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Reductive Dechlorination of *p*-Chlorophenol by Nanoscale Iron[1]

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Objective To investigate reductive dechlorination of 4-chlorophenol (4-CP) by nanoscale Fe^0 under different conditions. **Methods** Nanoscale Fe^0 was synthesized by using reductive method. 4-CP and its intermediate products were analyzed by HPLC. Chlorine ion was quantified with DX-100 ion chromatograph. Nano-iron particles were observed under a FEI Quanta 200 FEG environmental scanning electron microscope (ESEM). **Results** The size of the particles was in the range of 10-100 nm. The nano-iron particles could reduce 4-CP effectively. The initial concentration of 4-CP increased with the decrease of the relative degradation rate, whereas the reduced amount of 4-CP increased. Temperature could influence both the dechlorination rate and the reaction pathway. Moreover, the stability and durability of nanoscale Fe^0 was evaluated through batch studies over extended periods of time. **Conclusion** The nanoscale Fe^0 can be used for sustainable treatment of contaminants in groundwater.

Key words: Nanoscale iron; 4-CP; Phenol; Dechlorination; Priority pollutant

INTRODUCTION

Chlorinated phenols which are broadly used as antirust, antiseptics and herbicides have become an important contaminant in groundwater. Chlorinated phenols are mostly toxic, carcinogenic and intractable. Moreover, they can persist in the environment for a long time, and do harm to human health by bioaccumulation. Conventional processes such as biological ones fail to remove them effectively[1]. As a powerful reducing agent, zero-valent iron has attracted great attention since the 1980s. Extensive researches on zero-valent iron were carried out, especially in the 1990s. Degradation performance[2], kinetics[3], reaction conditions[4], and field tests[5] were developed. Due to their high specific surface area and high surface reactivity, nanoscale iron particles offer much more advantages over conventional iron particles for the treatment of chlorinated phenols[6-7]. The nanoparticles can also remain in suspension for extended periods of time to establish an *in situ* treatment zone. They provide enormous flexibility for both *in situ* and *ex situ* applications.

Synthesis of nanoscale iron particles was achieved from common precursors KBH_4 and $FeSO_4$ in this study. The experiments were performed to investigate the reduction of *p*-chlorophenol (4-CP) by nanoscale Fe^0 under different conditions. The effects of reaction conditions such as temperature and initial concentration of 4-CP were discussed.

MATERIALS AND METHODS

Synthesis and Characterization of Nanoscale Iron Particles

Synthesis of nanoscale iron particles was achieved by adding 0.04 mol/L $FeSO_4 \cdot 7H_2O$ aqueous solution dropwise to a three-necked flask containing 0.08 mol/L KBH_4 aqueous solution at ambient temperature. The process was performed in Ar atmosphere. Ferric iron was reduced by borohydrate according to the following reaction[8]:

$$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0 \downarrow + 2B(OH)_3 + 7H_2 \uparrow \quad (1)$$

Synthesized iron particles were deposited for 4 h in Ar atmosphere, and washed with ethanol. Then they were washed with deionized water after deposition for 3 h.

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Iron particles were observed under a FEI Quanta 200 FEG environmental scanning electron microscope.

Batch Experiments

Batch experiments for 4-CP transformation were conducted in 12-mL bottles. Iron particles (1 mL) were loaded into bottles containing 10 mL of aqueous solution of 4-CP. The bottles were sealed with rubber plugs and placed on a TZ-2EH rotary shaker (150 r/min) during the entire experiment period. 4-CP and its intermediate products were quantified with an Agilent 1100 HPLC equipped with a C^{18} column and a L-4000 UV-Vis detector. Chlorine ion was quantified with a DX-100 ion chromatograph. All samples were filtrated with 0.45-μm filter film.

RESULTS

Characterization of Fe Particles

Figure 1 displays an image of the synthesized Fe particles obtained with an ESEM under a magnification of 60 000×. The diameters of most particles ranged between 10 nm and 100 nm.

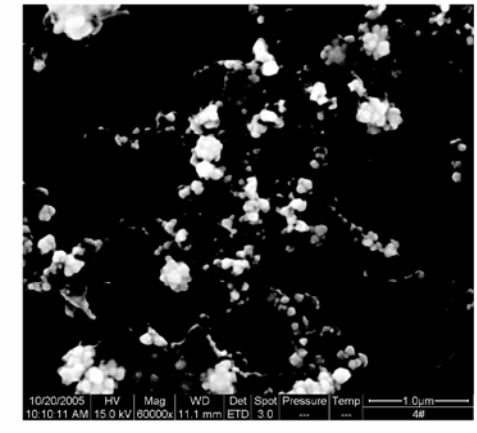

FIG. 1. ESEM image of nanoscale Fe particles.

Stability of the Synthesized Nanoscale Fe^0 Particles

An extended experiment was conducted to monitor the long-term performance of the synthesized nanoscale Fe^0 particles (Fig. 2). 4-CP solution (10 mL) was spiked 8 times into a 12-mL bottle containing 1 mL of synthesized Fe^0 particles.

Effect of Initial Concentrations

Figure 3 shows the reduction of 4-CP with different initial concentrations at 30℃. The release of chloride is depicted in Fig. 4.

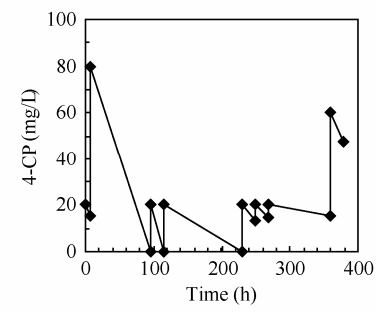

FIG. 2. Reduction of 4-CP over an extended period of time.

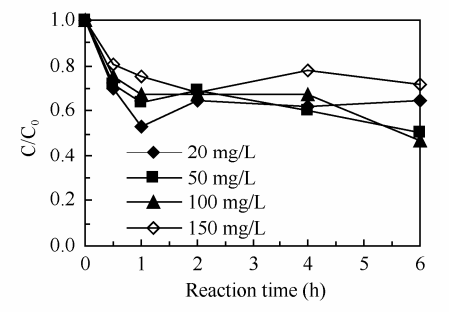

FIG. 3. Reaction of 4-CP with nanoscale Fe (Nano Fe) at 30℃.

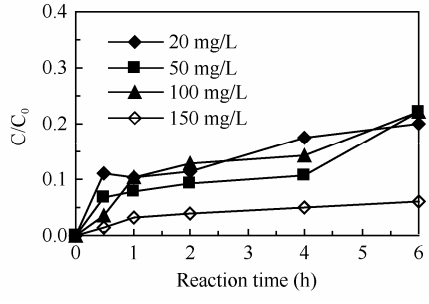

FIG. 4. Cl^- release during the reaction of 4-CP with Nano Fe.

Qualitative analysis shows that one major product is phenol, which presents a peak at 2.410 min in HPLC image (Fig. 5). The results of quantitative analysis for phenol are shown in Fig. 6.

Effect of Temperature

The temperature of rotary shaker was set at 10℃ and 30℃, respectively to investigate its effect. The results are shown in Fig. 7. The amounts of Cl^- and phenol formed at 30℃ were much more than those at 10℃, which implied that the dechlorination rate of 4-CP at 30℃ was higher than that at 10℃.

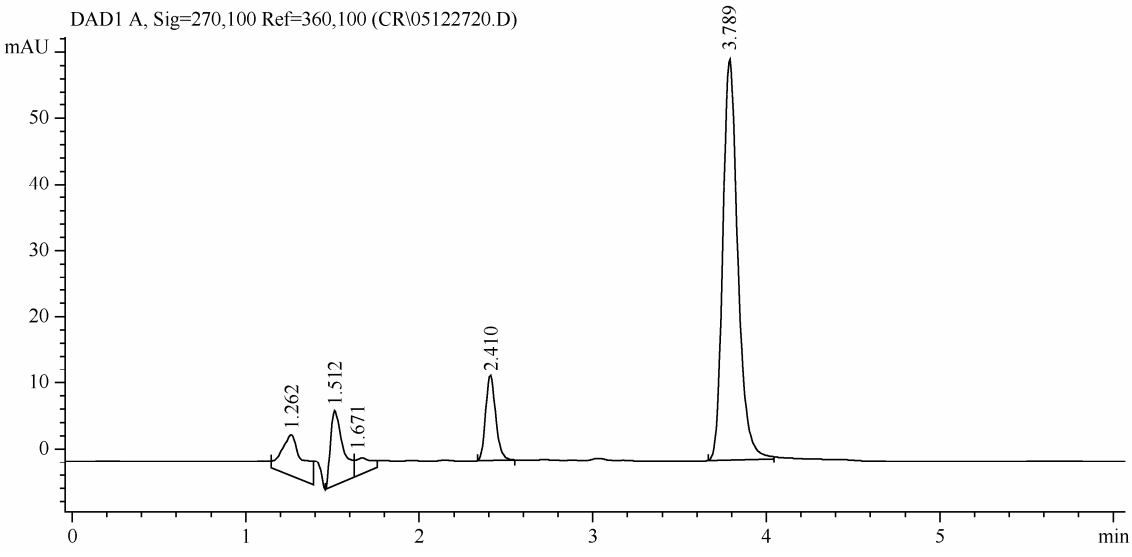

FIG. 5. HPLC image of products from the reaction of 4-CP with Nano Fe.

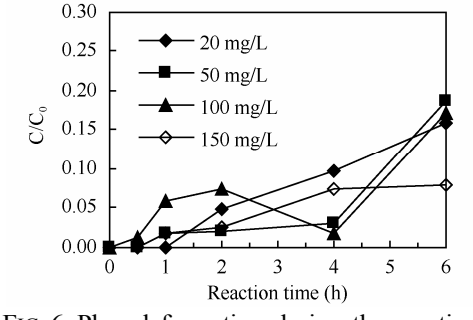

FIG. 6. Phenol formation during the reaction of 4-CP with Nano Fe.

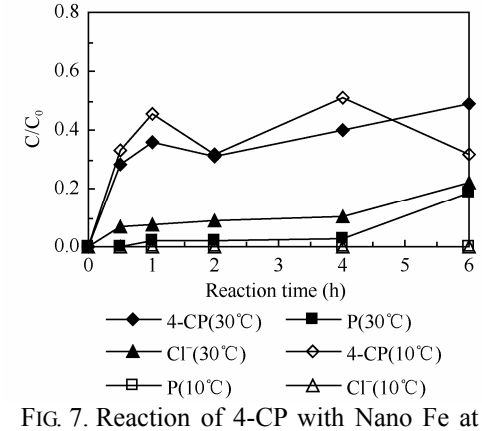

FIG. 7. Reaction of 4-CP with Nano Fe at different temperatures.

DISCUSSION

As shown in Fig. 2, 4-CP with the initial concentration of 20 mg/L could still be completely degraded by nanoscale Fe^0 particles within 20 h even after 4 batches. When the initial concentration of 4-CP was increased from 20 mg/L to 60 mg/L, the 4-CP concentration was reduced distinctly. For the 2nd batch, the initial concentration of 4-CP was increased from 20 mg/L to 80 mg/L, and then reduced to trace levels within 90 h, indicating that nanoscale Fe^0 particles could completely reduce the 4-CP solution with the initial concentration in the range of 20-80 mg/L within a few days (<4 days).

As seen in Fig. 3, the residual concentration of 4-CP increased when its initial concentration increased, especially during the first hour. That is to say, the reductive rate decreased when the initial concentration increased in the test range (20-150 mg/L). Cl^- release was quantified as well and the results implied the same trend (Fig. 4).

As illustrated in Fig. 6, the amount of phenol did not have the same regulation as that of Cl^-. When the initial concentration of 4-CP was 20 mg/L, no phenol was detectable in the first reaction hour. Also, no phenol was detectable in the first half hour when the initial concentration was 50 mg/L. The relative concentrations of Cl^- were 10.4% and 6.9%, respectively. It can be considered that there are other dechlorinated products in this reaction, which also can be discovered on the HPLC image, even though, the reduced amount of 4-CP increases along with the increase of initial concentration.

As seen in Fig. 7, the reductive ratio of 4-CP at 30℃ was lower than that at 10℃. But the relative concentrations of Cl^- and phenol detected at 30℃ were much higher than those at 10℃. This effect may possibly be attributed to the following two factors: adsorption and formation of chlorinated intermediate products.

Although the experimental conditions in this

research such as temperature and initial 4-CP concentrations are different from the actual application conditions, the results indicate that nanoscale Fe^0 can be used for the sustainable treatment of contaminants in groundwater. More research work needs to be done before nanoscale Fe^0 can be practically applied for the remediation of contaminated groundwater.

CONCLUSION

Synthesized nanoscale Fe^0 can reduce 4-CP effectively. The relative degradation rate decreases with the increase of the initial concentration of 4-CP. Temperature can influence both the dechlorination rate and the reaction pathway. Nanoscale Fe^0 can be used for the sustainable treatment of contaminants in groundwater.

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