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Debromination of decabromodiphenyl ether by organo-montmorillonite-supported nanoscale zero-valent iron: Preparation, characterization and influence factors

Zhihua Pang[1,2], Mengyue Yan[2], Xiaoshan Jia[1,*], Zhenxing Wang[2], Jianyu Chen[2]

1. School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510630, China. E-mail: Pangzhihua08@gmail.com
2. South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou 510655, China

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ABSTRACT

An organo-montmorillonite-supported nanoscale zero-valent iron material (M-NZVI) was synthesized to degrade decabromodiphenyl ether (BDE-209). The results showed that nanoscale zero-valent iron had good dispersion on organo-montmorillonite and was present as a core-shell structure with a particle size range of nanoscale iron between 30–90 nm, characterized by XRD, SEM, TEM, XRF, ICP-AES, and XPS. The results of the degradation of BDE-209 by M-NZVI showed that the efficiency of M-NZVI in removing BDE-209 was much higher than that of NZVI. The efficiency of M-NZVI in removing BDE-209 decreased as the pH and the initial dissolved oxygen content of the reaction solution increased, but increased as the proportion of water in the reaction solution increased.

Introduction

Due to its advantages of large specific surface area, good reactivity, strong reducing power and low cost, nanoscale zero-valent iron (NZVI) has recently attracted great interest (Li et al., 2006; Crane and Scott, 2012; Chen et al., 2011a). It can be used widely in the remediation and degradation of various kinds of pollutants, especially halogenated organic pollutants, such as nitrobenzene compounds (Dong et al., 2010), polychlorinated biphenyls (PCBs) (Lowry and Johnson, 2004), polybrominated diphenyl ethers (PBDEs) (Shih and Tai, 2010), and dioxins (Kim et al., 2008). However, as NZVI tends to aggregate (Sun et al., 2006; Zhan et al., 2008) and is easily oxidized to form an oxide layer on the surface of particles in the air (Liu and Lowry, 2006), both of which reduce the activity and efficiency of nanoscale zero-valent iron. By immobilizing or supporting NZVI on a solid material it is feasible to overcome its easy aggregation, easy oxidation and poor dispersion. In recent years, a number of materials, such as activated carbon (Xu et al., 2010), zeolite (Lee et al., 2007), porous silica (Qiu et al., 2011), and kaolin (Zhang et al., 2011a), have been used as carriers for NZVI, and these composites show great performance in the degradation of various kinds of pollutants.

Montmorillonite is a kind of clay mineral with a layered structure, high surface area and strong adsorption characteristics (Schoonheydt, 2002). Also, montmorillonite can be used as a good carrier and dispersant, to support NZVI prepared by a liquid phase reduction reaction (Fang et al., 2010). This composite was found to effectively remove a variety of organic pollutants, such as nitrobenzene compounds (Gu et al., 2010), methyl orange (Chen et al.,

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[*] Corresponding author. E-mail: eesjxs@mail.sysu.edu.cn

2011b), atrazine (Zhang et al., 2011b) and chlorophenols (Dorathi and Kandasamy, 2012). In addition, montmorillonite can be modified by surface-active agents (such as cetyl trimethyl ammonium bromide) through cation exchange to form organo-montmorillonite, which is hydrophobic instead of hydrophilic and therefore has high adsorption capacity for hydrophobic organic pollutants. Moreover, organo-montmorillonite can be used to support and disperse NZVI, and the prepared new composite materials can effectively degrade hydrophobic organic contaminants, such as pentachlorophenol (Li et al., 2011) and catechol tannin (Shakir et al., 2008).

PBDEs widely used in electronic, chemical, electrical, textile, and other industries as a typical kind of brominated flame retardants (Luo et al., 2009), are ubiquitous in the environment, with high hydrophobicity, persistence, bioaccumulation and toxicity (Law et al., 2006), among which decabromodiphenyl ether (BDE-209) is the only one that is still in production and large-scale use. There are many techniques to remove BDE-209, such as biological degradation (He et al., 2006), photocatalytic degradation (An et al., 2008) and zero-valent iron reduction. In particular, zero-valent iron reduction technology has gained great interest due to its high efficiency and low cost in the degradation of PBDEs. The use of zero-valent iron in the degradation of PBDEs was carried out by Keum and Li (2005) for the first time. Subsequently, nanoscale zero-valent iron was synthesized to degrade PBDEs (Qiu et al., 2011; Fang et al., 2011a, 2011b; Zhuang et al., 2010, 2011; Li et al., 2007), and showed high degradation efficiency, and Yu et al. studied the debromination of BDE-209 by a montmorillonite-clay-supported nanoscale iron material (Yu et al., 2012). However, there are still few studies about the use of organo-montmorillonite-supported nanoscale zero-valent iron in the degradation of BDE-209.

In this study, a supported nanoscale zero-valent iron material was prepared by a liquid phase reduction method with organo-montmorillonite as carrier and dispersant. Then, characterization was conducted by various means, such as XRD, BET, SEM, TEM, EDS, XPS, XRF, and ICP-AES. Finally, various factors influencing its degradation of BDE-209 were studied, including the pH, the initial dissolved oxygen content and the proportion of solvents.

1 Materials and methods

1.1 Chemicals

Sodium-montmorillonite, with a purity of montmorillonite of 95%, was purchased from Anji County, Zhejiang Province, China; its cation exchange capacity (CEC) was 112.0 mmol/100g. Decabromodiphenyl ether (BDE-209) standard solution was purchased from Accustandard Company and used to establish a standard curve. Chemical grade BDE-209 (pure type, solid, 99%) was purchased from Shanghai ANPEL Scientific Instrument Co., Ltd. (Shanghai, China) and used in the degradation tests. Methanol (HPLC grade) was purchased from Shanghai ANPEL Scientific Instrument Co., Ltd. (Shanghai, China). Other reagents such as cetyl trimethyl ammonium bromide (CTMAB), tetrahydrofuran (THF), ferrous sulfate heptahydrate, sodium borohydride, anhydrous ethanol, nitric acid, sodium bromide and sodium hydroxide were all of analytical purity, purchased from Guangzhou Chemicals Co., Ltd. (Guangzhou, China). The experimental water was self-made deionized deoxygenated pure water.

1.2 Preparation of materials

1.2.1 Preparation of organic-modified montmorillonite

The sodium-montmorillonite was organically modified mainly through an ion exchange process (Lowry et al., 2004; Zhu et al., 1997). A group of preliminary experiments were carried out to determine the optimum amount of modifier. The specific method was as follows: 5.0 g of sodium-montmorillonite (named MT) was added into a conical flask containing 200 mL deionized water, then 2.04 g cetyltrimethylammonium bromide (CTMAB) was added. After two hours of reaction with stirring at 60°C the modified product was centrifuged and washed several times, then dried at 70°C for 12 hr. The ground products were screened through a 100 mesh sieve, and finally activated at 115°C for 2 hr. The obtained organo-montmorillonite was named CMT.

1.2.2 Preparation of organo-montmorillonite supported nanoscale zero-valent iron

Organo-montmorillonite-supported nanoscale zero-valent iron was prepared mainly by a liquid phase reduction method of $FeSO_4$ and $NaBH_4$ according to the literature, (Fang et al., 2010; Shahwan et al., 2010) with some modification. The specific method was as follows: 5.0 g organo-montmorillonite was added into a beaker containing 200 mL deionized deoxygenated water, and a certain amount ($m_{\mathrm{CMT}}/m_{\mathrm{Fe}}$ = 4:1) of $FeSO_4{\cdot}7H_2O$ was added. A volume of 100 mL newly prepared $NaBH_4$ solution was added dropwise to yield a B/Fe molar ratio of 3:1 and stirred for 9 hr at room temperature. Then the product was separated by filtration and washed with alcohol three times, vacuum dried for 12 hr at 60°C and named M-NZVI. Also, nanoscale iron particles were prepared in the same way without participation of organo-montmorillonite in the reaction process, and the product was named NZVI.

1.3 Characterization of the materials

The BET surface area of the material was analyzed with an ASAP2020 system (Quantachrome Instruments Inc., USA).

The identification of crystalline phases of nanomaterials