

Comparison of reductive dechlorination of *p*-chlorophenol using Fe⁰ and nanosized Fe⁰

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Abstract

Chlorophenols, as a kind of important contaminants in groundwater, are toxic and difficult to biodegrade. Laboratory tests were conducted to examine zero-valent iron as an enhancing agent in the dechlorination of chlorinated organic compounds. Nanoscale iron particles were synthesized from common precursors KBH₄ and FeSO₄. Batch experiments were performed to investigate the reduction of *p*-chlorophenol (4-CP) by both common Fe⁰ and nanoscale Fe⁰. Comparison of 300 mesh/100 mesh/commercial reductive iron powders showed that size of iron particles played an important role in reduction process. Initial concentration and pretreatment of iron particles also influenced the chlorination rate. Nanoscale Fe⁰ offered much more advantages for treatment of 4-CP compared with common iron particles, such as stability and durability. And they can be used to treat contaminants in groundwater over a long time. Among different parts of synthesized nanoscale iron particle solution, the very fine particles were the major agent for treatment of pollutants. As for preservation of nanoscale Fe⁰, ethanol was recommended.

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Keywords: Iron; Nanoscale iron; 4-CP; Dechlorination; Stability; Preservation

1. Introduction

As wood preservatives, anti-rust agents, pesticides, chemical materials and intermediates, chlorinated phenols were used extensively. Then they came into environment through volatilising, container leaking, wastewater draining, pesticides using, and incinerating of some products [1]. Eventually, they became a kind of important contaminants in groundwater. Most of them are toxic, carcinogenic, and intractable [2]. Moreover, they could persist in the environment for a long time, and do harm to human health by bioaccumulation [3]. Most chlorophenols are listed as priority pollutants by the USEPA [4].

Due to the aryl structure and the presence of chlorine atom, chlorinated phenols are exceptionally recalcitrant towards chemical reactions aimed at their destruction. Biodegradation is a common treatment method of chlorophenols with the half-life

period being more than a few days [5,6]. But introducing chlorine atom greatly decreases the biodegradability of organic compounds. Advanced oxidation technologies have shown to be effective in degrading these pollutants using nanosized TiO₂, UV/O₃, UV/H₂O₂ or γ -radius [7–9], though the cost for such treatment is high. As a powerful reducing agent, zero-valent iron attracted a great deal of attention since 1980s. Especially in the 1990s, researches on zero-valent iron were carried out broadly. Degradation performance, kinetics, reaction conditions, field tests were developed [10–16]. Due to their high specific surface area and high surface reactivity, nanoscale iron particles offer much more advantages for treatment of chlorinated phenols compared to conventional iron particles [17–19]. The nanoparticles can also remain in suspension for extended periods of time to establish an in situ treatment zone. Equally important, they provide enormous flexibility for both in situ and ex situ applications.

Synthesis of nanoscale iron particles was achieved from common precursors KBH₄ and FeSO₄ in this paper. The experiments were performed to investigate the reduction of *p*-chlorophenol

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(4-CP) by both common Fe⁰ and nanoscale Fe⁰. The effects of reaction conditions and preservation method of nanoscale Fe⁰ were discussed.

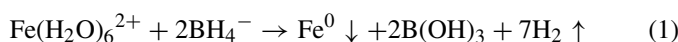
2. Experimental

2.1. Chemicals and materials

Iron powders (~100 mesh and ~300 mesh, reagent) were obtained from Beijing Wotai Technology Ltd. Company. Commercial reductive iron powders (≥98%, reagent) and *p*-chlorophenol (4-CP, ≥99%, reagent) were purchased from Tianjin Jinke Fine Chemical Industry Research Institute. Kalium borohydride (KBH₄, 96%) was supplied by Nankai Fine Chemical Factory. Ferrous sulfate (FeSO₄·7H₂O, 99.0%–101.0%) was supplied by Shenyang Reagent Factory. Methanol (99%, reagent), ethanol (99.7%, reagent) and sulfuric acid (98%, reagent) were supplied by Beijing Chemical Factory. Argon gas (Ar, 99.99%) and nitrogen gas (N₂, 98%) were supplied by Beijing Aolin Gas Company.

2.2. Preparation of nanoparticles

Synthesis of nanoscale iron particles was achieved by adding 100 mL 0.04M FeSO₄·7H₂O aqueous solution dropwise to a three-necked flask containing 250 mL 0.08M KBH₄ aqueous solution at ambient temperature. The process was performed in Ar atmosphere. Ferric iron was reduced by borohydrate according to the following reaction [20]:



Synthesized iron particles were deposited in Ar atmosphere, and then washed with ethanol. Then, they were washed with deionized water after deposited. Some solutions with iron particles were extracted before washing with ethanol/deionized water.

The morphology of common iron particles was viewed with a scanning electron microscope (SEM, JSM-6301F, JEOL). Synthesized iron particles were observed with an environmental scanning electron microscope (ESEM, FEI Quanta 200 FEG, Holand FEI Company).

2.3. Experimental procedure

Batch experiments for 4-CP transformation were conducted as two groups. The group with common iron particles was conducted in 250-mL three-necked flasks containing 150 mL of an aqueous solution of 4-CP. The initial concentration of 4-CP was 20 and 40 mg/L, respectively. Metal to solution ratio was 2 and 4 g/150 mL, accordingly. The flasks were sealed with rubber plugs and placed on a rotary shaker (TZ-2EH, Beijing Wode Company) during the entire experiment period. The rotate speed and the temperature of rotary shaker were set to 150 rpm and 30 °C separately. Some solutions were purged with N₂ and others not. Some solutions were pretreated using 0.1M H₂SO₄. All samples were filtrated with 0.45 μm filter film to be analyzed.

The group with synthesized iron particles was conducted in 12-mL bottles. Iron particles (1 mL, about 3 mg) were loaded into bottles containing 10 mL of an aqueous solution of 4-CP. Parallel control experiments were performed without the iron particles. Setting of rotary shaker was the same as the group above.

2.4. Analysis

4-CP and its products were quantified with an Agilent 1100 HPLC (Shanghai Agilent Ltd) equipped with a C¹⁸ column and an L-4000 UV-vis detector. The mobile phase for 4-CP consisted of 60% methanol and 40% water distilled three times. The flow rate was 1 mL/min and the detector wavelength was 280 nm for 4-CP. Chlorine ion was quantified with a DX-100 ion chromatogram (IC, DIONEX Company, Germany). The operational conditions were: eluent at 3.5 mM Na₂CO₃/1.0 mM NaHCO₃; eluent flow at 1.2 mL/min, sample loop volume at 250 μL, and run time at 6 min. Deionized water was used as blank. UV-vis recording spectrophotometer (UV-2401 PC, Japan) was used to measure the absorbance of 4-CP before and after reaction.

3. Results and discussion

3.1. Characterization of Fe particles

The surface morphology of different iron particles is shown in Fig. 1. The surface of commercial reductive iron powders was rough and the shape was anomalous (a). The size of particles differed a great deal. Most particles had an average diameter of 62 μm as observed with an SEM. The surface of iron powders (~100 mesh) was rough, too. But the sizes of particles did not differ a lot (b). The surface morphology of iron powders (~300 mesh) was nearly the same as the iron powders (~100 mesh). But the size was much smaller and had a better uniformity (c). The average diameters of these iron powders (~100 mesh and ~300 mesh) were 150 and 50 μm, separately. The image of the synthesized Fe particles was obtained with an ESEM under a magnification of 60,000× (d). Most particles had diameters in the range of 10–100 nm.

3.2. Transformation of 4-CP by common iron powder

Fig. 2 illustrated the reduction of 4-CP by different iron powders. The initial concentration of 4-CP was 20 mg/L. As shown in Fig. 2, the degradation rate of 4-CP treated by 300 mesh iron powders was much higher than the other two. One hundred mesh iron powders and commercial reductive iron showed comparative effects during the test periods. Commercial reductive iron powders produced however higher reductive rate than 100 mesh iron powders in the first 2 h. As seen in SEM images, the sizes of commercial reductive iron particles differed a great deal. Most particles had an average diameter of 62 μm, which was smaller than the 100 mesh iron powders diameter (150 μm). In view of the performances of these iron powders, it could be concluded that the size of iron particles played an important role in reduction process. The smaller the particle, the more active it is. And

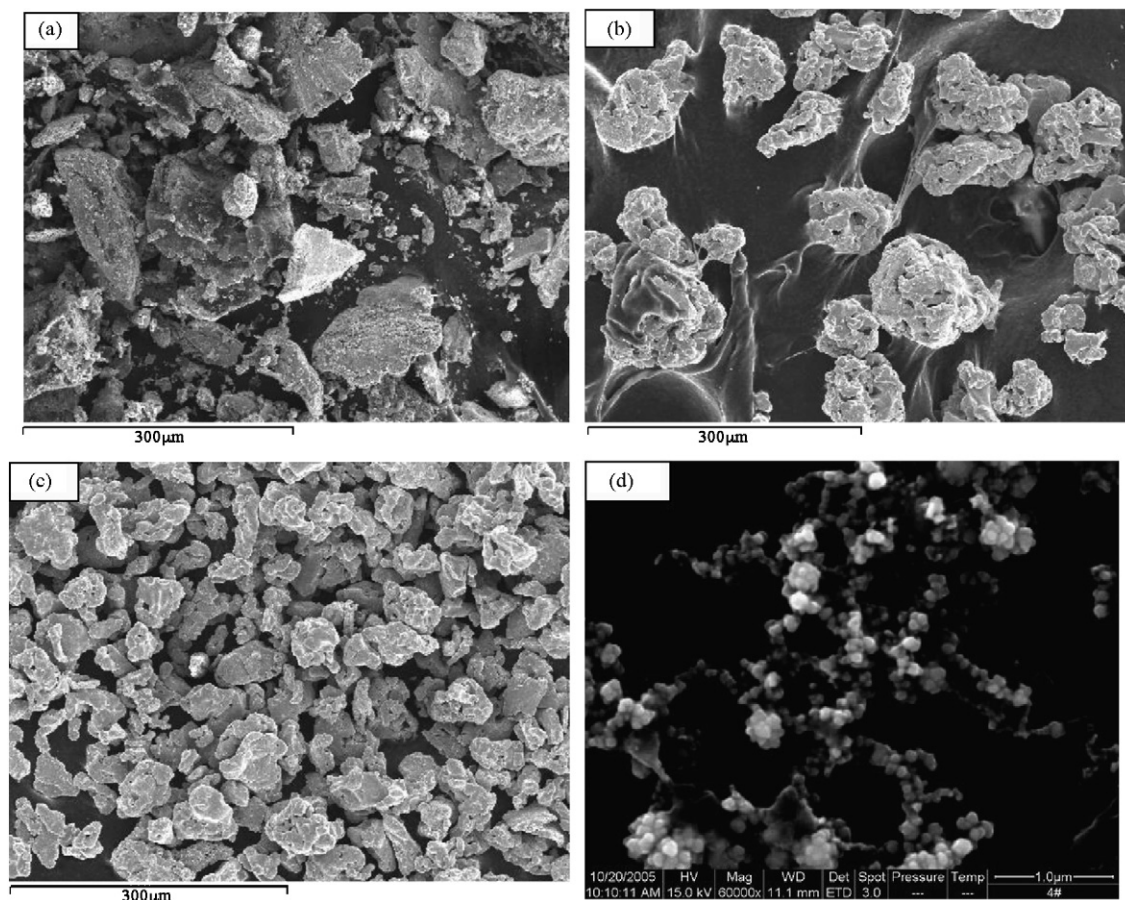


Fig. 1. SEM images of iron particles. (a) Commercial reductive iron powders; (b) iron powders (~ 100 mesh); (c) iron powders (~ 300 mesh); (d) nanosized iron particles.

the specific surface area increased with the decrease of particle size, which offered more interfaces for iron and 4-CP. Accordingly, the reaction rate increased. The results implied that the process was an interfacial reaction. He et al. [21] studied reduction of perchloroethylene (PCE) using Ni/Fe of different sizes, and similar results were obtained.

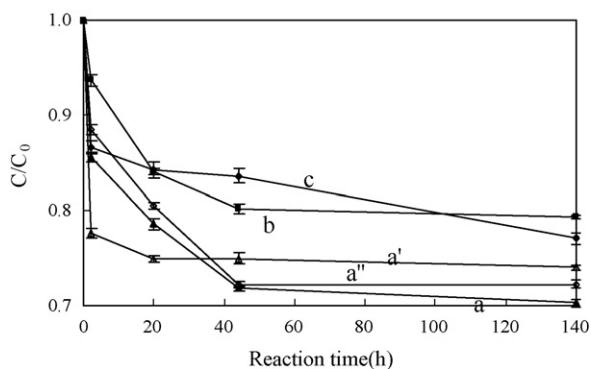


Fig. 2. Reduction of 4-CP by different iron particles. (a) Iron powders (~ 300 mesh); (b) iron powders (~ 100 mesh); (c) commercial reductive iron powders. Particles in (a)/(b)/(c) were pretreated with $0.1\text{ M H}_2\text{SO}_4$. The initial concentration of 4-CP was 20 mg/L . (a') Iron powders (~ 300 mesh); particles were pretreated; initial concentration of 4-CP was 40 mg/L . (a'') Iron powders (~ 300 mesh); particles were not pretreated; initial concentration of 4-CP was 20 mg/L .

Fig. 3 illustrated the reduction of 4-CP by nanosized Fe^0 . The initial concentration of 4-CP was 50 mg/L . As shown in Fig. 3, the degradation rate of 4-CP treated by nanosized iron particles was much higher than common iron powders. And the results implied that the nanoparticle is a better system than the common iron powders.

Effect of initial concentrations was studied in this paper. The curves (a) and (a') in Fig. 2 revealed that reductive rate increased when the initial concentration increased from 20 to 40 mg/L during the first 20 h . Later, the residual concentration of 4-CP

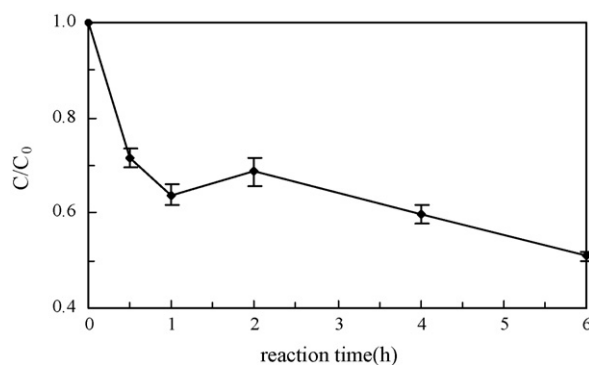


Fig. 3. Reduction of 4-CP by nanosized Fe^0 . Initial concentration of 4-CP was 50 mg/L . Metal to solution ratio was $3\text{ mg}/10\text{ mL}$.

increased when its initial concentration increased. That is to say, the reductive rate decreased when the initial concentration rose. Deng et al. [22] suggested that there were two types of surface sites on the iron: the reactive sites responsible for reduction, and the non reactive sites responsible for the bulk of adsorption. They found that the reactive site density was estimated to be only 2% of the total surface sites. Moreover, they proposed a two-site analytical model to explain the experimental results, in which adsorption took place on both reactive and non-reactive sites, but dechlorination reactions occurred only on reactive sites. In our experiment, we can infer that increase of initial concentration of 4-CP resulted in increase of adsorption and decrease of dechlorination. Also, adsorption was dominant in initial stages. When the adsorption process came into balance, dechlorination was dominant for reductive process. However, some researchers figured that dechlorination rates were pseudo-first-order in reactant concentration, and that initial concentration of pollutants did not impact dechlorination rate obviously in the test range [23,24]. Farrell et al. [25] studied reduction of trichloroethylene (TCE) with zero-valent iron, and concluded that TCE concentrations near aqueous saturation resulted in passivation of the iron surfaces and deviation from first-order reaction kinetics.

Curves (a) and (a'') in Fig. 2 illustrated effect of pretreatment of iron particles. Just as demonstrated in the figure, the pretreated particles offered a higher reductive rate for 4-CP than the non-treated ones. Iron is a kind of active metal and passivation of iron surface is easily occurred. Pretreatment with diluted acid can remove this passivation. Meanwhile, pretreatment corroded iron and increased the roughness of iron surface [26]. Consequently, more reactive sites were offered for organic substance, and reductive rate of 4-CP increased accordingly.

3.3. Transformation of 4-CP by nanoscale iron

Fig. 4 showed the differences of UV curves of 4-CP treated by synthesized nanoscale iron particles compared to the original solution. Peaks at 225 and 280 nm which were specific adsorption spectrum of 4-CP disappeared, and two new peaks arose at 210 and 270 nm. The peaks at 210 and 280 nm are specific adsorption spectrum of phenol [27]. This indicated that 4-CP was completely dechlorinated by nanoscale iron particles and that phenol was the major product. Nanoscale iron particles

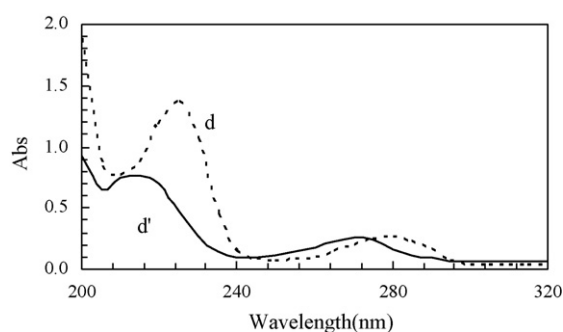


Fig. 4. UV curves of 4-CP solutions before (d)/after (d') treatment by nanoscale iron particles for 20 h. Initial concentration of 4-CP was 20 mg/L. Metal to solution ratio was 3 mg/10 mL.

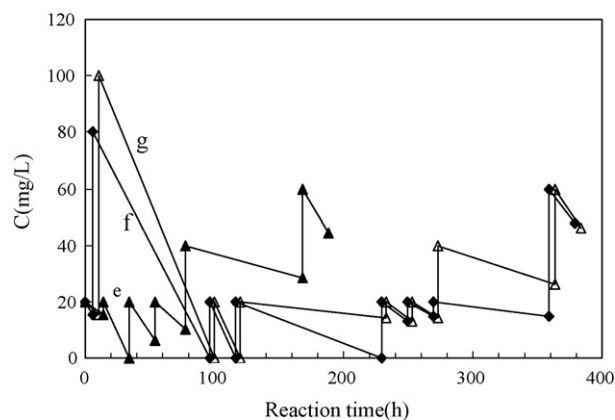
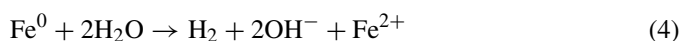
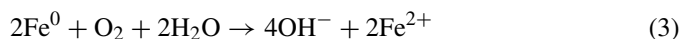


Fig. 5. Reduction of 4-CP solutions with nanoscale iron particles over extended periods of time. Curves (e), (f), (g) represent different series. Metal to solution ratio was 3 mg/10 mL.

offered much more advantages for treatment of 4-CP compared to common iron particles.

For different series, solutions were extracted after reaction for a period of time. And then the bottles containing residual iron particles were filled with fresh 4-CP solutions with different initial concentrations. Repeatedly, reduction of 4-CP solutions with nanoscale iron particles over extended periods of time was evaluated (Fig. 5). For the second batch, 4-CP with the initial concentration of 20 mg/L was completely degraded by nanoscale iron particles within 20 h (curve (e)). When the initial concentration of 4-CP was increased from 20 to 80 mg/L and 100 mg/L, it could also reduce to trace levels within 90 h (curves (f), (g)), which indicates that nanoscale iron particles can completely reduce 4-CP solutions with the initial concentration in the range of 20–100 mg/L within a few days (<4 days). As shown in the figure (curve (f)), 4-CP with the initial concentration of 20 mg/L could still be completely degraded by nanoscale iron particles within 20 h even after four batches. When the initial concentration of 4-CP was increased from 20 to 60 mg/L, the 4-CP concentration was reduced distinctly. It indicated that nanoscale iron particles were of stability and durability. And they can be used for treatment of contaminants in groundwater over a long time. Lien et al. [18] also tested the stability of nanoscale iron particles and concluded that nanoscale iron particles could maintain their activity over a long time (6–8 weeks). However, the activity of iron particles decreased along with the reaction process. It was due to $\text{Fe}(\text{OH})_3$ produced from the reaction process, which led to the passivation of iron surface. And therefore further reaction was blocked.

The general scheme of reactions between 4-CP and Fe^0 were discussed in some published systems [28–30]. As for this system, there are three main species (Fe^0 , 4-CP, H_2O) and a small quantity of O_2 in the initial solutions. The following reactions could take place according to electrochemistry theories:



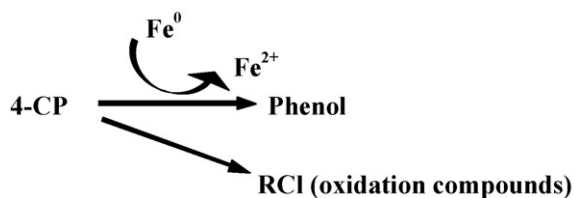
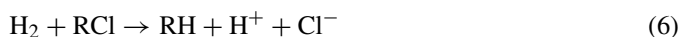
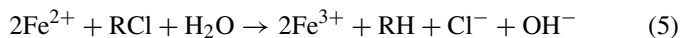


Fig. 6. Pathways for degradation of 4-CP by nanosized Fe⁰.

Considering the reductive activity of Fe²⁺ and H₂, which was produced from the above reactions, the following reactions may also theoretically take place:



In neutral or alkaline solutions,



Unstable Fe(OH)₂ could be transformed rapidly to Fe(OH)₃. So the reaction (5) would hardly occur [31]. Besides, there was very little H₂ produced and no effective catalyzer in this system, and the reaction (6) was very limited. However, not all the 4-CP would be dechlorinated to phenol. And some 4-CP may be transformed to oxidation compounds. So the pathway for degradation of 4-CP by nanosized Fe⁰ may be described as following: Fig. 6.

3.4. Role of different parts of synthesized nanoscale iron particle solution

Very few iron particles were found in the supernatant during the washing process when synthesizing nanoscale iron particles. Deionized water was used as solvent before the first washing process, while ethanol was used for the second. Using these supernatants for treatment of 4-CP solutions, we found that these supernatants were more active than the iron particles deposited. Fig. 7 illustrated reductive rate of 4-CP solution using differ-

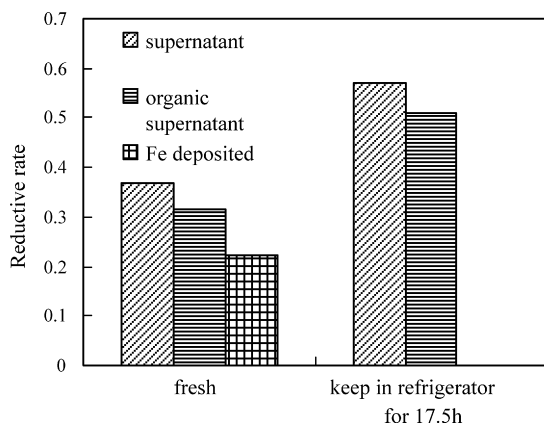


Fig. 7. Reduction of 4-CP solutions by different parts of synthesized iron particles. Initial concentration of 4-CP was 20 mg/L. Supernatant to 4-CP solution ratio was 10 mL/10 mL in the “fresh” group. Fe deposited to 4-CP solution ratio was 1 mL/10 mL. Reaction time was 2 h in “fresh” group, and 5 h in “kept in refrigerator for 17.5 h” group.

ent parts of synthesized nanoscale iron particle solution. The order for their reductive rates is as follows: supernatant > organic supernatant > particles deposited. Two 100-mL bottles were filled up separately with supernatant and organic supernatant and then kept in refrigerator. The temperature was 0 °C. After 17.5 h, particles in supernatant were all deposited at the bottom of the bottles. Using these particles for treatment of 4-CP solutions, they were still of high activities. Reductive rates of 4-CP were 57.2% and 51.1% within 5 h. Xu et al. [28] used synthesized nanoscale iron particles to degrade 4-CP with the initial concentration of 40 mg/L and got a dechlorination rate of 20% after 5 h. Thus, it can be seen that the particles in supernatant were much more capable of disposing 4-CP.

The quantity of iron particles in supernatant was so small that it could be ignored compared to iron particles deposited. But they had greater capability for treatment of 4-CP compared to the latter. As for supernatant and organic supernatant, particles in the former were smaller. It could be implied that the very fine particles were the major agent for treatment of pollutants. This was consistent with the results from common iron particles of different sizes.

3.5. Storage of synthesized nanoscale iron particles

As shown in Fig. 7, the nanoscale iron particles were still of high activities after being kept for 17.5 h in refrigerator, both in deionized water and ethanol. Nanoscale iron particles are quite active and may be easily oxidized even when there is little oxygen. So the storage of synthesized iron particles was a significant problem. Three methods were tested for the storage of nanoscale iron particles in this paper. One group of the solution was transferred to 10-mL bottles sealed with rubber plugs, and deionized water was the solvent. The second group of solution was also transferred to 10-mL bottles, and the solvent was ethanol. The two groups of solution were kept in refrigerator. Temperature in refrigerator was maintained to 0 °C all the time. The residual solution was kept in the three-necked flask that was used for synthesizing iron particles at room temperature. The flask was also sealed with rubber plugs. All the iron particles were deposited after 15 days. Reduction of 4-CP solution was conducted with these iron particles. The particles were used repeatedly the way in Fig. 5. As seen in Fig. 8, the particles from different storages

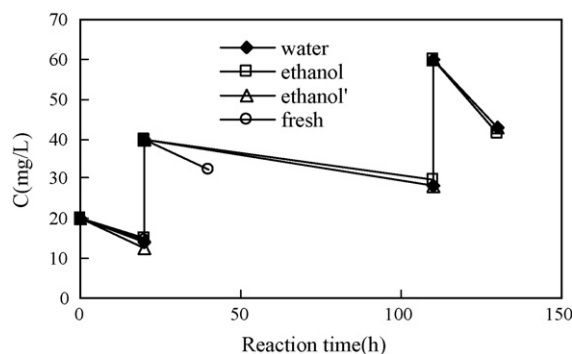


Fig. 8. Reduction of 4-CP solution with nanoscale iron particles from different storages over extended period of time.

performed comparative activity. Furthermore, the activity did not decrease very much compared to that of fresh particles.

Since H₂O molecule has a higher polarity than ethanol, and there is more dissolved oxygen in water, ethanol is considered to be more appropriate for the storage of nanoscale iron particles. It was found that nanoscale iron particles kept in water were easily oxidized during experiments.

Acknowledgements

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