Catalytic reductive dechlorination of p-chlorophenol in water using Ni/Fe nanoscale particles

ZHANG Wei-hua1,2,3, QUAN Xie2,∗, ZHANG Zhuo-yong1
1. College of Urban and Environmental Sciences, Northeast Normal University, Changchun 130024, China. E-mail: zhangwh282@163.com
2. School of Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116023, China
3. College of Chemistry, Inner Mongolia University for the Nationalities, Tongliao 028043, China

Received 12 January 2006; revised 10 October 2006; accepted 10 September 2006

Abstract

Nanoscale bimetallic Ni/Fe particles were synthesized from the reaction of sodium borohydride (NaBH4) with reduction of Ni2+ and Fe2+ in aqueous solution. The obtained Ni/Fe particles were characterized by TEM (transmission electron microscope), XRD (X-ray diffractometer), and N2-BET. The dechlorination activity of the Ni/Fe was investigated using p-chlorophenol (p-CP) as a probe agent. Results demonstrated that the nanoscale Ni/Fe could effectively dechlorinate p-CP at relatively low metal to solution ratio of 0.4 g/L (Ni 5 wt%). The target with initial concentration of p-CP 0.625 mmol/L was dechlorinated completely in 60 min under ambient temperature and pressure. Factors affecting dechlorination efficiency, including reaction temperature, pH, Ni loading percentage over Fe, and metal to solution ratio, were investigated. The possible mechanism of dechlorination of p-CP was proposed and discussed. The pseudo-first-order reaction took place on the surface of the Ni/Fe bimetallic particles, and the activation energy of the dechlorination reaction was determined to be 21.2 kJ/mol at the temperature rang of 287–313 K.

Key words: Ni/Fe bimetal; nanoscale particles; catalytic reduction; p-CP; dechlorination

Introduction

Chlorophenols are extensively used as the intermediates for organic synthesis, pesticides, and wood preservatives. Most chlorophenols are listed as priority pollutants by the United States Environmental Protection Agency (Larry and William, 1979) due to their high toxicity and resistance to degradation. There is an urgent need to understand their transport and fate in the environment and to develop effective control methods.

The use of zero valent iron for the treatment of contaminants of halogenated organic compounds (HOCs) in wastewater and groundwater represents one of the latest innovative technologies for environmental remediation (Gillham and O’Hannesin, 1994; Johnson et al., 1996; Arnold and Roberts, 2000; Lookman et al., 2004). Researchers have found that nanoscale Fe and Pd/Fe bimetallic particles exhibited much higher activity for the transformation of HOCs than commercially available iron powder due to their high activity in reduction and catalysis (Wang and Zhang, 1997; Lowry and Johnson, 2004; Wei et al., 2004; Liu et al., 2005). Pd, a precious metal, exhibited excellent catalysis capability in reductive dechlorination of HOCs (Wang and Zhang, 1997; Liu et al., 2001). However, high expense of Pd catalyst limited its wide application. Thus, it is of significance to explore lower price and more effective catalysts.

Clark II et al. (2003) found that Ni-plated Fe was more effective than the acid-treated and untreated Fe in perchloroethylene degradation. Wang et al. (2004) illustrated that Ni appeared to be a good catalyst in production of methane over chloroform (CF) during the reduction of carbon tetrachloride (CT). Nanoscale Ni/Fe particles were also prepared for treatment of trichloroethylene (TCE) (Schrick et al., 2002), CT and CF (Feng and Lim, 2005). Schrick et al. (2002) reported a 280-time faster dehalogenation of TCE with a lab-synthesized nanoscale Ni/Fe compared with a commercial Fe.

However, dechlorination of chlorophenols with nanoscale Ni/Fe bimetallic particles has not been reported in the literature so far. In the present work, zero-valent bimetallic Ni/Fe nanoscale particles were synthesized and used to dechlorinate p-chlorophenol (p-CP) in aqueous solution. The objective of this work was to investigate the reactivity of nanoscale Ni/Fe bimetallic particles on the dechlorination of chlorophenol and to identify the potential parameters affecting the dechlorination rates of p-CP by the Ni/Fe particles.

1 Materials and methods

1.1 Materials

The following chemicals were used: p-CP (≥99%, Fe-
xian Chemical Plant, Shanghai, China), ferrous sulfate (FeSO$_4$·7H$_2$O) and nickel sulfate (NiSO$_4$·7H$_2$O) (99%, Shenyang Agent Manufactory, China), sodium borohydride (NaBH$_4$, 96%, Shanghai Agent Company, China), and methanol (HPLC grade, Tedia Agent Company, USA).

1.2 Preparation and characterization of Ni/Fe nanoparticles

The bimetallic Ni/Fe nanoscale particles were prepared using the method similarly to that proposed by Schrick et al. (2002). After the pH was adjusted to 12 with 6 mol/L NaOH, the aqueous solution of NaBH$_4$ (0.5 mol/L) was added dropwise into an aqueous mixture of FeSO$_4$ (0.2 mol/L) and NiSO$_4$ (0.01 mol/L) at room temperature. The process is shown as below:

$$2\text{Fe}^{2+} (\text{Ni}^{2+}) + 2\text{H}_2\text{O} + \text{BH}_4^- \rightarrow 2\text{Fe(Ni)} \downarrow + \text{BO}_2^- + 4\text{H}^+ + 2\text{H}_2 \uparrow \quad (1)$$

NaBH$_4$ was added excessively to ensure the complete reduction of the metallic ions in the solution. During the addition of NaBH$_4$, the solution was stirred vigorously. No special precautions were taken to eliminate oxygen from the reaction vessel. After the addition of NaBH$_4$, the mixture was stirred for 5 min, and then filtered through a 0.45 µm membrane with a vacuum pump. To get rid of the excess borohydride, the particles were washed by deionized water for five times, rinsed with absolute ethanol to eliminate water, and followed by filtration as dry as possible. At last, black powder was spread in a thin layer on a filter paper and then dried at room temperature in argon. The dried Ni/Fe particles were then collected and stored at 4°C in refrigerator for subsequent use.

Brunauer-Emmett-Teller (BET) surface area of the obtained Ni/Fe nanoparticles were measured using the nitrogen adsorption method with a NOVA 4200e Surface Area and Pore Size Analyzer (USA). Morphology of the Ni/Fe nanoparticles was observed with a Philips EM 400T transmission electron microscope (TEM) to obtain the size and size distribution of the metal particles. X-ray diffraction patterns of the Ni/Fe nanoparticles were obtained using the X-ray diffractometer (XRD, LabxXRD-6000) with Cu Ka X-ray source.

1.3 Experimental procedure

The experiments for dechlorination of p-CP were carried out in a batch reactor. A given amount of the nanoscale Ni/Fe particles was placed in a 130-ml glass reactor, and a given amount of deionized water was added. The initial pH value of the mixture was adjusted with 0.1 mol/L H$_2$SO$_4$, then a given amount of stock solution of p-CP was added. The final volume of the mixture was 125 ml. The dechlorination reactions were performed under magnetic stirring (200 r/min) to disperse the Ni/Fe particles throughout the reactor evenly. In most cases, the reactions were conducted at the constant temperature of 25±1°C. After the reactions lasted for desired time, aliquots of the samples (5 ml) were transferred to a glass vial. In order to minimize the adsorption of p-CP and phenol on the particles, 1 mol/L NaOH was added to the vial to adjust the pH value to 12. The preliminary results indicated that the dechlorination reactions did not occur at pH value approximately 10, which was consistent with the work of Chen et al. (2001). Addition of NaOH can stop the dechlorination reaction immediately and desorb p-CP and its dechlorinated products from the surface of Ni/Fe particles to the solution. The mixture was then filtered with 0.45 µm membrane to remove the precipitates for subsequent analysis.

1.4 Analytical method

Concentrations of p-CP and phenol were determined with a high performance liquid chromatography (PU-1580) equipped with a UV-1575 detector and a Kromasil ODS column (5 µm, 4.6 mm × 250 mm, Jasco, Japan). A mobile phase of 67% methanol and 33% water was employed at a flow rate of 0.9 ml/min, and the wavelength was set at 280 nm.

Concentration of chloride ion was analyzed with an ion chromatography (HIC-VP Super, Shimadzu, Japan) coupled with a Shim-Pack IC-A3 non-suppressor column (4.6 mm×150 mm) and a CDD-10AVP conductivity detector. An eluent solution containing 8 mmol/L p-hydroxybenzoic acid, 3.2 mmol/L bis-tris, and 50 mmol/L boric acid was pumped at a flow rate of 1.2 ml/min.

The total content of iron and nickel in the bimetallic particles were measured by a flame atomic absorption spectrometer (AAS, Perkin Elmer Aanalyst 700).

2 Results and discussion

2.1 Characterization of Ni/Fe nanoscale particles

The morphology and size of the Ni/Fe bimetallic nanoscale particles, determined by transmission electron microscope (TEM), are shown in Fig.1. Most of the particles are in the range of 10–50 nm in diameter. It is believed that nanoscale zero-valent metal particles can offer several advantages, including high specific surface area, high surface reactivity, and flexibility in deployment (Zhang et al., 1998; Liu et al., 2005), so the Fe$^{0}$-based bimetallic particles with nanosize may be important in environmental applications.

![Fig. 1 TEM image of Ni/Fe nanoscale particles.](image-url)
Fig. 2 shows the XRD patterns of Ni/Fe nanoparticles before and after dechlorination reaction, respectively. Only one broad peak at around $2\theta = 45^\circ$ was observed, which indicated that Ni and Fe formed amorphous alloy. Similar results were reported by Schrick et al. (2002) and Liu et al. (2005). It is believed that such amorphous alloy structure was beneficial for both the activity and selectivity owing to the stronger synergistic effect between active sites (Liu et al., 2005; Yamashita et al., 1985). The BET surface area of the nanoscale particles was 22.8 m$^2$/g. In comparison, a commercially available fine iron powder (Jinshan Metallurgical Factory, $>98.0\%$, <100 mesh) has a specific surface area of approximately 0.49 m$^2$/g (Wei et al., 2004). Ni/Fe ratio of 1 : 20 w/w (Ni 5 wt%) was obtained by American Academy of Sciences (AAS).

2.2 Transformation of $p$-CP

Fig. 3 shows experimental results for the reaction of the nanoscale Ni/Fe particles with $p$-CP. Initial $p$-CP concentration was 0.625 mmol/L, metal to solution ratio was 50 mg/125 ml (0.4 g/L), the mass fraction of Ni in the bimetal was 5 wt%, and the initial pH was 5.2. As shown in Fig.3, the concentration of $p$-CP declined rapidly with reaction time. The $p$-CP was almost completely dechlorinated and transformed to phenol and chloride ion by nanoscale Ni/Fe within 60 min. It seemed that $p$-CP was adsorbed on the surface of Ni/Fe particles and then dechlorination reaction took place (Graham and Jovanovic, 1999). It can also be seen from Fig.3 that no other chlorinated intermediates or final products were generated.

2.3 Factors affecting reaction rate constants

2.3.1 Effect of initial pH

Fig.4 shows the dechlorination efficiency increased as initial pH decreased. When initial pH was selected at 3.0, 4.0, 5.2, and 6.5, the obtained dechlorination efficiencies within 20 min were 98%, 90%, 84% and 72%, respectively. The $p$-CP was completely dechlorinated within 30 min under initial pH of 3.0, whereas the reaction took more than 180 min under initial pH of 6.5 for completion (not shown in Fig.4).

The chlorinated compounds adsorbed on the bimetallic surface were reductively dechlorinated through a series of reactions. The current model for the dehalogenation reaction using Ni/Fe nanoparticles involved the oxidation of iron to galvanically protect Ni (Schrick et al., 2002). As iron corrodes, protons from solution were reduced to atomic and molecular hydrogen at the catalytic Ni surface. Chlorinated compounds were also adsorbed on the surface of Ni/Fe particles where the C–Cl bond was broken, and the chlorine atom was replaced by hydrogen. Similar to Graham and Jovanovic (1999), the chemical process can be represented as follows:

Surface reactions:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (2)$$
$$2H^+ + 2e^- \rightarrow H_2(g) \quad (3)$$
$$H^+ + e^- \rightarrow H^+ \quad (4)$$

Dechlorination reaction:

$$H^+ + R–Cl \rightarrow R–H + Cl^- \quad (5)$$

The overall dechlorination reaction process on bimetallic catalyst surface can be represented as:

$$Fe^0 + R–Cl + H^+ \rightarrow R–H + Fe^{2+} + Cl^- \quad (6)$$

At lower pH, more atomic hydrogen on the catalyst surface attacked chlorophenol to replace the chlorine and to form phenol and chlorine ion (Eqs. (4)–(6)).
surface passivating layers due to the precipitation of metal hydroxides and metal carbonates, which were developed at higher pH values, might not be easily formed at lower pH, and allowed more metal surfaces available for reaction with the chlorinated molecules or at least assists in the corrosion of the iron (Chen et al., 2001). Therefore, the dechlorination efficiency of p-CP was enhanced markedly.

2.3.2 Effect of Ni loading

An increase of Ni content in Ni/Fe bimetallic particles could promote the rate of dechlorination. To evaluate this hypothesis, bimetallic particles with various Ni mass fractions (0 wt%, 2 wt%, 5 wt%, and 10 wt%, respectively) were prepared and used to dechlorinate p-CP. As illustrated in Fig.5, the reaction rate constants (k_{obs}) under the four Ni loadings were determined as $3.924 \times 10^{-4}$, $1.602 \times 10^{-2}$, $9.066 \times 10^{-2}$, and $1.687 \times 10^{-1}$ min$^{-1}$, respectively. The k_{obs} became obviously larger as nickel content increased from zero to 10 wt%. This clearly shows that the addition of a hydrogenolysis catalyst has a tremendous effect on the dechlorination rate. Similar results were reported by Xu et al. (2005) with Pd/Fe bimetal to dechlorinate dichlorobenzene. It is well-known that nickel is an excellent catalyst for dechlorination reaction. Co-existence of nickel and iron in the particles has been proved to be very effective to accelerate the dechlorination reaction. The bimetallic particles effectively form a galvanic cell, in which Fe passes electrons to the catalytic metal, where the target was reduced (Schrick et al., 2002).

2.3.3 Effect of Ni/Fe mass loading

Fig.6 illustrates the increase of dechlorination efficiency with reaction time at the selected nanoscale Ni/Fe mass loading (ratio of nanoscale Ni/Fe to solution volume). When the nanoscale Ni/Fe mass concentration increased from 0.16 to 0.48 g/L, the dechlorination efficiency increased from approximately 15% to 91% within 20 min. As the Ni/Fe mass concentration increased, the reactive Fe site concentration and adsorptive Ni site concentration increased simultaneously, which led to the increase of reaction rate.

2.3.4 Effect of temperature and activation energy

The effect of reaction temperature on the dechlorination efficiency was investigated by varying the temperature from 287 to 313 K (Fig.7). It was observed that dechlorination reaction rate of p-CP increased with the increase of reaction temperature in the range investigated. The k_{obs} were determined to be 0.0666, 0.0777, 0.0906, 0.1081, 0.1151, and 0.1381 min$^{-1}$ at various reaction temperatures of 287, 292, 298, 303, 306 and 313 K, respectively. The experimental activation energy was calculated from these rate constants, and using Arrhenius equation:

$$\ln k = A - \frac{E_a}{RT}$$

(7)

Where $E_a$ is the activation energy (kJ/mol), A is the pre-exponential factor, $k$ is the reaction rate constant (min$^{-1}$), $R$ is the universal gas constant (8.314 J/(mol·K)), and $T$ is the reaction temperature (K).

The k_{obs} values calculated at various temperatures were correlated by Eq.(8), and estimated activation energy of 21.2 kJ/mol was obtained. This relatively small activation energy indicated that the reaction was kinetically and thermodynamically favorable on the Ni/Fe nanoscale particles surface.

$$\ln k = 6.172 - \frac{2550}{T}$$

(8)
3 Conclusions

The Ni/Fe bimetallic nanoscale particles were synthesized and were found to be quite effective for catalytic dechlorination of p-CP at ambient temperature and pressure. The dechlorination was believed to take place on the surface sites of the Ni/Fe particles following a pseudo-first-order reaction. The dechlorination reaction rate mainly depended on the reaction temperature, pH, Ni loading, and the ratio of Ni/Fe mass to solution. Phenol and chloride ion were the final products and no other chlorinated intermediates were found. The dechlorination reaction rate mainly depended on the reaction temperature, pH, Ni loading, and the ratio of Ni/Fe mass to solution. Phenol and chloride ion were the final products and no other chlorinated intermediates were found. The experimental results demonstrated that acidic conditions were more favorable than neutral ones because at low pH more Ni/Fe surfaces could be available for reaction with the chlorinated molecules. The dechlorination reaction rate benefited from the increase in bulk loading of Ni due to its ability to adsorb hydrogen and dissociated it into atomic hydrogen. The dechlorination reaction rate increased with the increases of reaction temperature and the reaction activation energy of 21.2 kJ/mol was obtained at the range of 287–313 K investigated. This relatively small activation energy indicated that the reaction was kinetically and thermodynamically favorable on the Ni/Fe nanoscale particles surface.

References