are detrimental to the Fe-catalytic activity of decomposing  $\text{H}_2\text{O}_2$  to generate hydroxyl radicals.

Surprisingly, unlike typical Fenton processes which usually require high temperature from 40 to 80 °C (Catrinescu et al., 2003; Liou et al., 2005), MNPs effectively catalyzed phenol degradation under temperatures varied from 16 to 95 °C (Fig. 3b). Over 85% phenol removal efficiency could still be achieved even at 16 °C. These data support that MNP catalysis is pH but not temperature dependent.



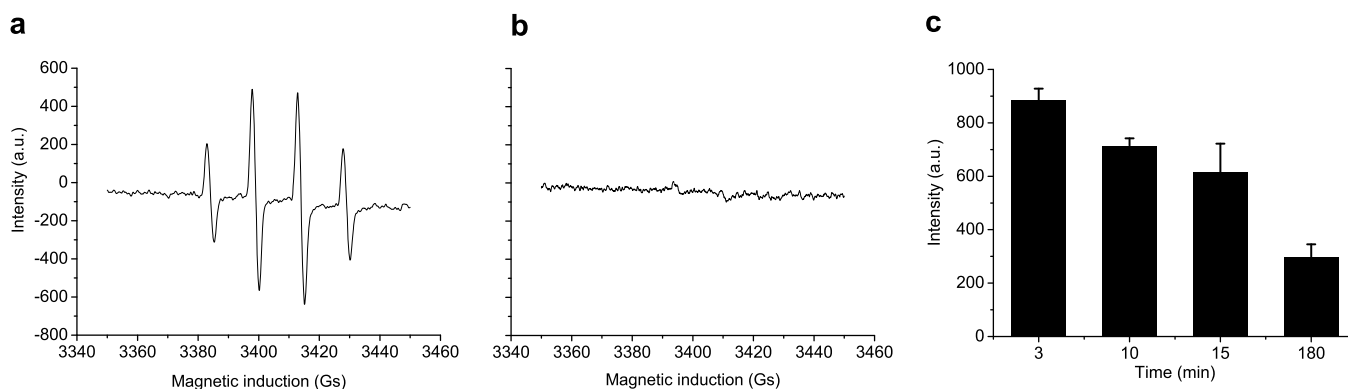
**Fig. 6.** TOC removal efficiency of MNPs. MNPs catalyzed reactions were stopped at different time points when samples were analyzed for both TOC and phenol concentration.

### 3.4. MNPs are thermo-stable

As inorganic nanomaterial, MNPs are expected to be more stable than the enzyme-HRP which is a protein and easy to be denatured. To examine the stability of MNPs, we first treated the HRP and MNPs at a range of temperatures from 5 to 90 °C for 3 h, and then the heat-treated catalysts were applied for phenol removal experiment under the optimal conditions. As shown in Fig. 4, the MNPs appeared very good thermo-stability. Even after treated at 90 °C for 3 h, the MNPs still remained more than 80% activity in phenol removal. In contrast, the enzymatic activity of HRP dramatically decreased after treatment at temperatures greater than 60 °C. These data suggest that MNPs are thermo-stable, which can be easily stored at temperature from 0 to 90 °C.

### 3.5. MNPs are reusable

The catalytic property coupled with magnetically driven capture techniques endowed the MNPs a unique advantage in wastewater treatment. To examine the reusability of MNPs, we repeated phenol removal experiments for 5 times using the same MNPs regenerated simply by sonication and washing with deionized water. After 5 rounds of recycle, the MNPs still remained almost 100% catalytic activity (Fig. 5). The combination of catalytic activity and magnetic recovery of MNPs on the one hand prevents secondary contamination caused by MNP leakage, on the other hand further lower the cost per treatment. Considering both the cost of preparation ( $\$2.5 \text{ kg}^{-1}$ ) and the reusability of MNPs, it would be very cheap when applied in wastewater treatment.



**Fig. 7.** ESR spectrum detected in phenol removal reaction with MNPs (a) or not (b). (c) ESR signal of DMPO-OH radical observed in MNP catalysis at different time points.

### 3.6. Analysis of phenol degradation product

In order to figure out whether all the phenol was mineralized during the MNP catalysis, we further tested the TOC values of reactions carried on for different times. The results showed that 30% of phenol was mineralized by MNPs after 3 h reaction (Fig. 6). The rest of reaction products were identified by GC/MS to be small molecular organic acids, including lactic acid, tartaric acid, oxalic acid, succinic acid, maleic acid and 1,2-propylene glycol. These data suggest that MNPs degraded phenol partially by cleaving phenyl to form small molecular organic acids.

Furthermore, we used ESR assay to detect whether any hydroxyl radicals were produced during MNP catalysis. The four-line signal with a peak height ratio of 1:2:2:1 showed in the results is matched with the pattern of the typical DMPO-OH adduct (Fig. 7a) while in the contrast no signal was observed in control reactions (without MNPs, Fig. 7b), indicating the presence of hydroxyl radicals in the products. Moreover, although the phenol oxidation reaction was almost stopped after 3 h, the intensity of DMPO-OH radical was still about one third of that when the reaction started (Fig. 7c). This implies that the MNPs could drive the generation of hydroxyl radicals constantly which is in consistent with the reusability. Taken together, we speculate the mechanism of MNPs in phenol removal is that the MNPs catalyzed  $H_2O_2$  to generate hydroxyl radicals, which in turn attacked the phenyl and break down it into small molecular organic acids.

## 4. Conclusions

Our results demonstrated that MNPs can be used as a promising catalyst to remove phenolic pollutants from aqueous solutions. Over 85% phenol could be removed at optimal reaction condition. There are 4 significant advantages of using MNPs in wastewater treatment: (1) The MNPs are cheap and easy to prepare, which make them more feasible than other effective but expensive reagents or processes. (2) As being composed of inorganic materials, MNPs are robust and thermo-stable. (3) With the chemical essential of  $Fe_3O_4$ , MNPs are nontoxic and environmental friendly. (4) The MNPs could be recycled and regenerated. These attractive features endowed them broad applications in various processes such as phenolic wastewater treatment.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.05.050.

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