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Cation exchange resin immobilized bimetallic nickel–iron nanoparticles to facilitate their application in pollutants degradation

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ABSTRACT

Nanoscale zerovalent iron (nZVI) usually suffers from reduction of reactivity by aggregation, difficulty of assembling, environmental release and health concerns. Furthermore, data are lacking on the effect of cheap nickel on debromination of decabromodiphenyl ether (DBDE) by immobilized nZVI in aqueous system. In this study, strong acid polystyrene cation-exchange resins with particle diameter from 0.4 to 0.6 mm were utilized as matrices to immobilize bimetallic nickel–iron nanoparticles in order to minimize aggregation and environmental leakage risks of nZVI and to enhance their reactivity. Elemental distribution mapping showed that iron particles distributed uniformly on the surface of the resin and nickel particles were dispersed homogeneously into Fe phase. The reaction rate of resin-bound nZVI is about 55% higher than that of dispersed nZVI. The immobilized bimetallic nanoparticles with 9.69% Ni had the highest debromination percent (96%) and reaction rate (0.493 1/h). The existence of Ni significantly improved the debromination rate, due to the surface coverage of catalytic metal on the reductive metal and the formation of a galvanic cell. The environmental dominant congeners, such as BDE 154, 153, 100, 99 and 47, were produced during the process. Outstanding reactive performance, along with magnetic separation assured that resin-bound bimetallic nickel–iron nanoparticles are promising material that can be utilized to remediate a wide variety of pollutants contaminated sites including polybrominated diphenyl ethers.

1. Introduction

The use of zerovalent metals (ZVMs), especially zerovalent iron (ZVI), for the treatment of organic pollutants in wastewaters and groundwaters has received much attention due to the environmental benignity and high activities of these materials. The majority of these studies are concerned with compounds such as chlorinated methanes, ethanes, ethenes, and pentachlorophenol [1]. The characteristics of ZVM treatments may also be advantageous for the treatment of persistent contaminants such as polybrominated diphenyl ethers (PBDEs) [2], which are in the list of persistent organic pollutants (POPs). Commonly, the decrease in ZVI particle size from microscale to nanoscale can greatly improve reaction rate due to the higher surface reactivity on larger specific surface area (SSA) [3]. But nanoscale ZVI (nZVI) usually suffers from aggregation leading to a reduction of reactivity [2]. Besides, due to the difficulty of assembling, the application of nanosized particles can be problematic with a view to engineering practice [4]. Occupational safety and health are also important concerns with respect to nanoparticles in combination with the risks of fire or explosion during storage and handling [5]. Literature review showed that boron nitride nanosheets, clay, resins, silica and starch have been utilized as matrices to facilitate the dispersion of ZVI particles in suspension, in order to minimize aggregation and environmental leaking risks [2,6–10].

The introduction of a second, catalytic metal has been found to improve the rate of dechlorination for chlorinated aromatics, such as PCBs, PCDDs, and pentachlorophenol [1,11,12]. A limited number of studies reported that palladium (Pd) promotes debromination of PBDEs by ZVI and magnesium [13,14], but the expensive Pd greatly restricts its wide application. Meanwhile, cheap nickel (Ni) has been widely used as an alternative catalyst to dechlorinate chlorinated organic compounds [1,15]. Few reports are available regarding the degradation of brominated aromatics by bimetallic ZVI/Ni. Fe/Ni bimetal has been found to be unable to destroy 2,2′,4,4′-tetrabromodiphenyl ether in methanol [13]. This failure is predictable since the product ratios formed during the dehalogenation reaction have been found to be dependent on the identity of the metals employed and the concentration of hydrogen in the aqueous phase [16]. To the best of our knowledge, data are lacking on the effect of Ni on debromination of PBDEs by ZVI in aqueous system.

In this study, zerovalent bimetallic nickel–iron nanoparticles were immobilized onto the resin surface of a strong acid type cation-exchange resin. The assembling and aggregation problems

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of dispersed nZVI were solved by the immobilization of the nanoparticles by the microscale resins. The dehalogenation of model PBDEs, decabromodiphenyl ether (DBDE, BDE 209) was compared in a series of contact experiments for three types of reductants: nZVI, resin-bound nZVI, and resin-bound bimetallic nanoparticles (nZVI/Ni). To elucidate the improvement in dehalogenation rate and particularly in product distributions from a mechanistic standpoint, the roles of nickel and iron in the debromination of DBDE were studied by measuring kinetics and product distributions.

2. Materials and methods

2.1. Materials

A mixture of eight PBDE congeners (Code BDE-CSM) each having from three to seven bromine atoms and DBDE, was obtained from Accustandard Inc. (New Haven, CT, USA). The individual congener of DBDE was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). All the other reagents used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). $NaBH_4$, $FeCl_2{\cdot}4H_2O$, and $NiCl_2$ were of CP grade, the other entire reagents used were of AR grade.

2.2. Sample preparation

A strong acid polystyrene cation-exchange resin with particulate diameter ranging from 0.4 to 0.6 mm was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Before use, the resins were washed by 10% (m/m) hydrochloric acid and 5% (m/m) sodium hydroxide solution twice to remove inorganic and organic impurities followed by the treatment of ethanol and distilled water. The synthesis of resin-bound nZVI and resin-bound bimetallic nZVI/Ni were modified from the literature [4]. Briefly, 2 g of $FeCl_2{\cdot}4H_2O$ or the mixture of $FeCl_2{\cdot}4H_2O$ and $NiCl_2$ was thoroughly dissolved in 40 mL of distilled water before adding 10 g of the resin. After the mixture was stirred for 2 h for the exchange of Fe^{2+} and Ni^{2+}, the resin was taken out and washed thoroughly with distilled water. Then, the resin was dispersed in 30 mL of distilled water in 10 °C water bath, and 10 mL of 10% (m/v) $NaBH_4$ was added with stirring to reduce the Fe^{2+} and Ni^{2+}. After 0.5 h reaction, the resin was separated and washed thoroughly to remove the residual $NaBH_4$ before the freeze dry process. The dispersed nZVI was prepared by dropwise addition of aqueous $NaBH_4$ solution (1.6 M) to 1.0 M $FeCl_3$ solution under continuous stirring [2]. The resin-bound nanoscale zerovalent nickel (nZVNi) was prepared by dissolving 2 g of $NiCl_2$ in 40 mL of distilled water before adding 10 g of the resin. Then the samples were treated following the above mentioned procedure. The 2 h reaction time was enough as the adsorption of Ni (II) on cation exchange resin could reach its equilibrium in 1 h [17].

2.3. Dehalogenation experiments

A certain amount (0.46 g nZVI or 2 g resin containing 0.46 g nZVI) of nZVI, resin-bound nZVI and resin-bound bimetallic nZVI/Ni was added each separately to a respective series of serum vials, in which different concentrations of DBDE stock solution was mixed with an equal volume of ultrapure water to form a 10 mL solution. Control experiments were carried out in the same solution without the addition of nZVI or with the addition of resin only. The PBDEs stock solution was prepared by dissolving DBDE in dimethyl sulfoxide (DMSO). The sample bottle was sealed, and sonicated in a water bath for 1 min to disperse the particles. The prepared samples were placed on a shaker incubator at 200 rpm at room temperature and covered to avoid photodegradation. Blank samples without contaminants but using the same solvent were set up in the same way. At preselected time intervals, samples were sacrificed to measure the parent compound and the reaction products. All samples were prepared in triplicate.

2.4. Instrumental analysis

The morphology and structure of the resin-bound products (resin-bound nZVI, nZVNi and nZVI/Ni) were investigated by scanning electron microscopy (SEM, JSM-6700F, JEOL). X-ray spectroscopy (EDS) was used to characterize the morphology and elemental mapping of the Ni–Fe bimetal as well as Fe and Ni contents in different positions. The specific surface area was estimated by the Brunauer–Emmet–Teller (BET) equation based on the nitrogen adsorption isotherm (77 K) using a QuadraSorb SI analyzer (Quantachrome Instruments, USA). Magnetic characterization was carried out on a superconducting quantum interference device (SQUID) magnetometry.

For the detection of DBDE, samples were directly analyzed by a high performance liquid chromatography (HPLC, P1201, Elite Analytical Instruments, Dalian, China) with a UV detector (UV 1201) and a Sinochrom ODS-BP C18 column (200 mm × 4.6 mm). HPLC-grade methanol was used as mobile phase at a rate of 1.0 mL/min. To analyze the reaction products, sample chromatograms were compared with the standard solution of PBDEs (BDE-CSM).

3. Results and discussion

3.1. Characterization of bimetallic nickel–iron nanoparticles

3.1.1. Structural analysis

Fig. 1A–C shows the scanning electron microscopy images of the ion-exchange resin particles before the immobilization of ZVM. Before the immobilization of the nZVI and nickel, the surface of the resin was smooth (Fig. 1A, B), except for unknown impurities (Fig. 1C). Fig. 1D–F shows the images of the resin immobilized with nZVI particles on the surface. The ZVI particles formed from the reduction of Fe^{2+} by $NaBH_4$ were mostly spherical. According to the SEM result, the particle size of the particles was mainly in the range of 150–200 nm in diameter (Fig. 1F). These nZVI balls aggregated to form a dense layer on the resin surface (Fig. 1E). Fig. 1G and H shows the images of the resin-bound nanoscale zerovalent nickel (nZVNi) particles on the surface. From Fig. 1 G and H, the nZVNi immobilized onto the surface of the resin more tightly with fewer cavities in comparison with resin-bound nZVI, and the particle size was smaller, mostly in the range of less than 100 nm in diameter. Obviously, the immobilization of the nZVI and nZVNi onto the resin resulted in similar structural changes in the resin surface. It can be interestingly observed from SEM images that the addition of Ni^{2+} changed the structure of nZVI. With 0.51% Ni in the bimetal, ZVI grew in the form of nanosheets or nanofilms (Fig. 1I). Higher content of 2.62% Ni changes nanosheet or film like materials to nanoflowers (Fig. 1J). The nanomaterials formed on the surface of the resin became spherical nanoparticles again with more loading of Ni, i.e. 3.57% (Fig. 1K). Li et al. found that 0.01–0.07 g of iron/g of resin was optimal for the formation of nanoparticles (∼60 nm) and channels with a depth of about 3 μm and width of about 10 μm were formed [4]. While in this study, no channel was observed and large diameter nanoparticles were formed with higher iron loading on resin. In the later experiments with BDE 209, the resin with 0.23 g of iron/g of resin was used.