Remediation and Biological Activity of Nano Zero-valent Iron Supported by Biomass Carbon on Soil Contaminated With Polybrominated Diphenyl Ethers

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Abstract

Polybrominated diphenyl ethers (PBDEs) are toxic to humans and can easily accumulate in the environment. Nanoscale zero-valent iron (NZVI) and modified NZVI have been developed to remediate PBDE contamination. However, their degradation in soil systems and their microbial toxicity have not been widely explored. In this study, NZVI supported on biomass carbon was applied to remove decabromodiphenyl ether (BDE-209) from contaminated soil. A removal efficiency of 100% was achieved within 384 h as BDE-209 reacted with 0.10 g/g soil biomass carbon NZVI particles (BC–NZVI) at pH 7.00. The reaction followed pseudo-first-order kinetics, and the BDE-209 removal efficiency increased with increasing BC–NZVI dosage and decreasing initial BDE-209 concentration, pH, and moisture content. Biological activity assays (dehydrogenase activity and soil basal respiration) were conducted to provide a preliminary risk assessment of the BC–NZVI application in BDE-209 contaminated soil. The results demonstrate that BC–NZVI has a strong potential for *in situ* remediation of organic-contaminated soil.

1 Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants over the past 30 years (Fang and Al-Abed 2008; Fang et al. 2010; Fang et al. 2011). PBDEs and their metabolites have been detected in various environmental media (water, air, and soil) worldwide. In addition, their concentrations in live organisms and their tissues and secretions, such as humans and their milk and blood, have increased significantly (Hites 2004; Meng et al. 2021) owing to their high hydrophobicity, bioaccumulation, and persistence in the environment (Jakobsson et al. 2002; McDonald 2002; Bezares-Cruz et al. 2004; Sjodin et al. 2004; Luo et al. 2007; Luo et al. 2008). PBDEs can act as endocrine disruptors, which can induce neurodevelopmental defects and lead to cancer (Hardy 2005). Therefore, practical and effective technologies to remediate PBDE contamination in the environment are of high importance.

Recent studies have shown that the use of nano zero-valent iron (NZVI) is promising for PBDE remediation (Fang et al. 2010; Keum and Li 2005) because of its strong reduction property. However, the strong tendency of NZVI particles to aggregate owing to Van der Waals and magnetic forces limits their application (Zhang et al. 2010). Therefore, immobilization technologies have been developed to increase the transport ability of NZVI in soil systems (Parshetti and Doong 2009; Alidokht et al. 2010). Previous studies have reported the immobilization of NZVI particles onto functional carriers, such as clay, nylon membrane, zeolite, potato starch, and resin (Li et al. 2007b; Choi et al. 2008; Choi et al. 2009). In this study, we explored a novel method to immobilize NZVI on biomass carbon, which has good decabromodiphenyl ether (BDE-209) removal efficiency, which can reach 97.94% in 120 min at a concentration of 8 g/L (Fu et al. 2016). Therefore, we investigated the application of biomass carbon NZVI particles (BC–NZVI) for the remediation of PBDE contaminated soil systems.

Previous studies have mainly focused on the development of novel materials and technologies for PBDE degradation (Luo et al. 2007; Luo et al. 2008; Shih et al. 2011). However, the possible ecotoxicity of the

byproducts and residues that remain in the soil system after the reaction have not been reported. Therefore, there is an urgent need for studies on the ecotoxicity of soils treated by NZVI. For that, soil enzymes and basal respiration can be used as soil quality indicators (He et al. 2015).

In this study, we investigated the BDE-209 degradation by BC–NZVI in a soil system. We also evaluated the ecotoxicity of the treated soils based on soil hydrogenase activity and soil respiration to assess the potential risks associated with the application of BC–NZVI nanoparticles for *in situ* remediation of PBDE polluted soil.

2 Materials And Methods

2.1 Chemicals

The standard BDE-209 solution, standard mixture of 39 PBDE congeners (EO-5113), and additional mixture of 14 PBDE congeners (BDE-COC) were obtained from AccuStandard, Inc. (New Haven, CT, USA). Three individual congeners (BDE 206, BDE 207, BDE 208) were obtained from Wellington Laboratories (Guelph, Canada), and methanol (HPLC grade) was purchased from Fisher Scientific (Leicestershire, UK). Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ > 99%), sodium borohydride (NaBH_4 > 96%), n-hexane (HPLC grade), tetrahydrofuran (THF > 99.8%), ethanol (GR > 99.8%), anhydrous sodium sulfate (Na_2SO_4), barium chloride (BaCl_2), hydrochloric acid (HCl), sodium hydroxide (NaOH), hydrofluoric acid (HF ~ 48%), and nitric acid (HNO_3 ~ 67%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PRC). Walnut shells were sampled from Chuxiong Yunnan Province.

2.2 Soil sampling and preparation

The soil material (without BDE-209) used in all experiments (pH 8.31, water content 1.56%, organic matter 16.85%, Fe 2.99%) was sampled from an open green space in Tongji University (31°15' N, 121°30' E, Shanghai, PRC). The samples were obtained from the topsoil layer (0–20-cm soil depth) and were fully homogenized. The soil was air dried and sieved through a 2.0-mm-mesh sieve to remove plant and organic residues. Subsequently, the soil material was spiked with a BDE-209 solution (100 mg/L, dissolved in tetrahydrofuran solution) and dried in fume hood at $25 \pm 1^\circ\text{C}$ until the tetrahydrofuran had thoroughly volatilized.

2.3 Synthesis of BC–NZVI particles

The BC–NZVI material was prepared and characterized according to our previous study (Fu et al. 2016), and its measured specific area was $248.67 \text{ m}^2/\text{g}$.

2.4 Batch experiments

For the remediation experiments, 5 g of contaminated soil was mixed with certain amounts of deionized (DI) water and BC–NZVI particles in glass vials (25 mL) with plugs. The glass vials were shaken in a thermostat vibrator (ZD-85, Changzhou Guoyu Instrument Manufacturing Co., Ltd., China) at 300 rpm and

25 ± 1°C. The initial pH was adjusted to 5–9 using HCl or NaOH. At different time intervals, sample vials were withdrawn. The samples were extracted with 50 mL of n-hexane/acetone (1:1, v:v) and then sonicated under 100 W and 51 Hz for 30 min. The samples were centrifuged for 6 min at 8000 rpm to separate the solid from the aqueous phase. The supernatant was transferred to a round-bottom flask. The entire procedure was repeated twice. The well mixed extracts were concentrated to approximately 1 mL via rotary evaporation. Subsequently, the concentrated extract was diluted to 10 mL with n-hexane and filtered through a 0.22-µm-mesh filter. The BDE-209 concentration was measured with a gas chromatograph–mass spectrometer (GC–MG QP2010 SE, Shimadzu, Japan) (Sanchez-Brunete et al. 2006).

2.5 Kinetic analysis

A pseudo-first-order kinetics model was applied to describe the degradation of BDE-209 (Shi et al. 2011):

$$\frac{dC_t}{dt} = -k_{\text{obs}}C_t,$$

1

where k_{obs} is the rate constant of a reaction, and C_t represents the concentration of BDE-209 both in the solid and aqueous phases at any experimental sampling time. The rate constants were calculated by regression of a natural log of the BDE-209 concentration based on the reaction time:

$$\text{Ln} \frac{C_t}{C_0} = -k_{\text{obs}}t,$$

2

where C_0 is the initial concentration of BDE-209.

2.6 Bromide measurement

For the bromide measurement, 5 g of contaminated soil (10 mg/kg BDE-209) was mixed with DI water (moisture content 40%) and BC–NZVI particles (0.1 g/g soil) in glass flasks (100 mL) with plugs. The initial pH was adjusted to 7.0 with HCl or NaOH. The glass vials were shaken in a thermostat vibrator at 300 rpm and 25 ± 1°C. For the bromide extraction, DI water was added for a soil/water ratio of 1/10. Subsequently, 50 mL of this extract was transferred into a 100-mL flask, to which 10 mL of an acetic acid buffer (pH = 5) was added. Bromides were quantified using a bromide ion selective electrode (Orion 9635BNWP, Thermo Fisher Scientific, Waltham, MA, USA).

2.7 Soil hydrogenase activity

The soil was pre-incubated at 25 ± 1°C in the dark for 7 d with 40% maximum water holding capacity to stabilize the microbial activity (He et al. 2015). After incubation, 300 g of the contaminated soil was artificially treated with the BC–NZVI suspension at 0.1 g/g soil (dry soil) in glass flasks. The control

without BC–NZVI or BDE-209 addition received the same amount of DI water. The soil was completely mixed to keep the BC–NZVI homogeneously distributed in the soil system. All treatments were performed in triplicates. The soil moisture content was adjusted to 40% before incubation. The soil samples were incubated for 112 d at $25 \pm 1^\circ\text{C}$ in the dark. Hydrogenase activity of the soil samples at certain time intervals was measured and then analyzed according to Friedel et al. (1994) and Li et al. (2015).

2.8 Soil basal respiration

The hydrochloric acid (HCl) titration method (Chen et al. 2014; He et al. 2015) was used to analyze the soil basal respiration. For that, a 50-mL beaker containing 50 g of soil treated with BC–NZVI (moisture content: 40%) and a vial containing 25 mL of 0.2-M NaOH were incubated in a 2500-mL sealable serum vial at $25 \pm 1^\circ\text{C}$. The titration method was used to determine the redundant NaOH after BaCO_3 precipitation. The respiration rate was determined by computing the HCl quantity. The soil respiration activity was expressed as $\text{mg CO}_2 \text{ g}^{-1} \text{ soil in 24 h}$.

3 Results And Discussion

3.1 Effect of BC–NZVI on BDE-209 removal

As show in Fig. 1, the removal efficiencies increased with increasing BC–NZVI concentration. The BDE-209 concentration decreased during 288 h of reaction time, and it reached a plateau after 336 h. When we plotted the k_{obs} against the BC–NZVI dosages, linear equations with correlation coefficients (R^2) of 0.9548 were obtained. This correlation indicated that k_{obs} were proportional to BC–NZVI dosage. The interaction between soil BDE-209 and BC–NZVI fitted well a pseudo-first-order kinetics mode. This result confirmed that the interaction occurred on the surface of the materials and that the surface reaction was the control step, which suggests that surface area was crucial for BDE-209 removal. According to Qiu et al. (2011), the reduction reaction between modified NZVI particles and BDE-209 fits well the Langmuir–Hinshelwood model, which also demonstrates that the surface reaction was a crucial step. Large surface areas lead to a greate number of reaction sites, which results in improved adsorption and degradation capacities. Therefore, the increase in BC–NZVI dosage resulted in more reaction sites and better removal efficiencies than that of low BC–NZVI dosage (Wang and Zhang 1997; Zhang et al. 2009). Moreover, as the BC–NZVI dosage increased from 0.10 to 0.12 g/g soil, the removal efficiency increased to 9.30%. This result suggested the stoichiometric of BC–NZVI particles, which indicated an optimum BC–NZVI dosage of 0.10 g/g soil.

3.2 Effect of initial BDE-209 concentration on its removal

Figure 2 shows the effect of initial BDE-209 concentration (1–15 mg/kg soil) on its removal efficiency at a fixed BC–NZVI dosage of 0.1 g/g soil. The removal efficiencies decreased with increasing BDE-209 initial concentrations, and they were 100%, 92.80%, 87.60%, and 49.47% after 288 h of reaction for 1, 5, 10, and 15 mg/kg of initial BDE-209 concentration. BDE-209 was almost completely degraded within 384

h at initial concentrations of 1, 5, and 10 mg/kg. The removal efficiency of BDE-209 for the initial concentrations of 1, 5, and 10 mg/kg showed increasing trends at the beginning of the reactions and then reached a balance of 100% at 288, 336, and 384 h respectively (Fig. 2A). Figure 2B shows that k_{obs} decreased from 0.0096 to 0.0021/h as the BDE-209 initial concentrations increased. This was also confirmed by the degradation of organic pollutants by $\text{SiO}_2@\text{FeOOH}@\text{Fe}$ and Fe–Ni bimetallic particles (Bokare et al. 2008; Xie et al. 2016; Li et al. 2019). The BDE-209 removal by BC–NZVI was likely a process including BDE-209 adsorption on the BC–NZVI surface and subsequent surface reduction reaction. For a fixed adsorption reaction area of BC–NZVI, an increase in the BDE-209 initial concentration led to competitive adsorption among BDE-209 molecules. This decreased the amount of BDE-209 adsorbed and reduced on the BC–NZVI surface, which decreased the removal efficiency. Moreover, as the addition of BC–NZVI was maintained, and the concentration of BDE-209 increased, the reaction products of BDE-209 on BC–NZVI could compete with BDE-209 and occupy the reaction sites on the BC–NZVI surface.

3.3 Effect of initial pH on BDE-209 removal

Figure 3A shows the effect of pH (5 to 9) on BDE-209 removal. The removal efficiencies increased from 31.00–100% as the pH decreased from 9 to 5 after 336 h. The removal efficiencies increased rapidly at the beginning of the reaction before reaching a balance, which occurred because the BDE-209 concentration and BC–NZVI reactivity were superior at the beginning of the reaction. The consumption of H^+ in the system increased the pH value. The k_{obs} for BDE-209 removal by BC–NZVI were 0.0086/h, 0.0064/h, and 0.0010/h at an initial pH of 5, 7, and 9, respectively (Fig. 3B). These results demonstrated a negative correlation between k_{obs} and pH of 5–9, which was consistent with the findings of previous studies (Li et al. 2007b; Fang and Al-Abed 2008). The results also suggest that relative acidic conditions were beneficial for the production of H^+ , which likely prevent iron from being reduced. However, alkaline conditions were favorable for the formation of iron oxides and iron hydroxides on the BC–NZVI surface, which inhibited the electron transfer from zero-valent iron surface to biomass carbon (Tang et al. 2011).

3.4 Effect of moisture content on BDE-209 removal

As show in Fig. 4, the removal efficiencies increased with increasing moisture content. They increased rapidly during the first 96 h as the moisture content increased from 30–50%. Before the reaction reached a balance, the BDE-209 removal by BC–NZVI increased with increasing moisture content. The removal efficiency for 50% soil moisture content reached a balance (~ 100%) within 288 h. However, the removal efficiencies for 30% and 40% soil moisture reached a steady state within 336 h. The interaction between BDE-209 and BC–NZVI under different soil moisture contents was well fitted by a pseudo-first-order kinetics model. The k_{obs} for BDE-209 removal by BC–NZVI was 0.0052/h, 0.0064/h, and 0.0091/h as the soil moisture content increased from 30–50% (Fig. 4B). These values demonstrate a positive correlation between k_{obs} and soil moisture content at 30–50%. As water is a polar molecule, it can provide protons with strong ability to reduce pollutants and transfer protons in the reaction. Therefore, the water content was essential for the reaction between BC–NZVI and BDE-209 (Xie et al. 2016).

3.5 Reaction mechanism and reaction pathways

Figure 5 shows the intermediate and final products of BDE-209 degradation in the BC–NZVI system at different reaction times. Di- and mono-BDEs were observed after 16 and 24 d, respectively. Nona-, octa-, and hepta-BDEs were formed after BDE-209 lost one to three -Br on day 1. When the bromination reaction continued, more -Br of BDE-209 were substituted by hydrogen atoms. Most BDE-209 in the reaction system was debrominated to lower -Br substituted congeners and DE (diphenyl oxide) within 32 d (Fig. 5). In this study, bromides were measured to investigate the BDE-209 debromination, and the concentration of bromide ions after 336 h of reaction was 0.94×10^{-5} mol/L. If BDE-209 were thoroughly debrominated, the concentration of bromine ions would be 1.0425×10^{-5} mol/L for initial BDE-209 concentration of 10 mg/kg (pH 7.0, moisture content 40%, extraction rate 91%). The obtained debromination rate was 90.17%, which confirmed that the degradation mechanism of BDE-209 was mainly debromination. To investigate the remediation mechanism, we analyzed the transfer and reduction reactions associated with the BDE-209 degradation in soil by BC–NZVI. The adsorption behavior of PBDEs in the soil fitted well the Freundlich model, and the hydrophobic bonding between BDE-209 and soil particles was the main inter molecular force during the BDE-209 adsorption on soil (Liu et al. 2011), which was also confirmed by the octanol/water partition coefficients of BDE-209 ($\log_{K_{ow}} = 9.97$) (Liang et al. 2010). Moreover, the debromination of PBDEs by NZVI is caused by surface interactions (Lowry and Johnson 2004; Xie et al. 2014). The reduction reaction occurred on the BC–NZVI particle surfaces after the BDE-209 molecules came into contact with BC–NZVI as the biomass carbon acted as an electron shuttle (Tang et al. 2011). Therefore, the removal efficiency of BC–NZVI was significantly higher than that of other supported NZVI materials with similar NZVI concentrations.

Figure 6 shows the proposed pathway of BDE soil debromination in the presence of BC–NZVI. Similar debromination pathways of BDE-209 by NZVI have been reported by many researchers (Li et al. 2007a; Zhuang et al. 2012; Fu et al. 2017), which suggests that the pathways of BDE-209 debromination in the soil might be similar to those in water systems.

3.7 Effect of BC–NZVI on soil microbial activities

Dehydrogenase is considered a direct measure of soil microbial activity because only viable cells contain dehydrogenase (Makoi and Ndakidemi 2008; Li et al. 2015). In addition, soil basal respiration is a good indicator of the decomposition of organic matter and is often used as an indicator of total soil microbial activity (Lu et al. 2013; He et al. 2015). Figures 7 and 8 show the impact of BC–NZVI on soil dehydrogenase activity and respiration during incubation for 112 d. Within 112 d, the dehydrogenase activity and respiration of the different treatments showed similar trends. During this time, the dehydrogenase activity and respiration increased significantly more in the BC–NZVI-treated samples than in the samples without BC–NZVI. Higher dehydrogenase activity usually indicates higher soil respiration rates; this was observed in our results, as BC–NZVI increased both dehydrogenase activity and soil basal respiration (Makoi and Ndakidemi 2008; Li et al. 2015).

The control and BDE-209-treated soil samples presented low dehydrogenase activity, which was not significantly affected by pollutant addition. The dehydrogenase activity of the BDE-209 soil without BC–NZVI treatment was lower than that of the control samples, except on days 14 and 21. The control and BDE-209-treated soils presented low soil basal respiration, which did not differ significantly between the BDE-209 treated and control samples within the initial 21 d. After day 28, the soil basal respiration significantly decreased in the treated samples compared with the control ones. This result suggested that BDE-209 is toxic to soil microorganisms, which is consistent with the results of previous studies (Zhang et al. 2012; Han et al. 2016).

4. Conclusions

In this study, we evaluated the effectiveness of BC–NZVI for the removal of BDE-209 from soil and the biotoxicity of soil treated with BC–NZVI. Compared to conventional NZVI or other NZVI supported materials, BC–NZVI provided higher removal efficiencies because of its high mobility and stability as biomass carbon, which acted as electron shuttles during the reaction. A removal efficiency of 100.00% was achieved within 384 h when BDE-209 reacted with 0.10 g/g of BC–NZVI soil at pH 7.00 and 40% moisture content. Moreover, the reaction followed pseudo-first-order kinetics, and the removal efficiency of BDE-209 increased with increasing BC–NZVI dosage and decreasing initial BDE-209 concentration, pH, and moisture content. To assess the BC–NZVI potential for *in situ* remediation of PBDEs in the environment, we conducted biological activity assays (dehydrogenase activity and soil basal respiration). The results showed that although BDE-209 was toxic to soil microorganisms and that dehydrogenase activity and respiration increased significantly for BC–NZVI during the reaction time. Therefore, the results suggest that BC–NZVI can be applied to remediate BDE-209-contaminated soils and reduce the microbial toxicity of PBDEs.

Declarations

Ethics approval and consent to participate: not applicable

Consent for publication: not applicable

Availability of data and materials: All data generated or analysed during this study are included in this published article.

Competing interests: not applicable

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was written by ZX and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

Figure 1

(a) Effect of BC-NZVI dosage on BDE-209 removal; (b) correlation between logarithmic plots of BDE-209 concentration and BC-NZVI dosage with time (BDE-209 initial concentration of 10 mg/kg; 25 °C; pH 7.0; 40% soil moisture)

Figure 2

(a) Effect of BDE-209 initial concentration on BDE-209 removal; (b) correlation between logarithmic plots of BDE-209 concentration and BDE-209 initial concentration with time (0.1 g/g BC-NZVI; 25 °C; pH 7.0; 40% soil moisture)

Figure 3

(a) Effect of initial pH on BDE-209 removal; (b) correlation between logarithmic plots of BDE-209 concentration and pH with time (0.1 g/g BC-NZVI; BDE-209 initial concentration of 10 mg/L; 25 °C; 40% soil moisture)

Figure 4

(a) Effect of soil moisture on BDE-209 removal; (b) correlation between logarithmic plots of BDE-209 concentration and soil moisture content with time (0.1 g/g BC–NZVI; BDE-209 initial concentration of 10 mg/L; 25 °C; pH, 7.0)

Figure 5

Distribution percentage of congeners formed from BDE-209 debromination by BC-NZVI in soil

Figure 6

Proposed debromination pathways of BDE-209 by BC-NZVI in soil

Figure 7

Effect of BC-NZVI on soil dehydrogenase activity during incubation for 112 d (0.1 g/g BC–NZVI; BDE-209 initial concentration of 10 mg/L; 25 °C; pH, 7.0; 40% moisture content)

Figure 8

Effect of BC-NZVI on soil basal respiration during incubation for 112 d (0.1 g/g BC-NZVI; BDE-209 initial concentration of 10 mg/L; 25 °C; pH 7.0; 40% moisture content)