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Complete debromination of decabromodiphenyl ether using the integration of *Dehalococcoides* sp. strain CBDB1 and zero-valent iron

Guiying Xu [a,*], Jiangbo Wang [b], Mang Lu [c]

[a] College of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing 400067, China
[b] School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, China
[c] School of Materials Science and Engineering, Jingdezhen Ceramic Insitute, Jingdezhen 333403, Jiangxi Province, China

HIGHLIGHTS

- Strain CBDB1 was unable to debrominate octa- to deca-BDEs.
- Strain CBDB1 can fully reduce lower brominated congener to diphenyl ether.
- Strain CBDB1 can resist 0.25 g L^{-1} nZVI.

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ABSTRACT

This study investigated the effects of nano- and micro-scale zero-valent iron (nZVI and mZVI) particles on *Dehalococcoides* sp. strain CBDB1 participating in anaerobic reduction of polybrominated diphenyl ethers. nZVI (>0.25 g L^{-1}) had an inhibitory effect upon this strain, whereas 1.0 g L^{-1} mZVI showed no negative impact on bacterial growth. Strain CBDB1 could only utilize lower brominated congeners (<7 bromines) as electron acceptor. In the bio-ZVI system, decabromodiphenyl ether (BDE-209) was first reduced by ZVI to lower brominated congeners, which were then dehalogenated to diphenyl ether by CBDB1. Within 30 d, a BDE-209 debromination efficiency of 16% and 24% was obtained in the bio-nZVI (0.25 g L^{-1}) and bio-mZVI (1.0 g L^{-1}) systems with a corresponding diphenyl ether yield efficiency of 14% and 19%, respectively. The debromination efficiency increased significantly from 8% to 24% with an increase of mZVI dosage from 0.25 to 1.0 g L^{-1} in the bio-mZVI system.

1. Introduction

As a class of effective and economical flame retardants, polybrominated diphenyl ethers (PBDEs) have been widely used in various products such as textiles, polyurethane foams, plastics and electronic products, etc. (Alaee et al., 2003). Many of PBDE congeners have been widely detected in environmental media such as soils, sediments, air, water, animals and even humans (Watanabe and Sakai, 2003; Hites, 2004). This has drawn international concerns on public health and environmental safety

Among PBDE congeners, decabromodiphenyl ether (BDE-209) received the least attention due to its low volatility and relatively low toxicity (Gandhi et al., 2011). However, long range transport and bioaccumulation of BDE-209 have been found and its heavy global application could lead to significant environmental release and bioaccumulation over the long-term (Gandhi et al., 2011).

Reductive dehalogenation by microorganisms under anaerobic conditions is considered to be the major biotransformation process, which offers much promise for pollutant removal (Robrock et al., 2008). Anaerobic dehalogenation may increase the biodegradability of PBDEs in the environment and facilitate the natural attenuation. However, this process requires a relatively long period of time for effective debromination and bio-debromination rate decreases with the increasing bromination degree, which may cause the accumulation of more toxic lower brominated congeners (Robrock et al., 2008; Lee and He, 2010).

Zero-valent iron (ZVI) is an effective reductant which has been used successfully for the reductive dehalogenation of chlorinated organic compounds under anaerobic conditions in both laboratory and field studies (Kim et al., 2008; Truex et al., 2011). In recent years, the application of ZVI for dehalogenation of PBDEs has drawn research attention (Keum and Li, 2005). Because of the larger surface area and higher reactivity relative to ZVI, nano-scale ZVI (nZVI) has been developed to remediate a wide range of organic and inorganic pollutants (Tratnyek and Johnson, 2006).

* Corresponding author.
E-mail address: ilvy06@163.com (G. Xu).

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Recent studies also showed that debromination of PBDEs (including BDE-209) with nZVI was more rapid than that with normal-scale ZVI (Shih and Tai, 2010; Fang et al., 2011; Kim et al., 2014). However, nZVI particles are easily aggregated rapidly in water via Van der Waals and magnetic attraction forces (Tratnyek and Johnson, 2006). To solve this problem, surface modification (using surfactants, starches, cellulose, etc.) and embed-immobilization methods (using activated carbon, silica, clay, polymers, etc.) have been developed for avoiding the agglomeration of nZVI particles (Qiu et al., 2011; Yu et al., 2012). However, these approaches involve complex preparational processes or may introduce secondary pollutants. Additionally, previous work showed that nZVI alone could not efficiently reduce lesser-halogenated PBDE congeners (Zhuang et al., 2010). Although the effective debromination of PBDEs could be obtained by using nZVI/Pd and nZVI/Pd-activated carbon (Zhuang et al., 2011, 2012), noble metal Pd is required for synthesis of these complex nZVI materials, which raises the treatment cost especially for large-scale field application.

Recently, several publications reported that ZVI dosing in anaerobic processes could enhance microbial dehalogenation of pentachloronitrobenzene (Yin et al., 2012) and BDE-209 (Shih et al., 2012). H_2 evolved during iron corrosion was found to promote the reduction of halogenated organic compounds. However, Xiu et al. (2010) found that bacteria dechlorinating trichloroethylene were inhibited by nZVI over a long incubation time. The study of Shih et al. (2012) demonstrated the synergistic effect of ZVI and anaerobic sludge on the degradation kinetics, congeners and bromide ion generation, and the evolving of iron-reducing microorganisms. Considering the uncertainty and complexity of bio-iron system, therefore, there is an urgent need for more research into the development and evaluation of bio-iron interaction mechanisms to enable this approach to become more effective and more versatile in environmental restoration.

Dehalococcoides sp. strain CBDB1 has broad dehalogenation activity on halogenated aromatic compounds, such as chlorobenzenes, chlorinated phenols, polychlorinated biphenyls (PCBs), dioxins, and brominated benzenes (Adrian et al., 2009; Wagner et al., 2012). However, there is no information on BDE-209 debromination by this strain. Thus, the main aim of the present study was to investigate the effects of ZVI with different sizes (nano and micro scale) on the microbial reduction of BDE-209 by strain CBDB1. The degradation kinetics under single and integrated machinery was measured and compared with known microbial PBDE debromination processes.

2. Materials and methods

2.1. Chemicals

Standards of BDE-209, PCB-30, PCB-209 and BDE-77 with high purity (>98.5%) were purchased from Sigma (St. Louis, MO, USA). Surrogate standards (^{13}C-6-OH-BDE47 and ^{13}C-BDE99) and standard solution of PBDEs were obtained from Wellington Laboratories (Guelph, Ontario, Canada). All solvents used were of HPLC grade. Deoxygenated water was used for all experiments.

The micro-ZVI (mZVI) (purity > 99.2%, approx. 100 μm) and nZVI (purity > 99.9%, approx. 50 nm) were purchased from Beijing Dk Nano technology, China. The specific surface areas of these ZVI (determined by N_2 isothermal adsorption) were 0.4 and 28 $m^2\ g^{-1}$ for mZVI and nZVI, respectively.

2.2. Microorganisms

Strain CBDB1 used in this study was obtained from China General Microbiological Culture Collection Center. CBDB1 was grown in a basal medium containing 0.8 mM Ti(III) citrate as reducing agent, vitamin B12, 5 mM acetate as carbon source (Adrian et al., 2000). The electron acceptor 1,2-dichlorobenzene was added from 1 M stock solution in acetone to a final concentration of 20 mg L^{-1}. The bacteria were cultured under strictly anaerobic conditions in 300-mL flasks containing 250 mL medium and 50 mL gas phase. The headspace was flushed with CO_2/N_2 (1:4, v/v). Hydrogen was added with a syringe to the headspace of bottles to a 7.5 mM nominal concentration before sealed with Teflon-lined butyl-rubber septa, and then the flasks were incubated at 25 °C in the dark with constant agitation at 100 rpm.

2.3. Experimental setup

To investigate the reactivity of CBDB1, ZVI or both for debromination of BDE-209, batch experiments were performed in 120-mL serum bottles containing 5 mL inoculation culture, BDE-209 (10 mg L^{-1}) and/or ZVI (0.25, 0.50 or 1.0 g L^{-1}), 4-(2-hydroxyerhyl) piperazine-1-erhaesulfonic acid (HEPES) buffer (60 mM), and basal medium needed to achieve 50 mL final volume. BDE-209 was dissolved in ethyl acetate, and then the ethyl acetate was evaporated under nitrogen in the dark. The initial pH of the culture was adjusted to 6.0. The bottles were flushed with CO_2/N_2 (1:4, v/v) and sealed as described above. Chemical controls without inoculum and negative growth controls without electron acceptor were setup. In the absence of iron, hydrogen was added as electron donor to the bottles with a syringe to the headspace of bottles to a 7.5 mM nominal concentration before sealed. All operations were done in an anaerobic chamber. All cultivations were performed in triplicate at 25 °C with constant agitation at 100 rpm.

2.4. Analytical methods

2.4.1. PBDE analysis

At selected time intervals, three serum bottles were sacrificed for analysis. PBDEs were extracted with a mixture of dichloromethane/diethyl ether (1:1, v/v) for three times. The extracts were combined and concentrated to 1 mL under N_2. PCB-30 and PCB-209 were added as surrogate standards to the samples before extraction and BDE-77 was added to the final solutions as an internal standard. PBDEs in the extracts were analyzed with an Agilent 7890–5975c gas chromatography–mass spectrometer (GC–MS) equipped with a HP-5MS column (60 m × 0.25 mm × 0.25 μm). The operation conditions were as follows: column temperature, 50 °C for 1 min, raised to 120 °C at a rate of 20 °C min^{-1}, and then increased to 310 °C at a rate of 4 °C min^{-1} and held for 30 min. Carrier gas was helium at a flow rate of 1 mL min^{-1}.

2.4.2. Ion analysis

Dissolved iron concentration was determined by a flame atomic absorption spectrometry (F-AAS, Shimadzu AA-7000, Kyoto, Japan). Bromide ions were determined by ion chromatography (C196-E039A, Shimadzu, Japan) with a Shim-pack IC-A3 chromatographic column.

2.4.3. H_2 analysis

Analysis of H_2 was conducted by direct injection of headspace samples into a GC (Auto System, Shimadzu, Japan) equipped with a thermal conductivity detector and a packed column (6 m × 1.8 cm OD, 80/100, Shimadzu, Japan). Helium (20 mL min^{-1}) was used as the carrier gas.

2.4.4. Bacterial count

The number of CBDB1 was counted after staining with SYBR-green by direct cell counting on agarose-coated slides as described by Adrian et al. (2007).