Journal of Hazardous Materials 165 (2009) 78–86

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Factors influencing the dechlorination of 2,4-dichlorophenol by Ni–Fe nanoparticles in the presence of humic acid

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ARTICLE INFO

Article history:
Received 26 May 2008
Received in revised form 8 September 2008
Accepted 19 September 2008
Available online 27 September 2008

Keywords:
2,4-DCP
Catalytic dechlorination
Ni–Fe nanoparticles
Humic acid
Mechanisms
Kinetics

ABSTRACT

The dechlorination of 2,4-dichlorophenol (2,4-DCP) by Ni–Fe nanoparticles in the presence of humic acid (HA) was investigated to understand the feasibility of using Ni–Fe for the in situ remediation of contaminated groundwater. 2,4-DCP was first adsorbed by Ni–Fe nanoparticles, then quickly reduced to *o*-chlorophenol (*o*-CP), *p*-chlorophenol (*p*-CP), and finally to phenol (P). However, the introduction of HA decreased the removal percentage of 2,4-DCP, as a result, the phenol production rates dropped from 86% (in the absence of HA) to 29% within 2 h. Our data suggested that the dechlorination rate was dependent on a number of factors including Ni–Fe availability, Ni loading percentage over Fe, temperature, pH, and HA concentration. In particular, the removal percentage of 2,4-DCP was determined to be 100, 99, 95, 84 and 69%, for HA concentrations of 0, 5, 10, 30 and 40 mg L^{-1}, respectively. The kinetic calculations for the dechlorination of 2,4-DCP indicated that k values for 2,4-DCP dechlorination dropped from 0.14, 0.051, 0.039, 0.021 to 0.011 min^{-1} with increasing concentrations of HA from 0, 5, 10, 30 to 40 mg L^{-1}.

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1. Introduction

Chlorinated organic compounds (COCs) have been so widely used that they can be found in nearly all major environmental compartments. For example, chloroaromatics have a wide range of industrial and domestic uses, and they are employed as industrial solvents or intermediates in the synthesis of other chemicals, dyestuffs, pesticides, lubricants, and dielectric [1]. Chloroaromatics are among the hazardous pollutants found in various waste oils and other organic liquids, and they are highly toxic, mutagenic and possibly carcinogenic. Furthermore, chloroaromatics are biorefractory and tend to accumulate in animal tissues. Once released into the environment, they accumulate in the surroundings and pose health threat to humans and ecosystems over a long period of time [2–5]. This raises an urgent need for efficient dechlorination methods to eliminate chloroaromatics from both concentrated industrial effluents and diluted polluted groundwater.

Recently, chemical reduction of hazardous compounds such as COCs using zero-valent iron (ZVI) has been intensively studied for both in situ and aboveground treatment of contaminated water. Recent study on metal iron technology showed that the use of zero-valent single metals to reduce chlorinated organics has some drawbacks [6–10]. For example, even when nanoscale zero-valent iron particles are used, the metal mass normalized observed rate constant for the dechlorination of trichloroethylene (TCE) is still very low, in the order of 10^{-2} L g^{-1} h^{-1} [11]. More importantly, the formation of a hydroxide or oxide layer on the particle surface, during the reaction or upon contact of the nanoparticles with air, significantly reduced their reactivity and decreased the effective use of the metal particles [12]. Further attempts have been made to enhance the dechlorination rate of COCs using hydrogen gas and noble bimetallic particles such as Ni/Fe, Pd/Fe and Cu/Fe [13–16]. Cheng and Wu [17] reported that the physical addition of Pd^0, Cu^0 or Ni^0 micron-sized powder could re-activate Fe^0 particles that have lost their surface activity. It is well known that the reduction of chlorinated organics by bimetallic particles occurs via hydrodechlorination instead of inter-metalic electron transfer, in which Fe acts as the reducing agent whereas Ni, Pd, or Cu acts as a catalyst. The latter are considered as good hydrogenation catalysts and have a high ability to dissociate H_2 [18]. The presence of a second metal not only increases the reactivity and reduces the accumulation of toxic byproducts, but also inhibits particle oxidation in air [19].

Although the bimetallic system and the nanoscale bimetallic system are effective in contaminant dechlorination, the reactivity of the zero-valent metals is highly controlled by the surface characteristics of metals and groundwater chemistry. In subsurface environments, natural humic substances (HS) such as humic acid (HA) are abundant and play important roles in both electron

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0304-3894/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2008.09.080

transfer and adsorption processes. The inhibition of chlorinated hydrocarbons dechlorination by zero-valent metals in the presence of natural HS was reported by Johnson et al. [20]. They depicted that any non-reactive adsorbates that out-compete the contaminants for reactive surface sites would result in decreased degradation rate. Tratnyek et al. found that the reduction rate of TCE by ZVI was inhibited by natural HS due to the competitive sorption onto the surface of ZVI [21]. However, HA also can act as an electron mediator to enhance the reduction efficiency of chlorinated aliphatic compounds in aqueous solutions containing bulk reductant and to facilitate the microbially mediated anaerobic dechlorination of chlorinated hydrocarbons under iron-reducing conditions [22,23]. So far, it is not clear whether HA enhances or inhibits the electron transfer process from a bimetallic system such as Ni–Fe to the target compounds during in situ treatment processes. Therefore, knowledge of the role of HA in the dechlorination of chlorinated hydrocarbons is thus required prior to applying it for in situ remediation treatment [24].

To evaluate the performance of the bimetallic systems in the remediation of contaminated groundwater under ambient condition, the role of HA in the dechlorination of 2,4-DCP by nanoscale Ni–Fe particles was investigated in this study. In addition, other factors contributing to 2,4-DCP reduction, such as Ni–Fe nanoparticles dosage, Ni content, initial 2,4-DCP concentration, initial pH values and temperature, were examined.

2. Experimental

2.1. Chemicals

Nickel sulfate hexahydrate, iron sulfate heptahydrate, 2,4-DCP, *o*-CP, *p*-CP, phenol (P) and other reagents were purchased from Sinopharm Group Chemical Reagent Co., Ltd., China, and used as received without further purification. HA was obtained from Sigma–Aldrich (ash ∼ 20%, Switzerland). A HA stock solution (500 mg L^{-1}) was prepared by dissolving 0.25 g of HA in 2 mL of a 0.1 M NaOH aqueous solution, followed by sonication, dilution with deionized water to 500 mL, the final pH of the solution was adjusted to 7. The solution was then filtered through a 0.45 μm pore diameter Millipore membrane to remove the insoluble solids, and stored at 4 °C before use. 2,4-DCP is dissolved in deionized water and stored at 4 °C. The nanoscale Fe^0 and Ni–Fe were synthesized immediately before use.

2.2. Synthesis procedure

Ni–Fe nanoparticles were prepared in a 1000 mL three-necked flask under nitrogen gas. The iron nanoparticles were synthesized by dropwise addition of stoichiometric amounts of $NaBH_4$ aqueous solution into the flask containing $FeSO_4{\cdot}7H_2O$ aqueous solution simultaneously with electrical stirring at 25 °C. The ferrous iron was reduced to zero-valent iron according to the following reaction:

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

The Fe^0 nanoparticles were then rinsed several times with deionized water. Subsequently, the nanoparticles were prepared by the reaction of the wet Fe^0 nanoparticles with an aqueous solution of nickel sulfate hexahydrate under stirring according to the following equation:

$$Fe^0 + Ni^{2+} \rightarrow Fe^{2+} + Ni \quad (2)$$

The nanoparticles were then rinsed with deionized water to remove excess ${SO_4}^{2-}$ ions.

2.3. Batch experimental procedures

The batch experiments for 2,4-DCP dechlorination in the presence of HA were performed in the same three-necked flask into which 3.0 g Ni–Fe nanoparticles were added. The benchmark experiment conditions were as following: 5 mL 1.0 g L^{-1} HA, 10 mL 1.0 g L^{-1} 2,4-DCP stock solution and a certain amount of deoxygenated deionized water were added into the flask containing freshly prepared nanoscale Ni–Fe particles, total reaction volume was 500 mL. The reaction solution was stirred under nitrogen flow to simulate anaerobic environment in groundwater in 25 °C, and the initial pH was 5.7, the hydraulic retention time were 2 h. Samples were periodically collected in 0, 10, 30, 60, 90, and 120 min with glass syringes and the reaction was stopped by passing the aliquots through 0.22 μm membrane filters, then analyzed in 4 h. Condition experiments were conducted under the benchmark experiment conditions except the change in corresponding conditions.

2.4. Analyses procedures

Fresh metal particles (with a Ni bulk loading of 2.0%) were visualized under a JEOL JEM 200CX transmission electron microscope (TEM) at 160 kV for morphological measurements. Prior to TEM analysis, the particles immersed in deionized water were dispersed by an ultrasonicator.

Organic compounds such as 2,4-DCP, *p*-CP, *o*-CP and phenol were measured by SHIMADZU High Performance Liquid Chromatography [25]. Agilent TC-C18 Column, 150 × 4.6. Mobile phase: $MeOH/H_2O$ (60/40, v/v), flow rate: 1.0 mL min^{-1}, detector: UV at 280 nm, sample size: 20 μL.

3. Results and discussion

3.1. Inhibition by humic acid

Catalytic dechlorination of 2,4-DCP over Ni–Fe nanoparticles with and without 40 mg L^{-1} HA is shown in Fig. 1. 2,4-DCP was first adsorbed by the nanoparticles then reduced to *o*-CP or *p*-CP, and later converted to phenol, phenol was the sole final organic product. No other chlorinated intermediates or final organic products were detected.

The concentration of 2,4-DCP decreased rapidly and the removal percentage reached 99% in 30 min, then reached 100% in 120 min for Ni–Fe nanoscale particles in the absence of HA. In contrast, only about 50% and 69% of removal percentage was obtained in the presence of 40 mg L^{-1} HA in 30 and 120 min, respectively. And the concentration of *p*-CP remained low during the whole reaction with or without the addition of 40 mg L^{-1} HA. As for *o*-CP, it is the concentration peaked at 10 min in the absence of HA. The addition of 40 mg L^{-1} HA made the removal of 2,4-DCP slowed down, and *o*-CP peaked at 30 min. Meanwhile, the addition of 40 mg L^{-1} HA lowered the production rate of phenol, which was expressed as the ratio of the actual amount of phenol produced to the theoretical amount of phenol during the total dechlorination of 2,4-DCP, from 86% in the absence of HA to 29% in 2 h. Phenol and inorganic chlorine were detected as final products. Compared to initial concentration (20 mg L^{-1}), approximately 15% mass loss was observed. This suggests that a fraction of organic compounds was absorbed or covered by surface passivating layers, most likely due to the precipitation of metal hydroxides and metal carbonates on the surface of iron and Ni–Fe particles for their large surface areas. This is also evidenced by that the 2,4-DCP concentration dropped rapidly in the first 10 min, but the phenol generated was much less than the maximum attainable. The non-detected fraction of intermediates may be attributed to the fact that the high surface area to volume ratios

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