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Degradation of decabromodiphenyl ether by nano zero-valent iron immobilized in mesoporous silica microspheres

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ABSTRACT

The agglomeration of nanoparticles reduces the surface area and reactivity of nano zero-valent iron (NZVI). In this paper, highly dispersive and reactive NZVI immobilized in mesoporous silica microspheres covered with FeOOH was synthesized to form reactive mesoporous silica microspheres (SiO_2@FeOOH@Fe). The characteristics of SiO_2@FeOOH@Fe were analyzed by transmission electron microscopy, Fourier transform infrared spectroscopy simultaneous thermal analysis, X-ray photoelectron spectroscopy, and Brunnaer–Emmett–Teller surface area analysis. The mean particle size of the reactive mesoporous silica microspheres was 450 nm, and its specific surface area was 383.477 $m^2\,g^{-1}$. The degradation of dcabromodiphenyl ether (BDE209) was followed pseudo-first-order kinetics, and the observed reaction rate constant could be improved by increasing the SiO_2@FeOOH@Fe dosage and by decreasing the initial BDE209 concentration. The stability and longevity of the immobilized Fe nanoparticles were evaluated by repeatedly renewing the BDE209 solution in the reactor. The stable degradation of BDE209 by SiO_2@FeOOH@Fe was observed within 10 cycles. Agglomeration-resistance and magnetic separation of SiO_2@FeOOH@Fe were also performed. The improved dispersion of SiO_2@FeOOH@Fe in solution after one-month storage and its good performance in magnetic separation indicated that SiO_2@FeOOH@Fe has the potential to be efficiently applied to environmental remediation.

1. Introduction

Polybromodiphenyl ethers (PBDEs), as efficient flame retardants, have been widely used in electronics, chemicals, electrical, textile and other industries [1,2]. Some studies have been confirmed that PBDEs are ubiquitous persistent organic pollutants in the environment as well as in human and animal bodies [3–5]. The presence of PBDEs in the animal body has been found to affect the balance of thyroid and cause neurotoxicity [6]. Therefore, it is necessary to seek for methods, which have high degradation efficiency and can be used in engineering practice.

Recently, using nanoscale elementary metals, metal oxides, and their composites is a promising method of environmental remediation [7–9]. Compared with zero-valent iron (ZVI), nano zero-valent iron (NZVI) has a larger specific surface area and higher reactivity [10]. NZVI is often used for treating contaminants in aqueous solutions because it could effectively degrade many pollutants, such as organic halogenated hydrocarbons [11,12], nitrates [13], heavy metals [14], insecticides [15], and dyes [16]. And it also showed good reactive ability in BDE209 degradation. In 2010, Shih and Tai [11] reported that the 2.8 $mg\,L^{-1}$ BDE209 can be rapidly removed by NZVI within 40 min in water solution and the efficiency was much better than that of ZVI. Recently, in our lab, the NZVI was prepared from steel pickling waste liquor and used to remove BDE209 in a water/tetrahydrofuran (4/6, v/v) solution [17]. The results showed that 97.92% of 2 $mg\,L^{-1}$ BDE209 was removed within 24 h by 4 $g\,L^{-1}$ NZVI, which was more effective than ZVI under the same conditions.

Aside from its faster reaction rate than ZVI, NZVI can also be directly injected into polluted groundwater and soil, resulting in the immediate degradation of pollutants [18]. However, due to their small size effect and surface effect, NZVI particles are easily aggregated via Van der Waals and magnetic attraction forces, forming particles with diameters ranging from several microns to several millimeters, or even larger in water [19,20]. The agglomeration of these nanoparticles can reduce the surface area and reactivity of NZVI [20,21]. In addition, the poor transport properties of NZVI in aquifers will limit its practical application in the remediation of toxic pollutants in contaminated environments [22].

Two methods are generally adopted to avoid the agglomeration of nanoscale zero-valent iron particles. One is the use of surfactants [23], starches [24], and cellulose [25] to modify the surface of NZVI. By increasing the steric or electrostatic repulsion between particles, nanoscale particles are stabilized and dispersed. The second

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method involves the embed-immobilization technique, wherein NZVI is loaded onto a functional carrier, such as activated carbon [26,27], a nylon membrane [20,28], or a resin [29]. Radical groups and channels in the carriers can obstruct nanoparticles' clustered. Some carriers can even play certain roles during the degradation process. For instance, Choi et al. [26] developed a new strategy wherein nanoscale Fe was loaded onto activated carbon particles to prepare reactive activated carbon. The particles were avoided to be clustered in the process, and the adsorption capacity for lipophilic pollutants was greatly improved. Recently, the emergence of new materials, such as molecular sieve and silica sphere, which can provide potential carriers to solve the problem of NZVI agglomeration has been attracted interest since they can immobilize various nanoparticles for further applications [19,30]. Meanwhile, surface modification of inorganic core with different inorganic shell to form core–shell structures have shown several applications because these particles show some special properties in optics and catalysis by adjusting their chemical composition and structure order recently [31,32]. Since the good thermal and chemical stability, non-toxicity, and biocompatible capacity, silica spheres are widely used in fabricating core–shell for further application [33,34]. For example, Shen et al. [34] prepared and demonstrated the h-SiO_2/TiO_2 core/shell microspheres have significant photocatalytic activity in degradation of methyl orange in water. Unfortunately, reports on the preparation and application of composite functional materials with NZVI immobilized in mesoporous silica microspheres or other new carriers are limited, let alone using NZVI immobilized onto mesoporous silica spheres to form core–shell structure to remove toxic organic pollutants.

Hence, a new synthesis method was used to prepare reactive mesoporous silica microspheres with a core–shell structure in this study. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) were applied to analyze and characterize the material. BDE209 was selected as the contaminant to be removed to study the degradation capacity of the new composite material. The longevity and anti-agglomeration capacity of the composites were also tested.

2. Experimental

2.1. Materials

A standard solution of decabromodiphenyl ether was purchased from Cambridge Isotope Laboratories (CIL, Andover, U.S.) and used to establish the standard curve. Decabromodiphenyl ether (98%, AR grade) was purchased from Aladdin (Shanghai, China) and used as the degradation sample. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$, >99%), sodium borohydride ($NaBH_4$ > 98%), PEG, and ethanol (EtOH, 99.7%) were supplied by Tianjin Damao Chemical Agent Company (Tianjin, China). Tetraethoxysilane and dodecylamine were purchased from Aladdin (Shanghai, China). Methanol (HPLC grade) was supplied by Tianjin Kermel Chemical Reagents Company.

2.2. Synthesis of materials

2.2.1. Preparation of mesoporous silica microspheres

The synthesis of mesoporous silica microspheres was performed according to the method of Miyaka et al. [35]. The main synthesis steps were as follows: About 0.2224 g of dodecylamine was dissolved in EtOH (62.5 vol%) under magnetic stirring in a 50 mL conical flask. Then, 1.16 mL of undiluted liquid tetraethoxysilane were slowly dropped into the solution, which was then stirred for 30 s and allowed to stand for 3 h under room temperature. The products were separated by centrifugation (centrifugation speed, 4000 rpm; time, 10 min) and rinsed with water and EtOH. Afterwards, the products were kept in a vacuum drying chamber for 4 h at 60 °C, heated in a muffle furnace up to 600 °C at a rate of 10 °C min^{-1}, and maintained for 4 h to remove the organic template under high temperature calcination. To regenerate the OH^- groups lost from the surface of SiO_2 during calcination, the silica microspheres were boiled in water for 2 h [36], and then dried in a drying chamber at 60 °C after centrifugation.

2.2.2. Coating the mesoporous silica microspheres with FeOOH

About 0.5 g $FeSO_4{\cdot}7H_2O$ was added to a 50 mL solution containing 0.5 g PEG. The solution was then treated via ultrasonic vibration for 15 min for complete dissociation. About 0.5 g boiled silica spheres was immersed in the solution for 30 min. The pH of the solution as this time was 4.85. Afterwards, the particles were removed and placed in a drying chamber for 3 h at 110 °C. The dried particles were flushed with water and EtOH and then dried in a vacuum drying chamber for 4 h at 60 °C. This produced silica microspheres covered with FeOOH, presented as SiO_2@FeOOH.

2.2.3. Synthesis of reactive mesoporous silica microspheres

About 0.2 g SiO_2@FeOOH was put into three flasks, after which 50 mL EtOH (30 vol%) containing 0.2 g $FeSO_4{\cdot}7H_2O$ was added. The solution was stirred well. Then, 20 mL EtOH (30 vol%) with 0.16 g $NaBH_4$ was added drop-wise while stirring continuously for 10 min. The solution system turned from yellow to black. The products were separated by vacuum filtration and then separately rinsed thrice with water and EtOH. The products were then placed in a drying chamber at 60 °C. Reactive mesoporous silica microspheres, SiO_2@FeOOH@Fe, with core–shell structures were obtained. The overall process of SiO_2@FeOOH@Fe synthesis is shown in Fig. 1. Meanwhile, in order to study the effect of FeOOH on degradation efficiency, the SiO_2@ Fe was also prepared as well as SiO_2@FeOOH@Fe but used SiO_2 as a carrier.

To compare the degradation efficiency of the new synthetic material and NZVI on BDE209, NZVI was synthesized according to previous literature [37]. Briefly, EtOH (30 vol%) was used to prepare 0.2 g L^{-1} $FeSO_4{\cdot}7H_2O$ and 0.16 g L^{-1} $NaBH_4$. Under mechanical stirring, the $NaBH_4$ aqueous solution was added to $FeSO_4{\cdot}7H_2O$; the resulting solution was continuously stirred until it turned black. The particles were separated by vacuum filtration, and separately rinsed thrice with deoxygenated water and EtOH. Finally, the particles were stored in a vacuum drying chamber until further use.

2.3. Characterization

TEM (TECNAI 10, PHILIPS, The Netherlands) was used to observe the size and morphology of the particles. Thermogravimetric and differential thermal simultaneous analyses (STA 409 PC/4/H, NETZSCH, Germany) were performed in the atmosphere from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. Particle surface elemental analysis was performed using XPS (ESCALAB 250, Thermo-VG Scientific, USA) with light as the mono Al Kα (energy: 1486.6 eV, scan mode: CAE, full spectrum scan: pass energy of 150 eV, narrow spectrum scan: pass energy of 20 eV). The crystalline phase of different particles was determined using an X-ray diffractometer (Y-2000, Dandong, China) with a Cu Kα radiation. The accelerating voltage and applied current were 30 kV and 20 mA, respectively. FT-IR spectra of SiO_2@FeOOH and SiO_2 was recorded on a IR-prespige-21 spectrometer (Shimadzu, Japan). The specific surface area and porosity were measured by an ASAP2020M instrument (Micromeritics Instrument Corp, USA). Fe content was measured by an inductively coupled plasma (ICP) optical emission spectrometer (IRIS Intrepid II XSP, Thermo Elemental Company, USA).