

Degradation of 4-chlorophenol by mixed Fe⁰/Fe₃O₄ nanoparticles: from the perspective of mechanisms

Rong Cheng, Xingyan Xue, Lei Shi, Tao Zhang, Yaping Liu, Mi Kang and Xiang Zheng

ABSTRACT

Fe⁰ nanoparticles have been widely studied for pollution abatement in recent years; however, regarding the mechanism for pollutant degradation, studies have mainly focused on the reductive dechlorination by Fe⁰, and the dynamic process has not been clarified completely. As reported, some organics could be degraded during the oxidation of Fe⁰ by O₂, and hydrogen peroxide was supposed to be produced. In this study, Fe₃O₄, an oxidation product of Fe⁰, was used to treat the pollutant combining with Fe⁰ nanoparticles, and 4-chlorophenol (4-CP) was used as the model pollutant. The results showed that the addition of Fe₃O₄ nanoparticles hindered the removal of 4-CP by Fe⁰ nanoparticles under anoxic conditions. However, the dechlorination efficiency was improved in the initial 6 h. Under aerobic conditions, the reused Fe₃O₄ nanoparticles would improve the removal and dechlorination of 4-CP. Especially, the dechlorination efficiency was obviously increased. It is proposed that the removal of 4-CP was due to the effects of both nanosized Fe⁰ and Fe₃O₄ – reducing action of Fe⁰ and catalytic oxidation action of Fe₃O₄. The reducing action of Fe⁰ was the major factor under anoxic conditions. And the catalytic oxidation action of Fe₃O₄ became an important reason under aerobic conditions.

Key words | catalytic oxidation, dechlorination, Fe⁰ nanoparticles, Fe₃O₄ nanoparticles, mechanism

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INTRODUCTION

Chlorophenols are important chemical materials with wide application including biocides, disinfectants, dyes, preservatives and pesticides. They occur as pollutants and industrial waste in the environment, and are widely detected in water and soil (Gao *et al.* 2008). Most chlorophenols are listed as priority pollutants by the United States Environmental Protection Agency due to their toxicity and carcinogenicity (Hwang *et al.* 2015). Moreover, they can persist in the environment for a long time, and resist chemical and biological degradation (Wang & Qian 1999). As a result, the exposure to chlorophenols in the environment would do harm to human health by bioaccumulation and pose a series of environmental problems. Therefore, necessary measures must be taken to remove chlorophenols from the environment.

Zero-valent iron (Fe⁰) has been applied for recalcitrant chemicals treatment including pesticides, nitro-aromatic compounds, chlorinated solvents, azo dyes and chloric organic pollutants (Dror *et al.* 2005; Liu *et al.* 2015). However, surface passivation of iron would seriously decrease

the activity of iron and further decrease pollutant removal efficiency (Carniato *et al.* 2012). Due to large specific surface area and high surface reactivity, Fe⁰ nanoparticles have been studied increasingly for pollution abatement. In previous studies, degradation performance (Cheng *et al.* 2007; Kim *et al.* 2010), kinetics (Yang & Lee 2005), mechanisms (Shih *et al.* 2011; Chen *et al.* 2012; Kaifas *et al.* 2014), and reaction conditions (Tian *et al.* 2009) for Fe⁰ nanoparticles removing chlorinated organics were studied. However, regarding the mechanisms for pollutant degradation, studies have mainly focused on the reductive dechlorination by Fe⁰, and the dynamic process has not been clarified completely. It has been reported that some organics could be degraded during the oxidation process of Fe⁰ by O₂, and hydrogen peroxide was supposed to be produced (Joo *et al.* 2005; Keenan & Sedlak 2008). Moreover, Fe₃O₄, the main oxidation product of Fe⁰ nanoparticles (Kumar *et al.* 2014a; Cheng *et al.* 2015), could catalyze the oxidation of 4-chlorophenol (4-CP) with hydrogen peroxide (Cheng *et al.* 2015). However, the

study of the role of Fe₃O₄ in the nanosized Fe⁰/pollutants system is limited to date.

In this study, Fe₃O₄, the main oxidation product of Fe⁰ nanoparticles, was used to treat the pollutant combining with Fe⁰ nanoparticles; and 4-CP, a representative chlorophenol which is highly toxic and recalcitrant towards chemical and biological degradation in the environment, was used as the model compound. The removal of 4-CP by Fe⁰ nanoparticles and mixed Fe⁰/Fe₃O₄ nanoparticles was studied, and the transformation of nanoparticles was also studied. Moreover, the mechanisms of 4-CP removal were analyzed. The results would analyze the role of Fe₃O₄ and provide a complement for the current pollutant degradation mechanism with Fe⁰ nanoparticles.

MATERIALS AND METHODS

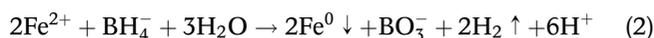
Chemicals and materials

Chemicals used in the experiments were of reagent grade. 4-CP was supplied by Tianjin Jinke Fine Chemical Industry Research Institute. Ferrous sulfate (FeSO₄·7H₂O) was provided by Shenyang Reagent Factory. Ferric sulfate (Fe₂(SO₄)₃) was provided by Nankai Fine Chemical Factory. Hydrogen peroxide, sodium borohydride, sodium hydroxide, sulfuric acid, methanol and ethanol were purchased from Beijing Chemical Factory. Argon gas was purchased from Beijing Aolin Gas Company.

Synthesis and characterization of nanoparticles

The synthesis of nanoparticles was conducted in a four-neck flask. The reaction was carried out in argon gas atmosphere to keep the anaerobic condition. Fe₃O₄ nanoparticles were prepared by the Massart hydrolysis method (Massart 1981). Briefly, mixed aqueous solution (100 mL) of ferric sulfate (0.07 mol L⁻¹) and ferrous sulfate (0.07 mol L⁻¹) was added dropwise into a four-neck flask containing sodium hydroxide aqueous solution (100 mL; 1 mol L⁻¹). Fe₃O₄ nanoparticles were obtained through the reaction shown in Equation (1). Fe⁰ nanoparticles were prepared by chemical reduction method (Glavec et al. 1995). Briefly, the aqueous solution (100 mL) of sodium borohydride was added dropwise into a four-neck flask containing ferrous sulfate aqueous solution (100 mL). The molar ratio of sodium borohydride to ferrous sulfate was more than 2:1. Fe⁰ nanoparticles were

obtained through the reaction given in Equation (2).



The synthesized particles were washed three times with degassed ultrapure water, and then dried in a vacuum dryer.

Morphology of the synthesized Fe⁰ nanoparticles and Fe₃O₄ nanoparticles was observed using a transmission electron microscope (TEM, Hitachi H-7650B) and a scanning electron microscope (SEM, JSM-6301F). The crystal structure and transformation products of nanoparticles were characterized using X-ray powder diffraction (XRD, D8-advance) on a Rigaku D/max-RB X-ray diffractometer with Cu K α radiation ($\lambda = 0.1542$ nm).

The TEM and SEM results showed that the two samples were relatively uniform. The average particle size of Fe⁰ nanoparticles was 50 nm, and the average particle size of Fe₃O₄ nanoparticles was 30 nm. Peaks identified on the two XRD patterns of synthesized particles were Fe⁰ and Fe₃O₄, respectively. No other peaks were detected in the two XRD patterns, indicating the high purity of the samples.

In addition, a microscopic confocal Raman spectrometer (RM2000, Renishaw) was used to investigate the transformation of nanoparticles under anoxic conditions and aerobic conditions.

Experimental procedure

In the test of 4-CP removal by Fe⁰ nanoparticles and mixed Fe⁰/Fe₃O₄ nanoparticles, experiments were conducted in 20 mL flasks containing 15 mL solutions of 4-CP. The initial concentration of 4-CP was 20 mg L⁻¹. Fe⁰ nanoparticles (20 mg) and mixed Fe⁰ (20 mg)/Fe₃O₄ (20 mg) nanoparticles were added to the Fe⁰ nanoparticles system and mixed Fe⁰/Fe₃O₄ nanoparticles system, respectively. The initial pH value of the systems was not adjusted. In order to keep the reactions under anoxic condition, the flasks were sealed completely and placed on a rotary shaker (150 rpm, 30 °C). Samples were withdrawn from various test groups at predetermined time intervals and then filtered by 0.22 μm membranes before analysis.

In the test of 4-CP removal by mixed Fe⁰/reused Fe₃O₄ nanoparticles, experiments were conducted in 50 mL flasks containing 15 mL solutions of 4-CP (20 mg L⁻¹). The reused Fe₃O₄ nanoparticles were the solid residues from the reaction of the 4-CP/Fe₃O₄/H₂O₂ system. In the

4-CP/Fe₃O₄/H₂O₂ system, Fe₃O₄ nanoparticles (20 mg) and hydrogen peroxide (1.0 ‰) were added to the 50 mL flask with 15 mL solutions of 4-CP (20 mg L⁻¹), and the flask was sealed with the sealing film for sterile culture vessel and placed on a rotary shaker (150 rpm, 30 °C). After 30 h, the flask was taken out of the rotary shaker and the solutions were withdrawn completely. The solid residues were the reused Fe₃O₄ nanoparticles. After this, new 4-CP solutions (20 mg L⁻¹) and Fe⁰ nanoparticles (20 mg) were added into the flask containing the reused Fe₃O₄ nanoparticles. The initial pH value of the system was not adjusted. The flask with mixed Fe⁰/reused Fe₃O₄ nanoparticles was sealed with sealing film to create a sterile culture vessel and the systems were under aerobic conditions. The reaction conditions were the same as mentioned above (150 rpm, 30 °C). Samples were withdrawn from various test groups at predetermined time intervals and then filtered by 0.22 μm membranes before analysis.

Analytical methods

4-CP and its byproducts were quantified using a high-performance liquid chromatograph (HPLC) (Agilent 1100, Shanghai Agilent Ltd, China). The HPLC was equipped with an L-4000 UV-visible detector and a C¹⁸ column. The mobile phase for 4-CP consisted of 60% methanol and 40% distilled water. The detection wavelength was 280 nm for 4-CP and the flow rate was 1 mL min⁻¹. Chlorine ions were quantified using a DX-100 ion chromatograph (DIONEX Company, Germany). Eluent was Na₂CO₃ (3.5 mM) and NaHCO₃ (1.0 mM), and eluent flow was 1.2 mL min⁻¹.

RESULTS AND DISCUSSION

Removal of 4-CP by Fe⁰ and mixed Fe⁰/Fe₃O₄ nanoparticles

Based on the previous studies, 4-CP adsorbed by Fe₃O₄ nanoparticles (<10%) was rather limited after 24 h (Cheng *et al.* 2015). As shown in Figure 1, the removal efficiency of 4-CP by Fe⁰ (9.4–48.1%) nanoparticles was higher than that of mixed Fe⁰/Fe₃O₄ nanoparticles (9.4–31.6%). Hydrogen peroxide could be produced by the reaction between Fe⁰ nanoparticles and oxygen in solution (Bhowmick *et al.* 2014). The Fenton-like reaction between hydrogen peroxide and Fe₃O₄ nanoparticles could produce hydroxyl radical. And the hydroxyl radical plays a significant role in removing

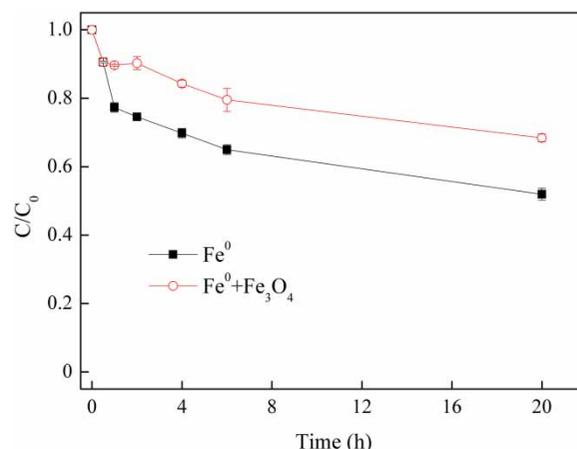


Figure 1 | Removal of 4-CP by Fe⁰ and mixed Fe⁰/Fe₃O₄ nanoparticles (Fe⁰ nanoparticles: 20 mg, Fe₃O₄ nanoparticles: 20 mg, vol.: 15 mL; T: 30 °C, shaking rate: 150 rpm).

4-CP due to strong oxidizing capability (Xu & Wang 2012; Cheng *et al.* 2015; Girit *et al.* 2015). However, hydrogen peroxide generated in the mixed Fe⁰/Fe₃O₄ system was rather limited since the oxygen contained in the system was very limited. As a result, the amount of hydroxyl radicals generated from Fe₃O₄ nanoparticles and hydrogen peroxide were very little. In addition, the dosage of Fe⁰ nanoparticles and Fe₃O₄ nanoparticles was high in the system. It was not conducive to the dispersion of nanoparticles. Moreover, parts of the reactive sites on the surface of Fe⁰ nanoparticles were occupied by Fe₃O₄ nanoparticles. As a result, the reaction between Fe⁰ nanoparticles and 4-CP was hindered by the addition of Fe₃O₄ nanoparticles.

The removal mechanism of chlorophenols involved dechlorination (Xu *et al.* 2013). Thus, chlorine ions were also determined in the system. As shown in Figure 2, the

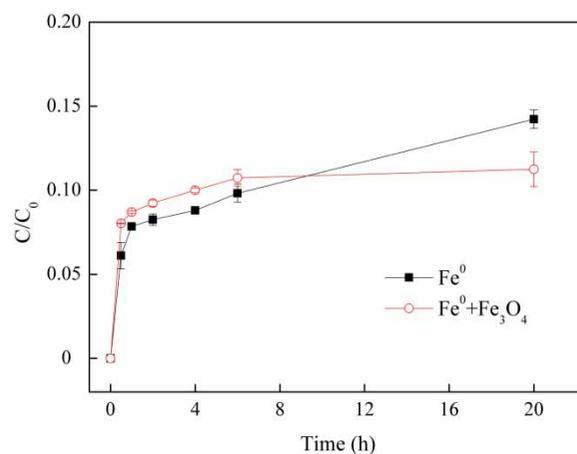


Figure 2 | Dechlorination of 4-CP by Fe⁰ and mixed Fe⁰/Fe₃O₄ nanoparticles (Fe⁰ nanoparticles: 20 mg, Fe₃O₄ nanoparticles: 20 mg, vol.: 15 mL; T: 30 °C, shaking rate: 150 rpm).

dechlorination efficiency by mixed Fe⁰/Fe₃O₄ nanoparticles was higher than that by Fe⁰ nanoparticles in the initial 6 h. And then dechlorination continued. However, when the reaction time was extended to 20 h, the dechlorination efficiency by mixed Fe⁰/Fe₃O₄ nanoparticles (11.3%) was lower than that by Fe⁰ nanoparticles (14.2%). Clearly, chlorine ion in the Fe⁰ nanoparticles system was increased continuously during the reaction, but chlorine ion in the mixed Fe⁰/Fe₃O₄ nanoparticles system was increased slowly and tended to be stagnant after 6 h. It illustrated that the addition of Fe₃O₄ nanoparticles was conducive to the dechlorination of 4-CP at the start of the reaction, while the dechlorination of 4-CP was hindered as the reaction time extended. As explained above, at the beginning of the reaction, Fe⁰ nanoparticles and oxygen in the solution could react to generate hydrogen peroxide, and then Fe₃O₄ nanoparticles and hydrogen peroxide could react to generate hydroxyl radicals. As a result, the reductive dechlorination and oxidation dechlorination of 4-CP could occur in the mixed Fe⁰/Fe₃O₄ nanoparticles system. However, hydrogen peroxide was no longer produced due to the consumption of oxygen with the increase of reaction time. And thus catalytic oxidation of 4-CP with Fe₃O₄ nanoparticles could not continue. In addition, parts of the reactive sites on the surface of Fe⁰ nanoparticles were occupied by Fe₃O₄ nanoparticles. As a result, the reaction between Fe⁰ nanoparticles and 4-CP was hindered by the addition of Fe₃O₄ nanoparticles.

Comparing the removal efficiency (Figure 1) with the dechlorination efficiency of 4-CP (Figure 2) by Fe⁰ and mixed Fe⁰/Fe₃O₄ nanoparticles, clearly, the removal efficiency of 4-CP was higher than the dechlorination efficiency in the two systems. Moreover, the difference between the removal efficiency and the dechlorination efficiency in mixed Fe⁰/Fe₃O₄ nanoparticles was less than that of Fe⁰ nanoparticles within 6 h. It illustrated that the proportion of the dechlorination in the 4-CP removal was increased by the addition of Fe₃O₄ nanoparticles. In other words, the catalytic oxidation of 4-CP with Fe₃O₄ nanoparticles contributed to the dechlorination. The difference between the removal efficiency and the dechlorination efficiency of 4-CP gradually increased with the increase of reaction time. It illustrated that the catalytic oxidation of 4-CP with Fe₃O₄ nanoparticles was gradually weakened, and the dechlorination was mainly attributed to the reducing action of Fe⁰ nanoparticles in the later stage of the reaction.

Moreover, the initial pH value was about 7.0, and pH values were decreased to about 5.0 and 6.0 after 20 h reaction in the Fe⁰ and mixed Fe⁰/Fe₃O₄ nanoparticles system, respectively. Opposite results were reported by other studies

(Kumar *et al.* 2013, 2014b). It could be due to the different experimental systems and conditions. Formic acid and acetic acid were also detected in the Fe⁰ and mixed Fe⁰/Fe₃O₄ nanoparticles systems. It illustrated that 4-CP could convert into the acids with low molecular weight as the reaction proceeded, which resulted in the decrease of pH value. However, the reducing action of Fe⁰ nanoparticles did not produce carboxylic acids. Thus, the catalytic oxidation action of Fe₃O₄ nanoparticles to remove 4-CP did take place. In the Fe⁰ nanoparticles system, Fe⁰ nanoparticles could convert into Fe₃O₄ (Cheng *et al.* 2010). And acids with low molecular weight could also be produced by catalytic oxidation of 4-CP.

Removal of 4-CP by mixed Fe⁰/reused Fe₃O₄ nanoparticles

As shown in Figure 3, the removal efficiency of 4-CP was increased from 15.8% to 41.9% as the time increased from 0.5 h to 6 h. And the dechlorination efficiency was increased from 12.7% to 37.1% as the time increased from 0.5 h to 6 h. Clearly, the removal efficiency of 4-CP was slightly higher than the dechlorination efficiency in the mixed Fe⁰/reused Fe₃O₄ nanoparticles system. It illustrated that the proportion of the dechlorination in the 4-CP removal was high. Moreover, pH value was decreased from 7.0 to about 5.0 in the mixed Fe⁰/reused Fe₃O₄ nanoparticles system. And acids with low molecular weight were also detected in the system.

Comparing to the mixed Fe⁰/Fe₃O₄ nanoparticles systems, both the removal efficiency and the dechlorination

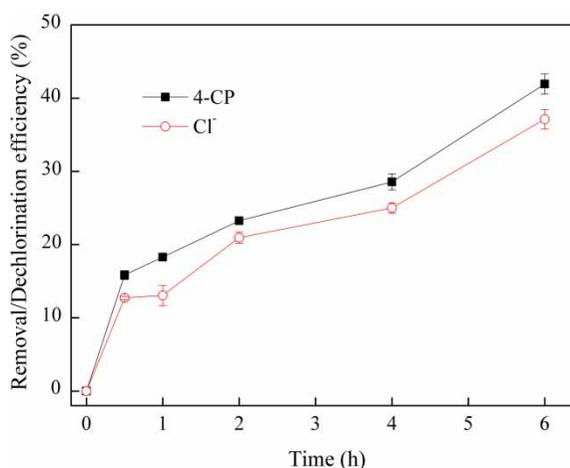


Figure 3 | Removal and dechlorination of 4-CP by mixed Fe⁰/reused Fe₃O₄ nanoparticles (Fe⁰ nanoparticles: 20 mg, Fe₃O₄ nanoparticles: 20 mg, vol.: 15 mL; T: 30 °C, shaking rate: 150 rpm).

efficiency of 4-CP were higher in the mixed Fe⁰/reused Fe₃O₄ nanoparticles system. On the one hand, hydrogen peroxide generated by Fe⁰ nanoparticles and oxygen in solution under aerobic conditions was higher than that in anoxic conditions. And then the catalytic oxidation of 4-CP with Fe₃O₄ nanoparticles could be improved. On the other hand, Fe₃O₄ nanoparticles were eroded and aggregated, and chain and flower structures were developed with the increase of reaction time, i.e. rough surfaces were formed. The erosion points were the sources of the surface active sites of Fe₃O₄ nanoparticles (Cheng *et al.* 2015). In addition, some surface defects of nanoscale iron could form, which could be used as active sites in the process of dechlorination (Gotpagar *et al.* 1999). Thus, surface active sites of Fe₃O₄ nanoparticles could increase after they were used. As a result, the removal efficiency and dechlorination efficiency of 4-CP were improved by the mixed Fe⁰/reused Fe₃O₄ nanoparticles.

The transformation of nanoparticles

The transformation of nanoparticles under anoxic conditions

As shown in Figure 4, in the Fe⁰ nanoparticles system, Fe₃O₄ and FeOOH were the main product of Fe⁰ nanoparticles. In the mixed Fe⁰/Fe₃O₄ nanoparticles system, the solid substance was mainly in the form of Fe₃O₄, and a weak peak of FeOOH was also observed in the XRD pattern. So, it was not possible

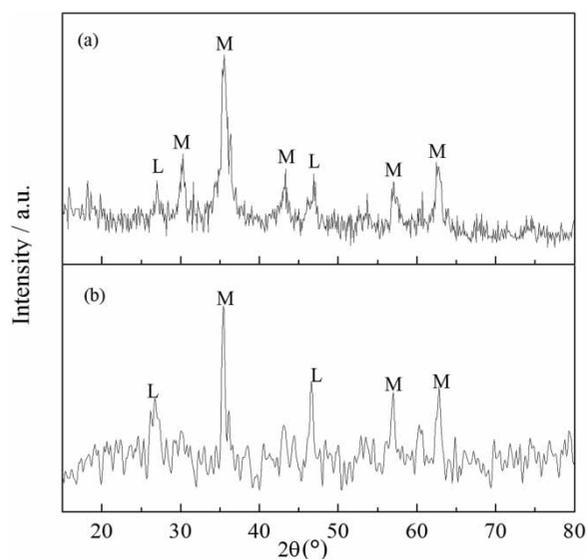


Figure 4 | XRD pattern of nanoparticles after reacting with 4-CP: (a) Fe⁰ + Fe₃O₄; (b) Fe (M: Fe₃O₄; L: FeOOH).

to determine whether Fe₃O₄ nanoparticles converted into FeOOH in the mixed Fe/Fe₃O₄ nanoparticles system.

To investigate the surface properties of the nanoparticles, Raman spectra of the nanoparticles after the reaction were obtained. As shown in Figure 5, the peak at 665 cm⁻¹ is the characteristic peak of Fe₃O₄ (Neff *et al.* 2006; Xue *et al.* 2009). Moreover, there were other obvious peaks at 250, 380, 514 and 1,294 cm⁻¹. In the Fe⁰ nanoparticles system, peak type of substance was sharper than that of the mixed Fe⁰/Fe₃O₄ nanoparticles system. However, higher Raman intensity was observed in the mixed Fe⁰/Fe₃O₄ nanoparticles system.

In addition, the peak at 380 cm⁻¹ could be produced by the molecular vibration of 4-CP adsorbed on the surface of nanoparticles (Cheng *et al.* 2015). The peak at 250 cm⁻¹ indicated the bending vibration produced by the aliphatic chain. Some acids with low molecular weight were produced in the system, and then they were adsorbed on the surface of nanoparticles, which could produce the vibration peaks. The peak at 514 cm⁻¹ might be produced by the stretching vibration of C-Cl, and the peak at 1,294 cm⁻¹ might be produced by the stretching vibration of C-C.

The transformation of nanoparticles under aerobic conditions

The catalytic oxidation of 4-CP with Fe₃O₄ nanoparticles was investigated in our previous studies, and the XRD pattern showed that no new solid matter was produced

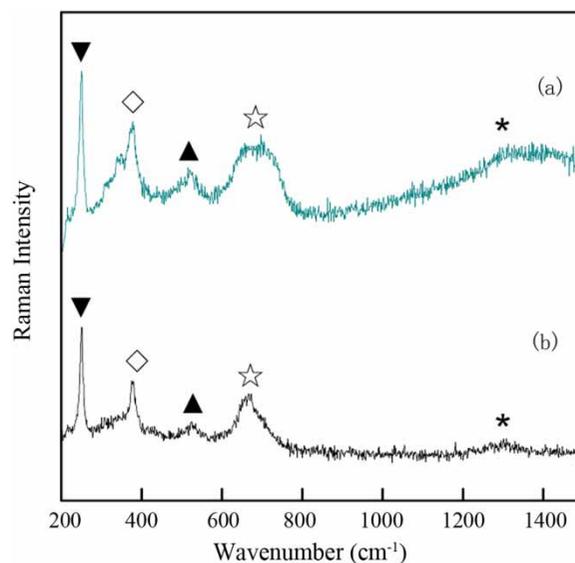


Figure 5 | Raman spectra of nanoparticles after reacting with 4-CP: (a) Fe⁰ + Fe₃O₄; (b) Fe.

(Cheng et al. 2015). It indicated that the Fe₃O₄ nanoparticles did not transform to another material after reaction. As shown in Figure 6, the composition of the mixed Fe⁰/reused Fe₃O₄ nanoparticles underwent change after reacting with 4-CP. In addition to Fe₃O₄, FeOOH was detected in the system. Moreover, similar to the Raman spectra of the mixed Fe⁰/Fe₃O₄ nanoparticles system under anoxic conditions (section on the transformation of nanoparticles under anoxic conditions), there were five different peaks at 250, 380, 514, 665 and 1,294 cm⁻¹ in the system under aerobic conditions (Figure 7).

The mechanisms of 4-CP removal

There was 4-CP, Fe⁰, Fe₃O₄, O₂ and H₂O in the mixed Fe⁰/Fe₃O₄ nanoparticles system. Fe⁰ is a reactive metal with standard redox potential of -0.440 V. As a result, Fe⁰

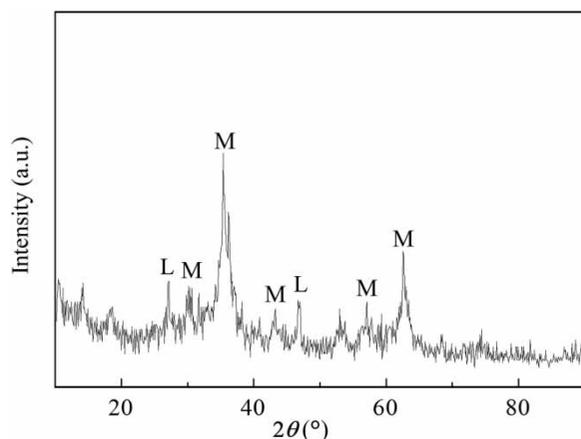


Figure 6 | XRD pattern of nanoparticles after reacting with 4-CP under aerobic conditions (M: Fe₃O₄; L: FeOOH).

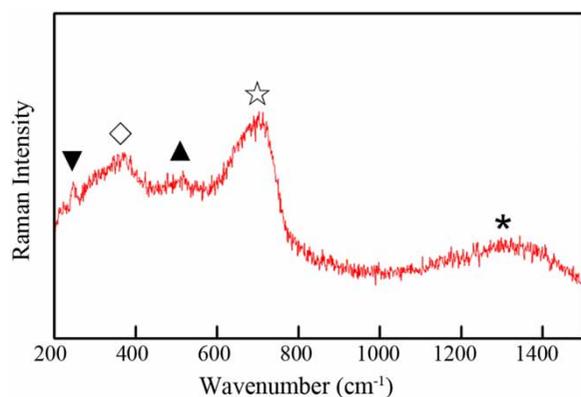


Figure 7 | Raman spectra of nanoparticles after reacting with 4-CP under aerobic conditions.

nanoparticles would be rapidly oxidized in the presence of oxygen. It was reported that two reaction pathways were involved in the reaction between Fe⁰ nanoparticles and oxygen (Figure 8). One pathway was that hydrogen peroxide could be generated by the reaction of oxygen and Fe⁰ nanoparticles through a two-electron-transfer step (Figure 8(a)) (Joo et al. 2004, 2005). The other pathway was that hydrogen peroxide could be generated by the reaction of oxygen and Fe⁰ nanoparticles through a series of single electron transfer steps (Figure 8(b)) (Leupin & Hug 2005; Englehardt et al. 2007). Anyway, hydrogen peroxide was produced in the system no matter what pathway is true. The essence of the reaction was hydroxyl radicals and other intermediate oxidants generated by Fe²⁺ and hydrogen peroxide through Fenton reaction. As a result, pollutants were removed by these oxidants. However, during the generation of hydrogen peroxide, oxygen played an important role.

4-CP could be catalytically oxidized by Fe₃O₄ nanoparticles in the presence of hydrogen peroxide (Cheng et al. 2015). In the mixed Fe⁰/Fe₃O₄ nanoparticles system under anoxic conditions, hydrogen peroxide was very limited due to the lack of oxygen. As a result, catalytic oxidation action of Fe₃O₄ nanoparticles only played a limited role for the 4-CP removal, and the removal of 4-CP was mainly attributed to the reducing action of Fe⁰. However, in the mixed Fe/Fe₃O₄ nanoparticles system under aerobic conditions, hydrogen peroxide was relatively high due to adequate oxygen. As a result, more 4-CP was catalytically oxidized by Fe₃O₄ nanoparticles. Meanwhile, the reducing action of Fe⁰ would be affected due to the oxidation of Fe⁰ nanoparticles.

In conclusion, the removal of 4-CP in the mixed Fe⁰/Fe₃O₄ nanoparticles system was mainly attributed to the effects of both Fe⁰ and Fe₃O₄ nanoparticles – reducing action of Fe⁰ nanoparticles and catalytic oxidation action of Fe₃O₄ nanoparticles. The proportion of the two actions would change with environmental conditions, and the two effects would restrict each other. The reducing action of Fe⁰ nanoparticles was the major factor under anoxic

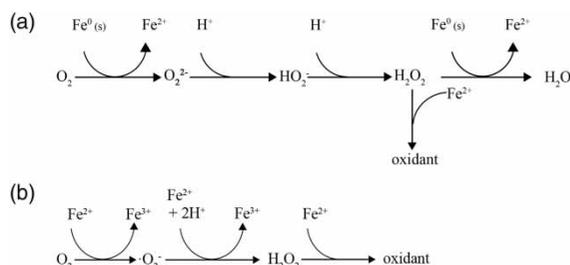


Figure 8 | Proposed mechanism of Fe⁰-oxygen reaction.

conditions. And the catalytic oxidation action of Fe₃O₄ nanoparticles became an important reason that could not be ignored under aerobic conditions; however, the proportion of the two effects would change with the content of oxygen in the system. Moreover, the dosage of Fe⁰ nanoparticles and Fe₃O₄ nanoparticles would influence the reactive sites on the surface of the nanoparticles, and thus the degradation and adsorption process were affected. Figure 9 demonstrates the mechanism of 4-CP removal by the mixed Fe/Fe₃O₄ nanoparticles. The process of oxygen converted to hydrogen peroxide is omitted, and the reaction of hydrogen peroxide and Fe₃O₄ is also omitted in Figure 9. The essence of 4-CP removal is the reductive dechlorination by Fe⁰ nanoparticles and the oxidative dechlorination by Fe₃O₄ nanoparticles, and the oxidation process and the reduction process were carried out respectively. As a result, both the reduction and the oxidation products were present in the mixed Fe⁰/Fe₃O₄ nanoparticles system. Moreover, in the Fe⁰ nanoparticles system, Fe₃O₄ could be generated as the reaction proceeded. Thus, the catalytic oxidation action of Fe₃O₄ might occur.

CONCLUSIONS

Under anoxic conditions, the removal efficiency of 4-CP was lower in the system with mixed Fe⁰/Fe₃O₄ nanoparticles than that with Fe⁰ nanoparticles alone, which suggested that the addition of Fe₃O₄ nanoparticles hindered the removal of 4-CP by Fe⁰ nanoparticles. However, the dechlorination efficiency of 4-CP was improved in the initial 6 h when Fe₃O₄ nanoparticles were added, which indicated that the catalytic oxidation of 4-CP with Fe₃O₄ nanoparticles contributed to the dechlorination. Under aerobic conditions, the reused Fe₃O₄ nanoparticles would improve the removal and dechlorination of 4-CP, and the

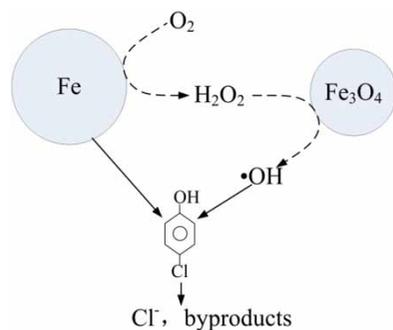


Figure 9 | Illustration of the mechanism for the 4-CP removal by mixed Fe⁰/Fe₃O₄ nanoparticles.

dechlorination efficiency of 4-CP was increased obviously. Fe⁰ nanoparticles were transformed to Fe₃O₄ and FeOOH during the process, and Raman spectra reflected that 4-CP, the acids with low molecular weight (products of 4-CP) and some other chlorinated byproducts could be adsorbed on the surface of Fe₃O₄ nanoparticles. It is proposed that the removal of 4-CP was due to the effects of both Fe⁰ and Fe₃O₄ nanoparticles – reducing action of Fe⁰ and catalytic oxidation action of Fe₃O₄. The reducing action of Fe⁰ was the major factor under anoxic conditions. And the catalytic oxidation action of Fe₃O₄ became an important reason that could not be ignored under aerobic conditions.

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