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Research article

Remediation and phytotoxicity of decabromodiphenyl ether contaminated soil by zero valent iron nanoparticles immobilized in mesoporous silica microspheres

Yingying Xie [a, b], Wen Cheng [a, b, **], Pokeung Eric Tsang [b, c], Zhanqiang Fang [a, b, *]

[a] School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, China
[b] Guangdong Technology Research Center for Ecological Management and Remediation of Urban Water System, Guangzhou, 510006, China
[c] Department of Science and Environmental Studies, The Hong Kong Institute of Education, Hong Kong, 00852, China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are a new class of environmental pollutants which easily accumulated in the soil, especially at e-waste sites. However, knowledge about their phytotoxicity after degradation is not well understood. Nano zero valent iron (nZVI) immobilized in mesoporous silica microspheres covered with FeOOH (SiO_2@FeOOH@Fe) synthesized in this study was utilized to remove decabromodiphenyl ether (BDE209) from soil. Results revealed that the removal efficiency of BDE209 can be achieved 78% within 120 h using a dosage of 0.165 g g^{-1} and a pH of 5.42. Furthermore, the removal efficiency enhanced with increasing soil moisture content and the decreasing of initial BDE209 concentration. Phytotoxicity assays (biomass and germination rate, shoots and roots elongation of Chinese cabbage) were carried out to provide a preliminary risk assessment of treated soil for the application of SiO_2@FeOOH@Fe.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), a new class of flame retardants have been widely used since the 1970s (Song et al., 2014). Owing to their persistence and bioaccumulation, they have been detected in various environmental matrices, including air, water, soil, sediments and biotic samples around the world (Mai et al., 2005). The low water solubility (<0.1 mg L^{-1}) and high lipophilicity (Log K_{ow} = 6.62–9.97) (Chou et al., 2013) of PBDEs cause them to accumulate in soils, especially at e-waste sites (Leung et al., 2007). For instance, road soils collected from an e-waste recycling region had total concentrations of PBDE ranging from 191 to 9156 ng g^{-1} dw in southern China (Luo et al., 2009). Possible adverse effects of PBDEs in wildlife and in humans (Mai et al., 2005) include disrupting the endocrine, reproductive and neural systems (Chou et al., 2013). Therefore, some approaches are expected to be valid for the remediation of PBDEs contaminated sites.

Recently, nano scale zero valent iron (nZVI) was known to be a reducing agent for the degradation of several different organic pollutants (Carroll et al., 2013), such as chlorinated organics (Katsenovich and Miralles-Wilhelm, 2009), nitrobenzene compounds (Satapanajaru et al., 2009), pesticides (Zhang et al., 2011), and several others. But to best of knowledge, the investigation into nZVI's applications in remediation has been limited, because bare nZVI particles have a strong tendency to agglomerate, due to their intrinsic magnetic and Van der Waals forces (Zhang et al., 2011). Consequently, to facilitate the delivery and mobility of nZVI in soils, various modification technologies have been explored. A common method is surface-modification of nZVI to increase colloidal stability, using PAA or Tween-20 (Dong and Lo, 2013). Another method involves immobilizing the nZVI onto a carrier, such as resin, potato starch (Fu et al., 2013), zeolite (Kim et al., 2013) or mesoporous silica (Qiu et al., 2011). In the study described herein, we have developed a new strategy wherein nZVI immobilized in mesoporous silica microspheres covered with FeOOH (SiO_2@FeOOH@Fe) which was certified to have higher mobility and good performance on degradation of BDE209 in THF/water, with a removal efficiency

* Corresponding author. School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, China.
** Corresponding author. School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, China.
E-mail addresses: pengyh@scnu.edu.cn (W. Cheng), zhqfang@scnu.edu.cn (Z. Fang).

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of 94.15% within 8 h when the dosage was 22 g L^{-1} (Qiu et al., 2011). Despite its successful demonstration in aqueous solution, very few studies have investigated the usage of SiO_2@FeOOH@Fe for the remediation of PBDEs contaminated soils.

Many studies have focused on the creation of technologies for the degradation of PBDEs (Luo et al., 2012; Shih et al., 2012). Nevertheless, residues of contaminants and the byproducts of degradation generally remain within the soil and it has not yet been demonstrated whether there is ecological risk in soils. As a consequence, concerns have been raised about the ecotoxicity of the residual contaminants which limits the engineering applications of nZVI remediation technology. Therefore, research on the ecotoxicity of the remediated soil by nanotechnology is urgently needed before field application can be considered (El-Temsah and Joner, 2013; Fjordbøge et al., 2013). Specially, plant-based tests are particularly useful and tractable as sensitive indicators of soil toxicity.

In this study, we investigated the degradation effectiveness of BDE209 in soils by SiO_2@FeOOH@Fe nanoparticles, and evaluated the phytotoxicity of the treated soils by using Chinese cabbage to assess the risks of SiO_2@FeOOH@Fe nanoparticles for in situ remediation of PBDEs contaminated soils.

2. Materials and methods

2.1. Soil collection and preparation

Soil studied in this paper was taken from surface soil samples (0–20 cm depth) from the higher education mega-center in South China. The preparation and properties of the soil used in this paper are shown in Supplementary material, Table S1.

2.2. Preparation and characterization of nZVI and SiO_2@FeOOH@Fe nanoparticles

The preparation and characterization of nano size zero-valent iron and SiO_2@FeOOH@Fe nanoparticles were performed as in our previous study (Fang et al., 2011; Qiu et al., 2011). The particle size and specific area of nZVI and SiO_2@FeOOH@Fe were measured to be 50–80 nm, 400–500 nm and 35 m^2 g^{-1}, 383 m^2 g^{-1}, respectively (Fang et al., 2011; Qiu et al., 2011).

2.3. Column breakthrough experiments

Silicon sand (30–50 mesh, Hainan, China) was selected for column breakthrough experiments. The sand was rinsed with deionized (DI) water by three times. Organic impurities were removed by soaking the rinsed sand in hydrogen peroxide (5%) for 3 h, rinsing the sand again with DI water and then soaking in hydrochloric acid (12 M HCl) overnight. And the sand was thoroughly rinsed with DI water and then air-dried. Transport studies were carried out in water-saturated silicon sand that was prepared as described above and packed in a vertical glass column 20 cm in length and 2.5 cm in inner diameter. A small nylon sieve (80 mesh) at the bottom of the column prevented loss of the sand. For each experiment, the column was packed wet (porosity = 34.5%) and fed a background ion (Mg^{2+} or Ca^{2+}) or natural organic matter (NOM) solution with a dual-channel peristaltic pump (HL-2, Chunding, Shanghai, China) for 2 h to remove background turbidity. After a 4 mL aliquot of nZVI or SiO_2@FeOOH@Fe was fed into the column, the same background solution was used to elute the materials in the column at a flow rate of 12 mL min^{-1}. The effluent samples were collected at selected time points. An aliquot of the nZVI effluent was digested with 1 M HCl for 2 h. The total iron concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Parallel experiments followed the same procedures.

2.4. Batch experiments

Batch tests were performed in 20 ml glass vials with plugs. For each batch, 2 g of contaminated soil, along with the appropriate amount of deionized water and SiO_2@FeOOH@Fe nanoparticles were placed in each vial. The vials were then placed in a rotary shaker with a speed of 300 rpm at 25 ± 2 °C. Samples were collected at time intervals, extracted with 10 ml acetonitrile for 30 min, and then centrifuged for 8 min at 716 g. This was repeated once and the extracted solutions were combined, and then filtered with a 0.22 μm filter. The concentration of BDE209 was then tested using high performance liquid chromatography (HPLC, HP1100, Shimadzu, Japan). Parallel experiments were performed following the same procedure. Control experiments without nanoparticles were also treated as described above.

2.5. Phytotoxicity tests

Soil culture experiments were conducted test for phytotoxicity. Standard analysis protocols were taken from guidelines used by international organizations (International Organizations for Standardization, 1993, 1995; OCED, 2003). And the soil was divided into five treatments which were shown as follows: S-1, Blank, unspiked soil; S-2, spiked soil with BDE209 (10 mg kg^{-1}); S-3, unspiked soil and SiO_2@FeOOH@Fe (0.165 g g^{-1}); S-4, soil spiked with BDE209 (10 mg kg^{-1}) and SiO_2@FeOOH@Fe (0.165 g g^{-1}); S-5, soil spiked with BDE209 (10 mg kg^{-1}) and SiO_2@FeOOH@Fe (0.165 g g^{-1}), after reaction for 5 days.

The five treatments were further examined using greenhouse soil culture experiments. The same plant species (Chinese cabbage) and seed density was used for all germination tests. A 90 mm petri dish was filled with 50 g prepared soil and wetted to 75% of the soil's water capacity using distilled water. Petri dishes were placed in the biochemical incubator for balance at 25 °C for 48 h. 20 seeds per dish were placed in the soil, with a spacing of 1 cm or more between each seed, to keep the seed radicle and the growth direction in a straight line. Petri dishes were covered with caps, and incubated for 14 days at 25 °C in the biochemical incubator. All treatments were harvested by recording germination percentage and measuring the lengths of shoots and roots when the controls had developed roots that were at least 20-mm long. Each soil treatment and control was replicated three times.

3. Results and discussion

3.1. Comparison of mobility and degradation of BDE209 in soils by SiO_2@FeOOH@Fe nanoparticles and nZVI

To compare mobility, experiments were conducted to explore breakthrough profiles of SiO_2@FeOOH@Fe and nZVI. As can be seen from Fig. 1, nearly 92.3% of the SiO_2@FeOOH@Fe particles were eluted from the silicon sand column under the specified conditions. The effluent Fe concentration from the SiO_2@FeOOH@Fe reached a plateau at ~8 pore volume (PV). In contrast, no significant elution of bare nZVI was observed, which is mainly due to strong magnetic interactions and Van der Waals forces in bare nZVI, which causes rapid aggregation, resulting in low mobility in silicon sand columns. A comparison of BDE209 degradation in soil by SiO_2@FeOOH@Fe and nZVI was shown in Fig. 1 (inset). SiO_2@FeOOH@Fe achieved 73% removal efficiency, whereas bare nZVI only achieved 18% efficiency under the same conditions. As noted above, these results suggest that SiO_2@FeOOH@Fe showed higher mobility and