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Dechlorination mechanism of 2,4-dichlorophenol by Ni/Fe nanoparticles in the presence of humic acid[*]

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Abstract: To understand the feasibility of its application to the in situ remediation of contaminated groundwater, the dechlorination of 2,4-dichlorophenol (2,4-DCP) by Ni/Fe nanoparticles in the presence of humic acid (HA) was investigated. We found that, as high performance liquid chromatography (HPLC) was used, the 2,4-DCP was first quickly reduced to *o*-chlorophenol (*o*-CP) and *p*-chlorophenol (*p*-CP), and then reduced to phenol as the final product. Our experimental results indicated that HA had an adverse effect on the dechlorination of 2,4-DCP by Ni/Fe nanoparticles, as the HA concentration increased, the removal rate decreased evidently. It also demonstrated that 2,4-DCP was reduced more easily to *o*-CP than to *p*-CP, and that the sequence of the tendency in dechlorination of intermediates was *p*-CP>*o*-CP. Transmission electron microscope (TEM) showed that HA could act as an adsorbate to compete reactive sites on the surface of Ni/Fe nanoparticles to decrease the dechlorination rate. Also we concluded that the dechlorination reaction of 2,4-DCP over Ni/Fe nanoparticles progressed through catalytic reductive dechlorination.

Key words: Dechlorination, Ni/Fe nanoparticles, 2,4-dichlorophenol (2,4-DCP), Humic acid (HA)
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INTRODUCTION

Chlorinated organic compounds (COCs) are so widely used that they are almost ubiquitous everywhere (Xu *et al.*, 2005a; 2005b). They are known for their biorefractory, bio-accumulation and toxicity, and they also pose a danger to life when released into the environment (Zhu *et al.*, 2006; Oliver and Nicol, 1982; Schwarzenbach *et al.*, 1979). By their nature, they are highly toxic, mutagenic and possibly carcinogenic compounds that are classified as the priority environmental pollutants by the US EPA (1988). It is definitely needed to have an efficient dechlorination method that is suitable for eliminating chlorophenol from both concentrated industrial effluents and diluted polluted groundwater (Xu *et al.*, 2005b).

Recently, chemical reduction of hazardous compounds such as COCs using zero-valent metals has been intensively studied for either in situ or aboveground treatment of contaminated groundwater. Zero-valent iron is found to serve as a donor of electrons (or the reducing agent) in the reaction (Matheson and Tratnyek, 1994; Xu *et al.*, 2005b), and to be able to react with water to produce hydrogen gas (which can react with COCs) and hydroxide ions (which lead to the increase of the pH of the solutions). The treatment of COCs by zero-valent iron represents one of the latest innovative technologies for environmental remediation (Xu *et al.*, 2005b). Further attempts have been made to increase the dechlorination rate of COCs using hydrogen and noble bimetallic agents such as Ni/Fe, Pd/Fe and Cu/Fe (Doong and Lai, 2005; He and Zhao, 2005; Wei *et al.*, 2006). Cheng and Wu (2001) reported that physical additions

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of Pd^0, Cu^0 or Ni^0 micro-sized powder could reactivate Fe^0 particles that have lost their surface activity. It is well known that the reduction of chlorinated organics by bimetallic particles happens via hydrodechlorination instead of electron transfer, in which Fe acts as the reducing agent, and Ni, Pb, or Cu acts as catalysts. The latter have considered as the good hydrogenation catalysts and have a strong ability to dissociate H_2 (Coq and Figueras, 2001; Schrick *et al.*, 2002; Wu and Stephen, 2006). The introduction of a second metal not only has increased the reactivity and reduced the accumulation of toxic byproducts, but also made the particles more stable in air by inhibiting the oxidation in some cases (Wu and Stephen, 2006; Zhang *et al.*, 1998; Lien and Zhang, 2001).

Although the nanoscale bimetallic systems are quite effective in the dechlorination of contaminants, the reactivity of the zero-valent metals is highly controlled by the surface characteristics of metals and water chemistry of groundwater. In subsurface environment, natural organic matter (NOM) is abundant and plays important roles in both electron transfer and adsorption processes (Doong and Lai, 2005). Johnson *et al.*(1998) depicted that any non-reactive adsorbate that out-competes the contaminants for reactive surface sites would result in the decrease of the degradation rate. Doong and Lai (2005) noted that humic acids (HAs) could act as inhibitors to compete the reactive sites on the Pd/Fe with tetrachloroethylene (PCE), or serve as electron shuttles to effectively accelerate the dechlorination efficiency and rate of PCE by Pd/Fe. However, the influence of HA on the reactivity of Ni/Fe toward the chlorinated hydrocarbons remains unclear. For the long-term application of iron wall to the remediation of the contaminated subsurface, the knowledge of the influence of HA in the dechlorination of chlorinated hydrocarbons is thus required (Doong and Lai, 2006).

In the research, we studied the role of HA in the dechlorination of 2,4-DCP by Ni/Fe nanoparticles, to estimate the capability of the bimetallic systems in the remediation of contaminated groundwater.

EXPERIMENTS AND METHODS

Chemicals

Most of the chemicals, such as nickel sulfate hexahydrate ($NiSO_4·6H_2O$, ≥99.0% (w/w)), iron(II) sulfate heptahydrate ($FeSO_4·7H_2O$, Analytical Reagent), 2,4-DCP, *o*-chlorophenol (*o*-CP), *p*-chlorophenol (*p*-CP), phenol and other reagents were used as received without further purification. HA was obtained from Sigma-Aldrich (ash to 20% (w/w); Switzerland). The HA stock solution (500 mg/L) was prepared by dissolving 0.25 g HA in 2 ml of 0.1 mol/L NaOH aqueous solution, followed by sonication and dilution with deionized water to 500 ml, and its final pH was adjusted to 7. The product was then filtered through a 0.45 μm pore diameter millipore membrane. Solution was stored at 4 °C before use. 2,4-DCP was dissolved in deionized water and stored at 4 °C. Fe^0 and Ni/Fe nanoparticles were synthesized immediately before use.

Ni/Fe synthesis procedure

Ni/Fe bimetallic nanoparticles were produced by adding 200 ml 0.54 mol/L $NaBH_4$ aqueous solution dropwise to a 1-L three-necked flask containing equal volume of 0.27 mol/L $FeSO_4·7H_2O$ aqueous solution with mechanical stirring at 25 °C for 10 min (Wei *et al.*, 2006). First of all, the ferrous iron was reduced to zero-valent iron according to the following reaction:

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

The Fe^0 nanoparticles were then washed 3 times with 400 ml deoxygenated deionized water in a nitrogen atmosphere. Subsequently, the Ni/Fe nanoparticles were synthesized by reacting the wet iron particles with a desired amount of nickel sulfate hexahydrate aqueous solution by stirring and in the nitrogen atmosphere according to the following equation (Wei *et al.*, 2006):

$$\mathrm{NiSO_4 + Fe^0 \rightarrow Fe^{2+} + Ni^0 + SO_4^{2-}}. \quad (2)$$

The Ni/Fe nanoparticles were then rinsed 3 times with 400 ml deoxygenated deionized water under nitrogen atmosphere to remove chloride ions.

Batch experimental procedures

The batch experiments for 2,4-DCP dechlorination were processed in the same three-necked flask, in which Ni/Fe nanoparticles were added. A desired volume of HA, 2,4-DCP stock solution, and 500 ml deoxygenated deionized water were added into the flask containing freshly prepared Ni/Fe nanoparticles (Wei *et al.*, 2006). The reaction solution was stirred in a nitrogen flowing environment. Samples were periodically collected with glass syringes and then immediately filtered through 0.22 μm membrane filters for analysis.

Analytical methods

Fresh metal nanoparticles (Ni bulk loading of 2.0 wt%) were visualized under a JEOL (Japan) JEM 200CX transmission electron microscope (TEM) at 160 kV for morphological measurement. Prior to TEM analysis, the particles were dispersed by an ultrasonicator.

Organic compounds such as 2,4-DCP, *p*-CP, *o*-CP and phenol were measured by SHIMADZU LC-10A (Japan) high performance liquid chromatography (HPLC), with the following conditions: agilent TC-C18 Column, 150 mm×4.6 mm; mobile phase, MeOH/H_2O (60/40, v/v); flow rate, 1.0 ml/min; detector, ultraviolet at 280 nm; and sample size, 20 μl.

RESULTS AND DISCUSSION

Dechlorination of 2,4-DCP

Fig.1 illustrates the HPLC chromatograms during the dechlorination of 2,4-DCP. 2,4-DCP was first transformed to chlorophenol, and then reduced to phenol quickly, because 2,4-DCP or chlorophenol was absorbed on the surface of Ni/Fe bimetal during the dechlorination (Xu *et al.*, 2005b). Some 2,4-DCP was reduced to chlorophenol or dechlorinated to phenol directly on the surface of Ni/Fe, and did not return to the solution. It can be seen that no other organic intermediates or final products were generated, except CP and phenol.

Inhibition effect of humic acid on 2,4-DCP dechlorination

HA had an adverse effect on the dechlorination of 2,4-DCP by Ni/Fe nanoparticles. As the HA concentration increased, the removal rate decreased.

Chlorophenol removal rates could be seen from Fig.2b. It is indicated that HA not only had an adverse effect on the removal of chlorophenol to phenol, but also remitted the creation of chlorophenol. During the experiment, little *o*-CP was identified and remained low concentration in the solution. The results demonstrated that 2,4-DCP was reduced more easily to *o*-CP than to *p*-CP, and the sequence of the tendency of the dechlorination was *p*-CP>*o*-CP. That is because the reaction rate constants were found to increase with the decrease in the Gibbs free energy of the formation of CPs (Xu *et al.*, 2005b).

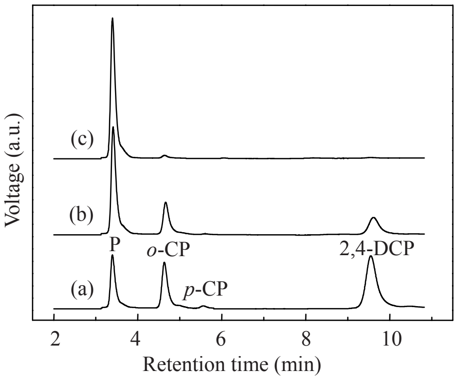

Fig.1 HPLC chromatograms of the reaction mixture during reaction. (a) 10 min; (b) 30 min; (c) 120 min

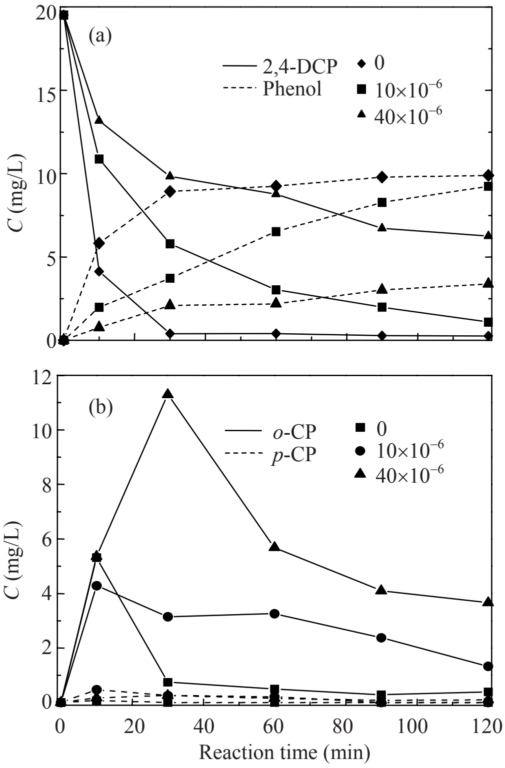

Fig.2 Effect of HA on 2,4-DCP dechlorination by Ni/Fe nanoparticles. (a) 2,4-DCP and phenol; (b) *o*-CP and *p*-CP. T=25 °C; pH_{in}=6.0; $C_{2,4\text{-DCP}}$=20 mg/L; $C_{Ni/Fe}$=6 g/L; stirring at 400 r/min; the nickel content of 2.0 wt%

The dependence of the reaction rate constant on the structure of the substrates is not surprising. Dolfing and Harrison (1992) had shown that the rate constant for the reduction of halogenated aromatics in anaerobic estuarine sediment was proportional to the Gibbs free energy or the activation energy of formation E_a which is one of the physical chemical parameters of compounds revealing the differences among molecular structures (Xu *et al.*, 2005b).

Characterization of Ni/Fe nanoparticles

Analysis of TEM micrographs are shown in Fig.3. Most of the particles tested were in the range of 20~100 nm in diameter. These spherical particles were connected together to form dendrites, which were the results of the geomagnetic forces between nanoscale particles and small particles, and their surface tension interactions. Fresh Ni/Fe nanoparticles in ethanol solution were clean. A mucous layer was bonded onto the surface of Ni/Fe in HA solution for 2 h, reflecting the possibility of lowering the dechlorination efficiency. And a more thickly mucous layer was shown on the surface of the Ni/Fe nanoparticles after 2 h reaction as shown in Figs.3c and 3d. More organic components such as HA and 2,4-DCP inhibited the active sites of Ni/Fe nanoparticles, likely lowering the dechlorination efficiency.

DISCUSSION ON MECHANISM

It is hypothesized that the reduction and dechlorination of 2,4-DCP occur when it is adsorbed on the surface of Ni/Fe particles (Niu *et al.*, 2006; Xu *et al.*, 2006). The Ni on the Fe surface acts as a receiver of hydrogen gas, which is produced by the reaction of Fe with water or hydrion. This process will increase the pH value of the solution. The corrosion reactions of iron are as follows:

$$Fe+2H_2O \rightarrow Fe^{2+}+H_2+2OH^-, \quad (3)$$

$$Fe+2H^+ \rightarrow Fe^{2+}+H_2. \quad (4)$$

On the nickel surface, the adsorbed hydrogen is dissociated into H atoms. The 2,4-DCP adsorbed on the Ni/Fe surface is reductively dechlorinated through the following reactions:

$$2,4\text{-}DCP+H_2 \rightarrow CP+Cl^-+H^+, \quad (5)$$

$$CP+H_2 \rightarrow P+Cl^-+H^+. \quad (6)$$

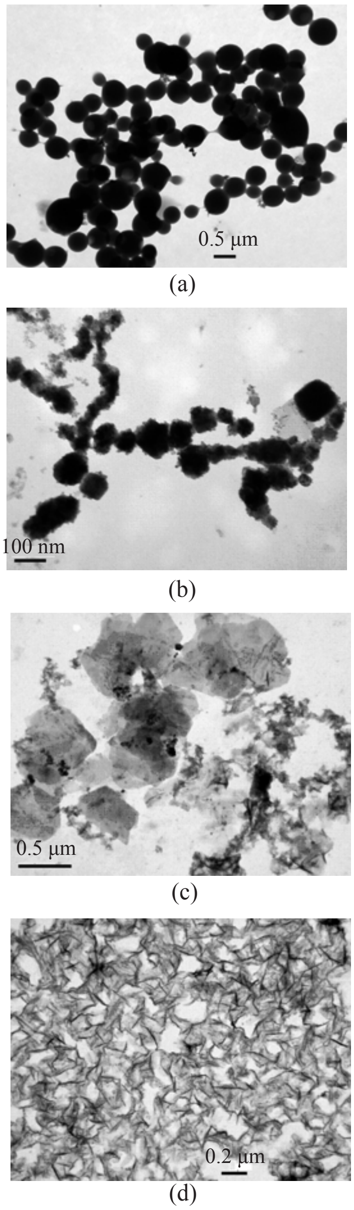

Fig.3 TEM images. (a) Ni/Fe nanoparticles in ethanol solution; (b) Ni/Fe nanoparticles with HA; (c) and (d) Ni/Fe nanoparticles after dechlorination reaction

Surface passivating layers are formed due to the precipitation of metal hydroxides and metal carbonates on the surface of iron and Ni/Fe particles (Burris *et al.*, 1995), which may hider the further reaction in the solution. In the presence of dissolved oxygen under weak acidic or neutral conditions, we propose the following reaction (Xu *et al.*, 2006):

$$4Fe^{2+}+10H_2O+O_2 \rightarrow 4Fe(OH)_3\downarrow+8H^+. \quad (7)$$

Under the current study, approximately 15% mass loss was observed. It was most likely that some organic compounds, including phenol, chlorophenol and HA, could be absorbed or covered by the surface passivating layers (Fig.4). The non-detected fraction of intermediates may be attributed to the fact that the high surface area to volume ratio of Ni/Fe nanoparticles appears to serve as non-reactive sorption sites for intermediates (Burris *et al.*, 1995).

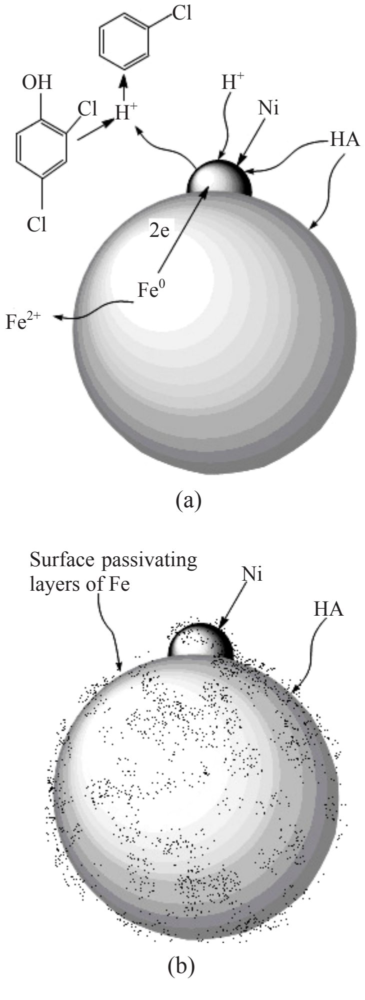

Fig.4 (a) Mechanism of 2,4-DCP dechlorination by Ni/Fe in the presence of humic acid; (b) In late reaction, some organic compounds, including phenol, chlorophenol and HA, were absorbed or covered by the surface passivating layers

CONCLUSION

Results obtained in this study clearly show that HA has inhibitory effect on the dechlorination of 2,4-DCP by Ni/Fe. During the dechlorination of chlorinated hydrocarbons, HA could out-compete reactive sites on Ni/Fe surface with 2,4-DCP to decrease the dechlorination efficiency and rate of 2,4-DCP. Our results show that 2,4-DCP is reduced more easily to *o*-CP than to *p*-CP, and the order of the tendency of the dechlorination is *p*-CP>*o*-CP. The present findings could be valuable for designing in situ treatment of contaminated water.

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