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Excellently reactive Ni/Fe bimetallic catalyst supported by biochar for the remediation of decabromodiphenyl contaminated soil: Reactivity, mechanism, pathways and reducing secondary risks

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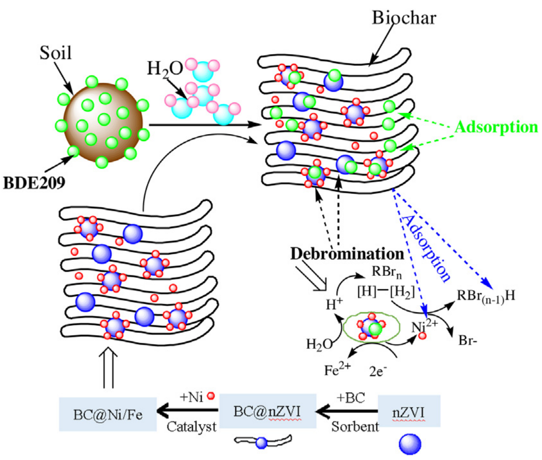
HIGHLIGHTS

- The PBDEs-contaminated soil was remedied by biochar-supported Ni/Fe particles.
- The reductive efficiency of BC@Ni(*)/Fe particles was enhanced.
- Removal of BDE209 was an interactive process combining degradation and adsorption.
- BC@Ni/Fe reduced the bioavailability of metals and adsorbed the byproducts in soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Ni/Fe bimetallic nanoparticles were synthesized using biochar as a support (BC@Ni/Fe) and their effectiveness in removing BDE209 from soil was investigated. BET, SEM, TEM, XPS and FTIR were used to characterize the catalyst, and the efficiencies of biochar, Ni/Fe nanoparticles and BC@Ni/Fe for removing BDE209 from soil were compared. The results showed that Ni/Fe bimetallic nanoparticles highly dispersed in the biochar, reducing its agglomeration. Thus, the reaction activity of BC@Ni/Fe was increased. The removal efficiency of BDE209 by BC@Ni/Fe was 30.2% and 69% higher than that by neat Ni/Fe and biochar, respectively. Meanwhile, an enhanced degradation efficiency of PBDEs in soil was realized by monitoring the formation of Br^- ions with time in the system. In addition, the degradation products identified by GC–MS showed that the reductive degradation of BDE209 proceeded through stepwise or multistage debromination, for which the degradation pathways and removal mechanisms were speculated. Furthermore, BC@Ni/Fe reduced the bioavailability of metals in soil and adsorbed the degradation products of BDE209, representing an improvement over neat Ni/Fe nanoparticles for the remediation of PBDEs-contaminated soil.

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1. Introduction

The contamination of soil by polybrominated diphenyl ethers (PBDEs), especially decabrominated diphenyl ether (DBDE), at electronic waste (e-waste) disposal and recycling sites has proven to be very serious [1–3]. This problem is worsening with the extensive use of brominated flame retardants and the development of the e-waste recycling industry [4]. With the growing interest in nano-zero-valent iron (nZVI), the modified nano zero-valent iron, especially in the form of iron-based bimetallic nanoparticles [5,6], has been intensively studied for the remediation of a wide range of contaminants. Although the modified metal can improve the reactivity of nZVI to a certain extent, it cannot effectively prevent the aggregation of nZVI particles, which diminishes their reaction efficiency. Moreover, the release of metal ions and the generation of high-toxicity intermediate products of organic contaminants during soil remediation by bimetallic nanoparticles, may pose a risk of secondary pollution. Therefore, it is necessary to modify the bimetallic nanoparticles to remedy these limitations [7,8].

Recently, support-modification technology has attracted increasing attention as a promising method for improving the reactivity of nZVI [9–11]. For example, Zhuang et al. [12] synthesized nZVI/Pd-impregnated activated carbon composite particles, which not only enhanced the degradation efficiency of BDE21 by reducing the agglomeration of nZVI, but also improved the adsorption capacity of these particles for the pollutants. Yu et al. [13] reported that smectite clay-templated subnanoscale zero-valent iron had an enhanced dispersibility and could rapidly degrade DBDE with a reaction rate 10 times greater than that by conventionally prepared nanoscale ZVI. Loading nZVI onto a carrier can effectively solve the problem of aggregation, thereby improving its degradation efficiency for organic pollutants. However, the above studies were carried out in aqueous or organic phases. Due to their hydrophobicity, PBDEs are readily adsorbed by soil particles, causing them to accumulate in soil rather than in water. Hence, it is more meaningful to use nZVI for the remediation of PBDEs-contaminated soil. Thus, the choice of a carrier, which would reduce the aggregation of nZVI to improve its reactivity and reduce the risk of secondary pollution, is a major challenge for the future application of nZVI to the remediation of contaminated soil.

Biochar(BC), a promising environmental remediation material, has been used to remediate a wide range of pollutants and has a significant effect on soil amelioration. It owes this behaviour to its high adsorption capacity, a consequence of its large specific surface area, abundantly porous structure and surface functional groups such as carboxyl (—COOH) and hydroxyl (—OH) [14–16]. Herein, the use of biochar as a supporting template to synthesize biochar-supported Ni/Fe bimetallic nanoparticles (BC@Ni/Fe) is shown to overcome the limitations of the neat bimetallic nanoparticles mentioned above. BC@Ni/Fe synergistically combines five properties: 1) biochar can be used as a carrier to facilitate the dispersion and lower the aggregation of nanoparticles; 2) leaching metal ions can be adsorbed and immobilized by biochar through complexation or electrostatic adsorption; 3) BDE209 in soil can be gathered into biochar to improve the degradation efficiency of bimetallic nanoparticles by adsorption and partition; 4) the bioavailability of intermediates can be decreased by biochar through adsorption and immobilization; and 5) biochar can also elevate the fertilizing effect of soil, which is advantageous for in situ soil remediation. Regrettably, there is no study have been focused on removing PBDEs from soil by the biochar −supported nZVI particles.

This study was the first to investigate the removal of PBDEs in soil using biochar-supported Ni/Fe bimetallic particles. Biochar-supported Ni/Fe bimetallic nanoparticles were synthesized, characterized and used for the remediation of PBDE-contaminated soil. The removal efficiencies and kinetics of BDE209 in soil were compared by a series of contact experiments for three types of materials: biochar, Ni/Fe bimetallic nanoparticles and biochar-supported Ni/Fe bimetallic nanoparticles. In addition, the degradation intermediates and products were identified to elucidate the reaction mechanism. Finally, the bioavailability of Ni ions in soil was evaluated by the diethylenetriaminepentaacetic acid (DTPA) and sequential extraction procedure (SEP) methods.

2. Experimental

2.1. Soil collection and preparation

The soil used in this study was collected from surface soil (top 0–20 cm) at the Higher Education Mega Center, southern China (23°03′12.59″N, 11323′25.81″E), then air-dried, sieved, mixed adequately and kept in a dryer before use and characterization. The physicochemical properties of the soil are shown in Table S1 (Supplementary material).

The soil was spiked with a BDE209 stock solution dissolved in 100 mL of THF solution, mixed thoroughly, stirred continuously in a fume hood in darkness until the soil was dried to completely evaporate the THF, and then balanced for 24 h. The final concentration of BDE209 in the spiked soil was 8.7 ± 0.9 mg/kg with a deviation of less than 5%.

2.2. Synthesis and characterization of particles

The chemicals used in this study were listed in Section S1 (Supplementary material). BC@Ni/Fe particles were synthesised by incipient wetness impregnation of $FeSO_4$, biochar, $NaBH_4$ reduction, Ni deposition with a slight modification of the method previously reported by Choi et al. [17]. Details of the synthetic method are described in Section S1. Ni/Fe bimetallic nanoparticles were prepared using the procedure reported in our previous report [5]. Biochar was produced by pyrolysis of bagasse in a muffle furnace at 600 °C for 2 h under the conditions of purging with nitrogen gas and then ground to pass through a 120-mesh sieve. Bagasse is a major crop waste because of sugarcane is one of the most important economic crops in china. So using bagasse to prepare biochar can achieve the purpose of waste utilization and the physicochemical properties of the biochar are shown in Table S2 (Supplementary material).

The N_2 Brunnaer–Emmett–Teller (BET) surface area analyses of the synthesized particles were performed using an ASAP2020M surface analyzer (Micromeritics Instruments, USA). The surface morphology of the particles was examined by a Hitachi S-3700N scanning electron microscope (SEM). Transmission electron microscopy (TEM) images of BC@Ni/Fe particles were obtained using an electron microscope (Hitachi H-3000). An X-ray energy dispersive detector (EDS) was utilized to identify the elemental composition and distribution. X-ray photoelectron spectroscopy (XPS) analysis with Al(K) radiation (photoenergy 1486.6 eV) was performed on an ESCALAB 250 instrument (Thermo-VG Scientific, USA) to survey iron and nickel speciation. The surface functional groups of the particles were analyzed using an FTIR spectrometer with a resolution of 4 cm^{-1} in the region of 4000–400 cm^{-1}.

2.3. Sacrificial batch experiments

Sacrificial experiments were conducted in ambient conditions without precautions to exclude oxygen. 0.06 g of BC, 0.06 g of Ni/Fe nanoparticles or 0.12 g of BC@Ni/Fe materials was added to a 20 mL glass vial containing a mixture (2 g of contaminated soil with appropriate amounts of deionized water), and the vial was tightly capped with PTFE liner. The mixture was placed on a horizontal shaker with