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Dechlorination of chlorinated hydrocarbons by bimetallic Ni/Fe immobilized on polyethylene glycol-grafted microfiltration membranes under anoxic conditions

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ABSTRACT

In this study, the dechlorination of chlorinated hydrocarbons including trichloroethylene (TCE), tetrachloroethylene (PCE) and carbon tetrachloride (CT) by bimetallic Ni/Fe nanoparticles immobilized on four different membranes was investigated under anoxic conditions. Effects of several parameters including the nature of membrane, initial concentration, pH value, and reaction temperature on the dechlorination efficiency were examined. The scanning electron microscopic images showed that the Ni/Fe nanoparticles were successfully immobilized inside the four membranes using polyethylene glycol as the cross-linker. The agglomeration of Ni/Fe were observed in poly(vinylidene fluoride), Millex GS and mixed cellulose ester membranes, while a relatively uniform distribution of Ni/Fe was found in nylon-66 membrane because of its hydrophilic nature. The immobilized Ni/Fe nanoparticles exhibited good reactivity towards the dechlorination of chlorinated hydrocarbons, and the pseudo-first-order rate constant for TCE dechlorination by Ni/Fe in nylon-66 were 3.7–11.7 times higher than those in other membranes. In addition, the dechlorination efficiency of chlorinated hydrocarbons followed the order TCE > PCE > CT. Ethane was the only end product for TCE and PCE dechlorination, while dichloromethane and methane were found to be the major products for CT dechlorination, clearly indicating the involvement of reactive hydrogen species in dechlorination. In addition, the initial rate constant for TCE dechlorination increased upon increasing initial TCE concentrations and the activation energy for TCE dechlorination by immobilized Ni/Fe was 34.9 kJ mol^{-1}, showing that the dechlorination of TCE by membrane-supported Ni/Fe nanoparticles is a surface-mediated reaction.

1. Introduction

Chlorinated hydrocarbons such as trichloroethylene (TCE) and tetrachloroethylene (PCE) are one of the most commonly found hazardous organic contaminants in subsurface environments (USEPA, 1997). These solvents are often used as degreasing agents in the automotive, metal, and electronic industries, and released into the environment via improper disposal. It has been demonstrated that both biotic and abiotic reactions contribute to the reductive transformation of contaminants under anoxic conditions (Lee et al., 2004; Doong and Chiang, 2005; Chu et al., 2006; Darlington et al., 2008; Elsner et al., 2008; Maithreepala and Doong, 2009; Lee and Doong, 2011). Over the past decades, zerovalent metals and bimetallic systems such as Pd/Fe, Ni/Fe, Ni/Si and Cu/Fe have been demonstrated to be an effective approach to treat the contaminated water containing chlorinated hydrocarbons by enhancing the dechlorination rate as well as by altering the dechlorination pathways (Li and Farrell, 2001; Zhang, 2003; Choi et al., 2008; Lee and Doong, 2008; Tee et al., 2009). However, the agglomeration and decrease in reactivity of nanoparticles resulting from the formation of metal oxide films have also been reported.

The attachment of metallic particles onto polymer membranes and supports can reduce the particle loss and particle agglomeration (Xu and Bhattacharya, 2008; Parshetti and Doong, 2009). Several stabilizers including starch (He et al., 2007), hydrophilic carbon, poly (acrylic acid) (PAA) (Schrick et al., 2004), and carboxymethyl cellulose (Wang et al., 2010) have been used to prevent the aggregation of nanoparticles in aqueous solutions. The use of porous microfiltration membranes as the support is of great interest because of their open structures and large pore sizes (Xu and Bhattacharya, 2008). PAA is one of the often used cross-linkers to immobilize bimetallic nanoparticles onto various membranes, such as poly(vinylidene fluoride) (PVDF) and cellulose acetate, for dechlorination of TCE (Xu and Bhattacharya, 2005, 2008; Wang et al., 2008). Xu et al. (2005) synthesized the bimetallic Ni/Fe and Pd/Fe nanoparticles in the PAA/PVDF composite membrane for the reductive dechlorination of TCE. In addition, the nanoscale zerovalent iron (NZVI) has been immobilized onto poly(vinyl alcohol) (Shimotori et al., 2004) and high-density polyethylene

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membranes (Shimotori et al., 2006) for effective removal of contaminants including carbon tetrachloride (CT), copper, nitrobenzene, 4-nitroacetophenone, and chromate.

In addition to PAA, other polyelectrolytes containing multifunctional chelating groups such as –OH, $–NH_2$, and $–CONH_2$ can also be used to functionalize the microfiltration membranes. However, not all the stabilizers can be applied to the NZVI because thiols and carboxylic acid can be reduced by NZVI (Xu et al., 2005). Poly(ethylene glycol) (PEG) is a bi-functional polymer with reactive OH groups on both ends, which is beneficial for metal ion adsorption onto membranes (He et al., 2007). The use of PEG as the cross-linker has several advantages including high water solubility, non-toxicity, low cost, environmental friendliness, and ease of thermal grafting. However, the reactivity of bimetallic Ni/Fe nanoparticles immobilized in different membranes has received less attention. In addition, only limited studies have been focused on the dechlorination of chlorinated hydrocarbons by Ni/Fe nanoparticles immobilized in PEG-grafted membranes. Moreover, the effect of environmental parameters on the reactivity of membrane-supported bimetallic nanoparticles towards the dechlorination of chlorinated hydrocarbons remains unclear.

The purpose of this study was to immobilize the bimetallic Ni/Fe nanoparticles onto four different microfiltration membranes and to understand the effect of membrane characteristics on the dechlorination efficiency and rate of chlorinated hydrocarbons under anoxic conditions. The morphology, particle sizes and distribution patterns of immobilized Ni/Fe nanoparticles were characterized by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The immobilized Ni/Fe nanoparticles were then used for the dechlorination of chlorinated hydrocarbons including TCE, PCE and CT. Effects of environmental parameters including concentration of chlorinated hydrocarbon, pH value, and reaction temperature on the dechlorination efficiency and rate of chlorinated hydrocarbon were investigated. In addition, the reaction products of chlorinated hydrocarbons by immobilized Ni/Fe nanoparticles were measured.

2. Materials and methods

2.1. Chemicals

TCE (>99.8%, GC grade), PCE (>99.8%, GC grade), and CT (>99.8%, GC grade), HEPES buffer (*N*-[2-Hydroxyethyl] piperazine-*N*′-[2-ethanesulfonic acid]) ($C_8H_{18}N_2O_4S$), and PEG were purchased from Sigma–Aldrich (Milwaukee, WI). Nickel chloride ($NiCl_2·6H_2O$) and ferrous sulfate ($FeSO_4·7H_2O$) were obtained from Riedel–de Haën (Seelze, Germany). Four membranes including nylon-66 (47 mm, 0.45 μm pore size, Supelco), PVDF (13 mm, 0.45 μm pore size, Millipore), mixed cellulose ester membrane (MCEM, 47 mm, 0.45 μm pore size, MFS), and Millex GS (47 mm, 0.45 μm pore size, Millipore) membranes were used for immobilization of nanoparticles. All other chemicals were of analytical grade and were used as received without further purification. Bidistilled deionized water (18.3 MΩ cm, Millipore) was used to prepare deoxygenated solutions unless otherwise mentioned. The deoxygenated solution was prepared by purging high-purity nitrogen gas (99.995%) in vacuum sealed bottles. This process was repeated 4–5 times to remove trace amount of oxygen (Maithreepala and Doong, 2004).

2.2. Synthesis of membrane-supported Ni/Fe nanoparticles

The membrane-immobilized Ni/Fe nanoparticles were prepared according to the procedures of Parshetti and Doong (2009). Briefly, membranes were first dipped into a 200-mL coating solution containing 2 mM PEG and 380 mM $FeSO_4·7H_2O$. After 10 min of reaction, mixtures were heated at 110 °C for 3 h, and soaked with 0.5 M $NaBH_4$ solution for 10 min. The Fe-containing membranes were then again dipped into the 100 mM $NiCl_2·6H_2O$ solution for 10 min, and the membrane-supported Ni/Fe nanoparticles were synthesized by adding 0.5 M $NaBH_4$ solution for another 10 min. In addition, the suspended Ni/Fe nanoparticles were synthesized using the similar procedures except the addition of membranes.

2.3. Dechlorination of chlorinated hydrocarbons

The dechlorination of chlorinated hydrocarbons by immobilized bimetallic Ni/Fe nanoparticles on different microfiltration membranes was investigated using 40-mL serum bottles sealed with Teflon-lined rubber septa and aluminum crimp caps. N_2-purged serum bottles were filled with 20 mL of 20 mM HEPES buffer solutions and membrane-immobilized Ni/Fe nanoparticles at pH 7. After being capped with rubber septa and aluminum caps, serum bottles were purged with N_2 immediately to maintain the anoxic conditions. The deoxygenated stock solutions of chlorinated hydrocarbons including PCE, TCE and CT were introduced into the system to get the final concentration of 10 μM. In addition, the effect of initial TCE concentration on dechlorination rate was examined by addition of stock solution into the system to get the final concentrations of 2, 5, 20, 40, 60, and 80 μM. The bottles were incubated in an orbital shaker at 100 rpm and at 25 ± 1 °C in the dark. Control experiments were also carried out with pristine membranes. In addition, all experiments were carried out in duplicate or triplicate and the average values were reported.

2.4. Analytical methods

The headspace analytical technique was used for the determination of chlorinated (PCE, TCE, CT, and dichloromethane) and non-chlorinated hydrocarbons (methane and ethane). The dimensionless Henry's constants for TCE, PCE, and CT are 0.421, 0.752 and 1.25, respectively (Washington, 1996). The details of analytical procedures can be obtained from our previous work (Parshetti and Doong, 2009). Briefly, concentrations of chlorinated hydrocarbons and byproducts in the headspace of test bottles were monitored by withdrawing 40 μL of gas using a 50-μL gas–tight syringe into a gas chromatograph equipped with an electron capture detector (ECD) and a flame ionization detector (FID). A VOLCOL fused-silica magebore capillary column was connected to the ECD and FID simultaneously by a Y-splitter to determine the concentrations of chlorinated and nonchlorinated hydrocarbons, respectively. In addition, concentrations of chlorinated hydrocarbons in aqueous solutions were calculated using the external standard method by preparing the known concentrations of chlorinated hydrocarbons in aqueous solutions.

The surface morphology of the microfiltration membranes containing bimetallic Ni/Fe nanoparticles was characterized by SEM (JEOL JSM-6700F OXFORD INCA ENERGY 400). The particle sizes of Ni/Fe nanoparticles were determined manually from the SEM by using the high magnification image. In addition, more than 100 immobilized nanoparticles were used to calculate the average particle size. EPMA was performed using an electron probe X-ray microanalyzer (JEOL JXA-8200) with an accelerating voltage of 20 kV and a beam current of 20 nA. The X-ray photoelectron spectroscopy (XPS) measurements were performed by an ESCA PHI 1600 photoelectron spectrometer (Physical Electronics, Eden Prairie, MN) using Al Kα X-ray source (1486.6 eV photon energy). The spherical capacitor analyzer with a multi-channel detector had a takeoff angle of 70° related to the horizontal plane of the sample. Data were recorded digitally, and all peak scans were signal averaged until an acceptable signal-to-noise ratio was obtained. During data acquisition, the pressure in the sample chamber maintained