Chemosphere 162 (2016) 235–242

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effects of Ni/Fe bimetallic nanoparticles on phytotoxicity and translocation of polybrominated diphenyl ethers in contaminated soil

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HIGHLIGHTS

- Chinese cabbages were able to uptake and accumulate PBDEs.
- Ni/Fe nanoparticles and BDE209 were both found to have phytotoxicity.
- Fresh nanoparticles promoted the translocation of PBDEs into plants.
- The phytotoxicity in the amended soil was decreased compared with other treatments.

ARTICLE INFO

Article history:
Received 10 April 2016
Received in revised form 29 July 2016
Accepted 29 July 2016

Handling Editor: T Cutright

Keywords:
Ni/Fe bimetallic nanoparticles
Polybrominated diphenyl ethers
Phytotoxicity
Translocation
Uptake
Soil

ABSTRACT

In vivo studies of the interactions of polybrominated diphenyl ethers (PBDEs) in plants have generally focused on uptake, translocation, metabolism and accumulation, but there were limited reports about the phytotoxicity and translocation of PBDEs in contaminated soil with the effects of nanoparticles. In this study, the effects of Ni/Fe bimetallic nanoparticles on translocation of polybrominated diphenyl ethers (PBDEs) in contaminated soil and its phytotoxicity to Chinese cabbage were investigated by soil culture experiments. The results showed that the plant biomass, germination rate, and shoot and root lengths of treated soil (S-5) increased by 0.0044 g, 15%, and 5 and 6 mm, respectively, compared with untreated soil (S-2B). The average Ni and Fe contents of the edible parts(stem and leaf) of the S-5 sample, which contained 0.03 g/g Ni/Fe and 10 mg/kg BDE209, were measured at 1.71 and 184 mg/kg, respectively. The superoxide dismutase, peroxidase and catalase activities in the S-5 sample decreased by 12%, 6.1% and 5.9%, respectively, while compared with the S-2B sample. In all treatments, the contents of BDE209 and the total PBDEs in sample S-5 were lowest, suggesting that the fresh Ni/Fe nanoparticles had higher toxicity than that of the aged nanoparticles. And the lower brominated PBDEs (tri-to nona-) were detected in samples, indicating uptake, debromination and/or metabolism of PBDEs existed in plants. The phytotoxicity and translocation of BDE209 in the contaminated soil decreased as a result of the effects of the Ni/Fe bimetallic nanoparticles.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), a class of brominated flame retardants (BFRs), are widely used in plastics, furniture, cars, textiles, construction materials and electronic equipments (Hamm, 2004). Due to the hydrophobic character of PBDEs, these chemicals are strongly bound to solid particles such as soil and sediments (Labunska et al., 2013). Soil is a major sink for organic contaminants in the terrestrial environment (Huang et al., 2010). As previously reported, the highest PBDE concentrations were tested to be 390,000 ng g^{-1} dw ($\sum$14 PBDEs) in a open-burning of e-waste site in Guiyu (Hale et al., 2006). Several observations showed that increasing concentration/burden of PBDEs had been detected in human tissues when exposing via food chain by soil-plant system (Pulkrabová et al., 2009). However, information related to the remediation of PBDE-contaminated soil was limited.

The application of nano zero valent iron (nZVI) has recently gained much attention due to its high efficiency in transforming

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http://dx.doi.org/10.1016/j.chemosphere.2016.07.101
0045-6535/

pollutants such as organic pollutants, nitrate and heavy metals (Li et al., 2007; Schrick et al., 2002) in soil. nZVI has been found to be effective in the treatments of PBDEs in aqueous phase (Fang et al., 2011; Li et al., 2007). Furthermore, iron-based bimetallic nanoparticles such as Pd/Fe and Ni/Fe have been synthesized to improve the performance of nZVI for the remediation of pollutants (Bokare et al., 2007; Fu et al., 2014). Our prior work successfully demonstrated that Ni/Fe nanoparticles performed significantly removal of the decabromodiphenyl ether (BDE-209) in soil with a removal efficiency of 72% (Xie et al., 2014). However, the lack of understanding is particularly disconcerting in terms of the possible negative effects of Ni/Fe nanoparticles on plants following their application to soil.

In soil-plant system, it is notable that a series of process about translocation and accumulation of the residues of the contaminants and products has been taken place by the application of nZVI in soil (El-Temsah and Joner, 2013; Gardea-Torresdey et al., 2014). Thus, there are three possible explanations. First, with regard to the adsorption of organic compounds by nZVI and the mobility of the nanoparticles, the translocation of organic compounds may be affected. Second, due to the novel physicochemical and structural properties of engineered nanoparticles (ENPs), some studies have suggested that nanoparticles were certified to have potential toxic effects on plants (Domingos et al., 2009; Lin and Xing, 2007; Nel et al., 2006). For this, it is likely to suppose that a combined phytotoxicity exists between the organic compounds and nanoparticles to plants. Finally, the reactivity of nZVI with contaminants leads to the degradation of organic compounds. Consequently, the translocation and phytotoxicity of organic compounds may be affected by the nanoparticles possibility (Fjordbøge et al., 2013).

According to the literature, the toxicity of nZVI has been focused on organisms such as plants or microorganisms (El-Temsah and Joner, 2012; Kim et al., 2014; Ma et al., 2013). For instance, it is shown that nZVI exhibits a strong toxic effect on typha at higher concentrations (>200 mg/L), and significantly decreases the transpiration and growth of hybrid poplar (Ma et al., 2013). For PBDEs, recent reviews documented those plant-PBDEs interactions have focused on the uptake, translocation, metabolism and accumulation, especially nearing the e-waste recycling site. As pointed by Wang et al. (2011a), BDEs-15, 28, and 47 can be uptaken and metabolised by maize, and results demonstrated that PBDEs showed a higher accumulation in maize roots, with the following the order of concentrations: roots >> stems > leaves. In particular, very little research has focused on the phytotoxicity and translocation of PBDEs in contaminated soil resulting from the effects of Ni/Fe nanoparticles.

Chinese cabbage, a leafy vegetable, is cultivated widely in China and other countries. The aim of this investigation was to provide information about effects of Ni/Fe bimetallic nanoparticles on phytotoxicity and translocation of polybrominated diphenyl ethers in contaminated soil for Chinese cabbage (the edible parts). Soil culture experiments were conducted to investigate the uptake and accumulation of Ni/Fe and PBDEs in plants, phytotoxicological effects on anti-oxidation ability of Chinese cabbage. Attempts were made to offer better understanding on phytotoxicity and translocation of PBDEs in contaminated soil with the effects of nanoparticles.

2. Experimental section

2.1. Materials and chemicals

A standard solution of decabromodiphenyl ether was purchased from Cambridge Isotope Laboratories (CIL, Andover, USA) and used to establish the standard curve. Decabromodiphenyl ether (BDE209 > 98%), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, >99%), sodium borohydride ($NaBH_4$>98%), nickel chloride ($NiCl_2 \cdot 6H_2O$, >99%), polyvinylpyrrolidone (PVP, K-30) and ethanol (EtOH, 99.7%) were purchased from Tianjin Damao Company. Acetonitrile and methanol (HPLC grade) were obtained from Tianjin Kermel Chemical Reagents Company. All of the chemicals were used as received without further purification.

The preparation of Ni/Fe bimetallic nanoparticles was described as follows: 50 mL 0.3 mol/L of $NaBH_4$ solution was added dropwise to a 250 ml erlenmeyer flask containing 100 mL 0.1 M $FeSO_4 \cdot 7H_2O$ ethanol/water (30/70, v/v) solution with appropriate PVP (nZVI/PVP, w/w = 1/1) and the mixture was stirred for 5 min at room temperature. The particles formed were magnetically separated and washed three times with deionized water and ethanol to remove the excess $NaBH_4$. Then, to get post-coated bimetallic nanoparticles, a specified amount of $NiCl_2 \cdot 6H_2O$ in 50 mL ethanol solution was rapidly added into the flask and constantly stirred for 30 min. The bimetallic nanoparticles were separated and washed again and finally vacuum dried at 60 °C overnight. The size and distribution of Ni/Fe was determined by dynamic laser and scattering and TEM. The average diameter of the Ni/Fe nanoparticles was about 20–50 nm(TEM), which was demonstrated in our previous report(Fang et al., 2011). Besides, the DLS measured average particles size of Ni/Fe are 28.4 nm (Fig. S1, Supplementary material). The other characterization of Ni/Fe bimetallic nanoparticles was as demonstrated in our previous report (Fang et al., 2011).

2.2. Soil collection and contamination

The red soil(type of loam), obtained from 0 to 20 cm surface soil at the Higher Education Mega Center, southern China (23°03′12.59″N, 11323′25.81″E), were sampled, homogenised, air dried and stored at 4 °C after ground to pass through a 60-mesh. The soil sample characterizations are shown in Supplementary material, Table S1. Soil was artificially contaminated with a BDE209 stock solution (5 mL, 100 mg/L) dissolved in 100 mL of tetrahydrofuran, then stirred until homogenised in the fume hood in darkness to achieve completely volatilised tetrahydrofuran, balanced for 24 h. The final concentration of BDE209 in soil after spiking was measured to be 8.5 ± 0.6 mg/kg.

2.3. Eco-toxicological effect experiments

Root elongation inhibition, seed germination and early plant growth tests are three methods of testing the toxicity of higher plants. This study referenced the ISO standards (ISO, 1993; 2005), performing soil culture experiment. The soil was divided into the following seven treatments: S-1 (blank, unspiked soil); S-2P(soil and PVP (0.03 g/g)); S-2B (spiked soil with BDE209, with a concentration of 10 mg/kg); S-2N (soil and nZVI (0.03 g/g)); S-3 (soil and Ni/Fe (0.03 g/g)); S-4 (soil spiked with BDE209 (10 mg/kg) and Ni/Fe (0.03 g/g)); and S-5 (soil spiked with BDE209 (10 mg/kg) and Ni/Fe (0.03 g/g), after reacting for 3 days).

The seven treatments were further tested in soil culture experiments. All seed germination tests were conducted using the same plant species and seed densities. 90 mm Petri dishes were filled with 50 g of prepared soil and then distilled water was added as required to maintain moisture content at 75% of its water-holding capacity by regular weighing. The dishes were placed in a biochemical incubator for balance at 25 °C for 48 h. Twenty seeds per dish were placed in the soil, with a spacing of 1 cm or more between each seed and to keep the seed radicle and growth direction in a straight line. The dishes were covered with caps and incubated for 14 days in the biochemical incubator which was maintained at 25 °C during the day and 20 °C at night. All