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Kinetics and Pathways for the Debromination of Polybrominated Diphenyl Ethers by Bimetallic and Nanoscale Zerovalent Iron: Effects of Particle Properties and Catalyst

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Abstract

Polybrominated diphenyl ethers (PBDEs) are recognized as a new class of widely-distributed and persistent contaminants for which effective treatment and remediation technologies are needed. In this study, two kinds of commercially available nanoscale Fe⁰ slurries (Nanofer N25 and N25S), a freeze-dried laboratory-synthesized Fe⁰ nanoparticle (nZVI), and their palladized forms were used to investigate the effect of particle properties and catalyst on PBDE debromination kinetics and pathways. Nanofer and their palladized forms were found to debrominate PBDEs effectively. The laboratory-synthesized Fe⁰ nanoparticles also debrominated PBDEs, but were slower due to deactivation by the freeze-drying and stabilization processes in the laboratory synthesis. An organic modifier, polyacrylic acid (PAA), bound on N25S slowed PBDE debromination by a factor of three to four compared to N25. The activity of palladized nZVI (nZVI/Pd) was optimized at 0.3 Pd/Fe wt% in our system. N25 could debrominate selected environmentally-abundant PBDEs, including BDE 209, 183, 153, 99, and 47, to end products di-BDEs, mono-BDEs and diphenyl ether (DE) in one week, while nZVI/Pd (0.3 Pd/Fe wt%) mainly resulted in DE as a final product. Step-wise major PBDE debromination pathways by unamended and palladized Fe⁰ are described and compared. Surface precursor complex formation is an important limiting factor for palladized Fe⁰ reduction as demonstrated by PBDE pathways where steric hindrance and rapid sequential debromination of adjacent bromines play an important role.

Keywords

Polybrominated diphenyl ether (PBDE); Nanoscale zero-valent iron (nZVI); Palladium; Nanofer; Debromination; Pathways

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of extensively-used brominated flame-retardants that are persistent and ubiquitous in the environment and in organisms (Hites, 2004). Three commonly used PBDE technical mixtures are penta-BDEs (mainly BDE 47 (2,2',4,4'-tetraBDE), BDE 99 (2,2',4,4',5-pentaBDE), BDE 100 (2,2',4,4',6-pentaBDE), and

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Supporting Information Available

BDE 153 (2,2',4,4',5,5'-hexaBDE)), octa-BDEs (mainly BDE 153, BDE 183 (2,2',3,4,4',5',6-heptaBDE), BDE 196 (2,2',3,3',4,4',5,6'-octaBDE), and BDE 207 (2,2',3,3',4,4',5,6,6'-nonaBDE)), and deca-BDEs (mainly BDE 209) (La Guardia et al., 2006). Growing environmental and human health concerns with respect to PBDEs led the European Union to ban the use of penta- and octa-BDEs in 2004, and in the United States the sole manufacturer of the penta- and octa-BDEs voluntarily ceased their production in 2004 (Renner, 2004). However, deca-BDE is still widely used and remains unregulated. Those banned PBDEs are still released from products currently in-service or from new products manufactured with recycled materials.

Several biotic and abiotic processes in the environment have been shown to degrade higher-brominated BDE mixtures to lower-brominated BDE congeners, which are more toxic (Gerberding, 2004), bioavailable (Ciparis and Hale, 2005) and persistent (Tokarz et al., 2008) than their parent PBDEs. Environmental degradation processes for PBDEs include photochemical degradation (Bezares-Cruz et al., 2004), reaction with sulfide minerals (Keum and Li, 2005), and anaerobic microbial debromination (Tokarz et al., 2008). These natural processes would gradually contribute to the accumulation of lesser-brominated BDEs from the very large burden of BDE 209 that already exists globally.

It is thus important to develop effective and feasible remediation technologies that can debrominate or mineralize PBDEs completely and rapidly. Zerovalent iron (Fe^0) is considered a strong reducing agent for many polyhalogenated organic contaminants, including PBDEs (Johnson et al., 1996; Keum and Li, 2005). In its nanoscale form, zerovalent iron (Fe^0) can greatly improve PBDE debromination rates compared to microscale Fe^0 due to the larger specific surface area (Li et al., 2007; Zhuang et al., 2010). Adding a metallic catalyst by doping Fe^0 with palladium (Zhuang et al., 2011) or nickel (Fang et al., 2011) is found to improve PBDE reduction kinetics. Our previous studies showed that laboratory-synthesized nanoscale zerovalent iron (nZVI) and palladized nZVI (nZVI/Pd) can debrominate lower-brominated BDEs to diphenyl ether (DE), which is their fully debrominated form (Zhuang et al., 2010; Zhuang et al., 2011). Thus, nZVI and nZVI/Pd assisted debromination of PBDEs is a potentially valuable treatment or remediation technique.

Due to the growing interest in nanoscale Fe^0 for waste treatment and remediation applications, nZVI is now commercially available from companies like Nano Iron and Toda Kogyo Corp. Reactive nanoscale iron particles (RNIP) from Toda Kogyo Corp. are synthesized by gas-phase reduction of iron oxides in H_2 (Liu et al., 2005). It was found that RNIP dechlorinated trichloroethene (TCE) at 4-fold lower rates than nanoscale Fe^0 synthesized by borohydride reduction of ferrous iron, which is probably due to the thicker and more crystalline Fe_3O_4 shell contained within RNIP (Liu et al., 2005). Nanofer slurries from Nano Iron are synthesized by a dry-phase production technique (Cernik, 2010). In the field trials, Nanofer slurries were more efficient than RNIP in dechlorinating chlorinated-ethenes but showed rates similar to those of RNIP in dechlorinating polychlorinated biphenyls (PCBs) (Cernik, 2010).

Better understanding of PBDE debromination kinetics and reaction products by different Fe^0 nanoparticles will foster the development of these materials for efficient application and help prevent unintended effects on ecosystems and human health. In this study, the effects of particle properties and palladium loading on PBDE debromination kinetics, pathways and mechanisms were investigated. Laboratory-synthesized nanoscale Fe^0 , two commercially available nanoscale Fe^0 slurries from Nano Iron, Nanofer 25 (N25) and Nanofer 25S (N25S), and their palladized forms were evaluated to debrominate PBDEs. Several environmentally-abundant PBDE congeners, including BDE 47, 99, 153, 183 and 209, were

selected to elucidate the overall debromination pathways and mechanisms for both unamended and palladized nanoscale Fe⁰.

2. Material and methods

2.1 Synthesis and characterization of particles

Details of the synthesis methods of nZVI and nZVI/Pd were described previously (Zhuang et al., 2010; Zhuang et al., 2011). Both nZVI and nZVI/Pd were dried by a vacuum freeze-drier (VirTis Freezemobile 12ES, SP industries inc., Gardiner, NY).

Two kinds of commercially available nanoscale Fe⁰ slurries, N25 and N25S, were obtained from Nano Iron s.r.o. (Czech Republic). N25 and N25S are aqueous dispersions of nanoscale Fe⁰ stabilized by iron oxides, and iron oxides plus a biodegradable organic modifier polyacrylic acid (PAA), respectively (Klimkova et al., 2011). A portion of each slurry was freeze-dried and then referred to as DN25 and DN25S. A portion of each slurry was dispersed and palladized by mixing with equal volumes of palladium acetate solution (in acetone) and then referred to as N25/Pd and N25S/Pd.

The N₂ Brunnaer–Emmett–Teller (BET) specific surface areas, the total iron and palladium contents, and zero-valent iron (Fe⁰) content of the particles were determined as reported in our previous work (Zhuang et al., 2010; Zhuang et al., 2011).

2.2 Debromination experiments

To investigate the debromination pathways and reaction kinetics, debromination tests of laboratory-synthesized and commercially-available nanoscale Fe⁰ (nZVI, N25, N25S, DN25, DN25S) or their palladized form (nZVI/Pd, N25/Pd, N25S/Pd) were conducted on selected PBDEs (Accustandard) under anoxic conditions. The PBDE stock solutions (around 200 µg/L) were prepared in an acetone/milli-Q water solution (50:50, v/v, pH=7) with 0.4 % sodium azide (Fisher) added to minimize microbial degradation. Either 1 g of nZVI, 0.1 g or 0.3 g of nZVI/Pd, 0.25g DN25 or DN25S, 2 ml N25 or N25S slurry, 0.5 ml N25/Pd or N25S/Pd slurry, was added to a 40 ml vial containing 10 ml of the individual PBDE stock solution. The sample vial was capped with Teflon septa, placed on a horizontal shaker at 60 rpm, and covered to avoid photodegradation. Blank samples without contaminants but using the same solvent were set up in the same way for all nanoscale Fe⁰ particles or slurries tested. At preselected time intervals, samples were sacrificed to measure headspace H₂, and the concentrations of the parent compound as well as the reaction products. Details on sample extraction and GC analysis are available in the Supporting Information.

2.3 Kinetics analysis

A pseudo-first-order kinetic model was applied to describe reductive debromination of PBDEs (Zhuang et al., 2010). Observed debromination rate constants (k_{obs}) and Fe⁰ concentration normalized rate constants (k_{Fe^0}) were calculated to compare reaction kinetics. A general indication of the efficiency of each particle can be demonstrated by the conversion fractions of the same compound at a certain time. The conversion fraction is defined as the removed fraction of the initial organic bromines of the parent congener, where all intermediates formed were taken into account (Agarwal et al., 2009). A sample calculation for BDE 47 debromination is shown in Equation S1 (Supporting Information).

3. Results and discussion

3.1 Effect of particle properties on PBDE debromination

The N₂-BET specific surface area and the elemental compositions of the nanoscale Fe⁰ particles studied are given in Table 1 and Table 2. The specific surface areas and particle size distributions of the laboratory-synthesized and Nanofer nanoscale Fe⁰ particles after the freeze-drying process were similar. The dispersed N25 and N25S slurries used in our study have an Fe⁰ content of 0.12 g/mL, and the Fe⁰ content decreased by half (0.06 g/mL) after the Pd deposition process where an equal volume of slurry and palladium acetate solution was mixed.

BDE 47, one of the most environmental-abundant PBDEs, was used to evaluate the debromination potential for laboratory-synthesized and Nanofer nanoscale Fe⁰. BDE 1 was used to evaluate the debromination potential for palladized nanoscale Fe⁰ for easier sampling due to its low activity towards the electron donor. A series of contact experiments for BDE 47 by nZVI, N25, N25S and for BDE 1 by nZVI/Pd, N25/Pd, N25S/Pd with similar Pd loadings (0.3 Pd/Fe wt%) were conducted to study the reaction kinetics (Figure S1 and S2). As illustrated in Figure S2, the debromination of BDE 1 by palladized nanoscale Fe⁰ slowed after 1 hr due to the deactivation of particles and increase of pH (Zhuang et al., 2011). Therefore, to better compare the debromination potentials of different palladized Fe⁰ nanoparticles, data within the same period (1 hr) were applied to obtain initial rate constants. The Fe⁰ concentration normalized rate constant (k_{Fe}) were calculated to compare the reaction efficiency of different particles when their specific surface area differences are not drastic and where Pd loadings (Pd/Fe wt %) are similar (Zhuang et al., 2010; Zhuang et al., 2011).

The values of k_{Fe} in Table 1 and Table 2, show that the N25 slurry was 3.3 times more efficient on debrominating BDE 47 than the N25S slurry, while the N25/Pd slurry was 3.5 times more efficient at debrominating BDE 1 than the N25S/Pd slurry. The surfactant PAA (3%), used to disperse N25 to form N25S, would account for the decrease in the PBDE debromination kinetics by N25S. In our solution, side chains of PAA would lose their protons and acquire a negative charge, which has a repelling effect on the hydrophobic PBDEs. This might hinder the contact of the iron surface with PBDE. However, it has been suggested that in a remedial application stabilization with PAA would increase nanoscale Fe⁰ mobility by reducing their aggregation and generating a negatively charged surface (Kanel et al., 2008; Jiemvarangkul et al., 2011). Another commonly used polymer for sterically stabilized aqueous dispersions, polyvinyl pyrrolidone (PVP) was observed to increase the catalytic activity of nZVI/Ni to debrominate BDE 209 (Fang et al., 2011). Such effects might relate to the blocking of reactive sites and the difference in the polarity of the polyelectrolyte, where PVP is less polar than PAA, resulting in a less negative effect on interaction between the iron surface and PBDEs.

The N25S slurry was twelve times more efficient in debrominating BDE 47 than nZVI, while the N25S/Pd slurry was nine times more efficient in debrominating BDE 1 than nZVI/Pd. To explore the reason, 2-day contact tests of BDE 47 with freeze-dried N25 and N25S (DN25, DN25S) were set up. From Table 1, the 2-day conversion fractions of BDE 47 for those freeze-dried particles were quite similar, but an order of magnitude less than those for the slurries. A similar finding was true for freeze-dried nZVI/Pd compared with either N25/Pd or N25S/Pd slurries, all of which had the same Pd loading (0.3 Pd/Fe wt%) for debromination of BDE 1. These results suggest that the freeze-drying and stabilization processes in the laboratory are the main factors contributing to the lower activity of the freeze-dried Fe⁰ nanoparticles.

Considering the differences of Fe^0 mass in each system, freeze-dried Nanofer particles had a three-fold higher activity than freeze-dried laboratory-synthesized nZVI. N25 slurry was also found to dechlorinate TCE faster than wet nZVI synthesized by the same method in this study (Cernik, 2010). Such differences in kinetics between the two particle types were likely caused by composition differences due to synthesis methods, particularly the presence of boron and other impurities, as well as the shell composition and thickness, as the two types have a similar particle size and surface area. Some other factors resulting from the composition differences, such as the extent to which each nanoparticle aggregates, would also contribute to the kinetics differences.

3.2 Effect of palladium loading on PBDE debromination

According to a previous study, the debromination reaction rate of PBDEs can be significantly increased by coating nZVI with Pd (Zhuang et al., 2011). But it is important to minimize the Pd loading while maintaining satisfactory catalytic activity, considering that Pd is noble metal and the addition of Pd to water may cause environmental problems (Feng and Lim, 2007). nZVI/Pd with ten different Pd loadings (0.05 – 1.1 Pd/Fe wt%), and N25/Pd and N25S/Pd with four different Pd loadings (0.08 – 0.6 Pd/Fe wt%) were synthesized, and they reacted with BDE 1 for 1 hour.

From Figure 1, the 1-hr conversion fractions of BDE 1 by nZVI/Pd were maximized at Pd loading of 0.3 Pd/Fe wt%. The Fe^0 -content normalized H_2 production rate, a good indicator of iron corrosion, increased logarithmically with increasing Pd loading from 0.05 to 1.1 Pd/Fe wt%. One explanation for the drop in reactivity above 0.3 Pd/Fe wt% is the deposition and growth mechanism of Pd on the nZVI surface. The active site for reduction, represented by the available surface area of Pd, increases roughly linearly with the Pd mass percentage for initial Pd nucleation and growth, but decreases with excessive Pd addition for which the Pd may coalesce as discrete deposits, and hence lose effectiveness at > 0.3 Pd/Fe wt%. Another explanation is that extensive H_2 bubbles formed from nZVI/Pd might hinder formation of active reductants on the Pd surface, which plays some role in the rate enhancements for PBDEs (Zhuang et al., 2011). In this case, the amount of Pd is a limiting factor affecting the BDE 1 debromination rate in our system at a Pd loading of < 0.3 Pd/Fe wt%, while the formation of surface active reductants becomes a limiting factor at a Pd loading of > 0.3 Pd/Fe wt%. Similarly, the reduction of chloroacetic acids (Wang et al., 2010) and TCE (He and Zhao, 2008) by nZVI/Pd were found to maximize at 0.1 Pd/Fe wt% under their laboratory conditions.

For 1-hr contact tests with N25/Pd, the optimum Pd loading was not identified because more than 98% of BDE 1 was debrominated by N25/Pd with all Pd loadings tested (0.08, 0.2, 0.3, 0.6 Pd/Fe wt%). For 1-hr contact tests with N25S/Pd, the BDE 1 conversion fraction increased logarithmically with increasing Pd loading from 0.08 to 0.6 Pd/Fe wt% (Figure S3). The debromination kinetics of BDE1 in the N25S/Pd system are not proportional to Pd loadings, probably due to the trends of active Pd growth and active reductants formation as demonstrated in our nZVI/Pd system. A loading of 0.3 Pd/Fe wt% for N25S/Pd was considered to be optimum, as the debromination kinetics for BDE 1 was close to the maximum kinetics at a higher Pd loading.

The effect of nZVI/Pd addition on removal efficiency was also investigated by time-series tests with BDE 1 using 10 g/L and 30 g/L nZVI/Pd (0.3 Pd/Fe wt%) (Figure S2). Data within 1 hr were used to obtain the initial observed debromination rate (k_{obs}), 0.48 /hr for the 10 g/L nZVI/Pd addition and 1.02 /hr for the 30 g/L nZVI/Pd addition, respectively. The faster observed kinetics with which BDE 1 was debrominated for the higher nZVI/Pd addition was probably due to a greater likelihood of its contact with Pd, indicating that Pd was still a limiting factor for debromination at an nZVI/Pd dose of 10 g/L. However, the

three-times higher nZVI/Pd addition only promoted debromination kinetics by a factor of two, resulting in a lower Fe° -concentration normalized debromination rate (k_{Fe°). It was found that the unit H_2 production rates were the same for both cases, indicating that the nZVI/Pd particles, with the same Pd loading, were deactivated at similar rates. Thus, the lower value of k_{Fe° for higher nZVI/Pd content could be caused by some other factors, such as inefficient mixing at higher metal addition.

3.3 Debromination of environmentally-abundant PBDEs by Fe° nanoparticles

The debromination of environmental-abundant higher-brominated BDEs, including BDE 47, 99, 153, 183, 209, was explored for both unamended and palladized nanoscale Fe° . Based on BDE 47 debromination tests with five kinds of nanoscale Fe° (nZVI, N25, N25S, DN25, DN25S) (Figure S4) and three kinds of palladized nanoscale Fe° (nZVI/Pd, N25/Pd, N25S/Pd) (Figure S5), although the specific pathways were dependent on whether Pd was present, the main debromination pathways remained the same with different particles, whether laboratory-synthesized or Nanofer. Therefore, the N25 slurry, the unamended nanoscale Fe° showing the fastest kinetics in our system, and freeze-dried nZVI/Pd (0.3 Pd/Fe wt%), the laboratory-synthesized palladized nanoscale Fe° with optimized Pd loading, were chosen to demonstrate the general differences in debromination preferences and mechanisms between unamended and palladized Fe° .

N25 was able to rapidly debrominate a wide range of selected PBDEs, from tetra- to deca-BDEs. The majority of parent PBDEs in the system was debrominated to their lower-brominated congeners and DE within 1 week, mainly di-BDEs, mono-BDEs and DE (Figure S6). Due to the persistence of di-BDEs and mono-BDEs, the aging of iron particles, and increasing the pH in the system (Zhuang et al., 2010; Zhuang et al., 2011), the product distributions for N25 at two weeks changed slightly compared to those at one week. In the nZVI/Pd (0.3 Pd/Fe wt%) system, a considerable amount of DE was detected after one hour, and the majority of the parent PBDEs was debrominated to DE within one week (Figure S7). By contrast, the debromination reactions with the N25 and nZVI/Pd were very much faster than anaerobic microbial debromination. More than half of BDE 47 was debrominated by N25 and nZVI/Pd within 6 hours, while the half life of BDE 47 was reported to be almost 58 days in a cosolvent-enhanced biomimetic system and several years in anaerobic sediment microcosms (Tokarz et al., 2008). Thus, abiotic debromination by nanoscale Fe° appears potentially advantageous for rapid reaction with PBDEs.

With N25, the major debromination pathways for the five selected PBDEs are shown in Figure 2(a). The overlapping pathways for those PBDE congeners suggest a stepwise reaction where inherent chemical properties play an important role in the debromination as indicated from the good linear free energy relationships for unamended Fe° nanoparticles (Hu et al., 2005; Keum and Li, 2005; Zhuang et al., 2010). The debromination pathways for BDE 209 are similar to those reported for nZVI (Shih and Tai, 2010). BDE 183 was the main hepta-BDE in the debromination pathways for BDE 209 resulting from debromination of two meta-Brs and one ortho-Br. Another major hepta-BDE from BDE 209 debromination was presumptively identified as BDE 184, resulting from the debromination of three meta-Brs. The main products for all selected PBDEs after one week were BDE 15 (4,4'-diBDE), BDE 3 (4-monoBDE) and DE, indicating the persistence of para-Br. The general debromination preference is meta-Br > ortho-Br > para-Br for unamended Fe° , which is consistent with previous studies (Keum and Li, 2005; Li et al., 2007; Shih and Tai, 2010; Zhuang et al., 2010).

With nZVI/Pd, the major debromination pathways including the top two reaction products in each homologue group for the five selected PBDEs are shown in Figure 2(b) and their major identified products with percentage within each congener are summarized in Figure S8. The

main hepta-BDE in the BDE 209 debromination pathways by nZVI/Pd was also BDE 183 and BDE 184, similar to that of unamended Fe^0 . A high fraction of BDE 183, BDE 184, BDE 153 and BDE 154, the reaction products of BDE 209 debromination was also observed photolytically and biologically (Tokarz et al., 2008; Zeng et al., 2008). Due to the crowded bromines around the two benzene rings for higher-brominated BDEs, the bromines were probably more vulnerable to nucleophilic substitution, as inferred from electron density distribution, rather than steric, considerations (Zhuang et al., 2010; Zhuang et al., 2011).

The main products for all selected PBDEs in reaction with nZVI/Pd after one week were BDE 4 (2,2'-diBDE), BDE 1 and DE, indicating the persistence of ortho-Br. The major one-level lower congeners from parent PBDEs tested were generated by debromination of para-Br. Thus, for PBDEs lower than hepta-bromo homologues, a steric hindrance could inhibit the formation of a precursor complex on the palladium surface (Noma et al., 2003), resulting in a general debromination preference of para-Br > meta-Br > ortho-Br for palladized Fe^0 (Zhuang et al., 2011). Although the toxicity of PBDEs has not been fully studied, researchers found that at least one para-bromine atom should be present beside two ortho (2, 6)-bromine atoms on one phenyl ring to form a common structural feature for estrogenic PBDEs (Meerts et al., 2001). Therefore, the fast and preferred elimination of para-bromines by palladized Fe^0 would reduce the potential estrogenic potencies for PBDE debromination intermediates.

Despite this debromination preference, the main reaction intermediates by palladized Fe^0 were also highly dependent on the parent PBDEs tested, which was different from the unamended Fe^0 system. A rapid sequential two/three-step, or simultaneous debromination due to the formation of active intermediates on the palladium surface, was shown to be significant for nZVI/Pd with BDE 183, 153, and 99. In these cases, adjacent bromines were quickly debrominated in sequence in the order of para-Br, meta-Br and ortho-Br. For example, the main intermediate congeners for BDE 183 were BDE 149 by para-Br debromination, followed by BDE 102 (2,2',4, 5,6'-pentaBDE) by adjacent meta-Br debromination, and then BDE 48 by adjacent ortho-Br debromination (simplified as 183-(P)-149-(M)-102-(O)-48). Similar phenomena were found for BDE 153 (153-(P)-101-(M)-48-(O)-29), and for BDE 99 (99-(P)-48-(M)-17).

A degradation pathway is both compound specific and reductant specific. The differences in PBDE debromination pathways between unamended and palladized Fe^0 is a consequence of the differences in debromination mechanisms. The main debromination mechanisms for unamended Fe^0 appears to be a direct electron transfer (Zhuang et al., 2010). Similarly, PBDE photodebromination is also caused by electron transfer, as there is a correlation between the debromination rate constants and the calculated lowest unoccupied molecular orbital energies (E_{LUMO}) (Zeng et al., 2010; Zhuang et al., 2010). Fe^0 reduction and photodebromination of PBDEs have similar major products (Zeng et al., 2010). Zeng et al. were able to build an energy-based debromination model to predict the major congeners and kinetics for PBDE- Fe^0 reduction and photodebromination, where the reactions are governed by the enthalpy of formation (Keum and Li, 2005; Zeng et al., 2008; Zeng et al., 2010).

In contrast, a greater role of H atom transfer was found to control PBDE debromination by palladized Fe^0 (Kim et al., 2008; Zhuang et al., 2011). Compared to reactions on an iron surface, the debromination reactions on a palladium surface highlight the steric hindrance and rapid sequential debromination of adjacent bromines, indicating the importance of surface precursor complex formation. Similarly, in addition to the enthalpy of formation and the type of microbial culture, steric effects also control PBDE anaerobic microbial debromination (Zeng et al., 2010). Moreover, preferential removal of para- and meta-bromines was observed in the PBDE debromination tests with sewage sludge collected from

a mesophilic digester (Gerecke et al., 2005) and three microbial cultures (Robrock et al., 2008). Therefore, as with palladized Fe⁰ reduction of PBDEs, an energy-based model cannot predict well the major congeners and kinetics for anaerobic microbial debromination of PBDEs.

4. Conclusions

Remediation of PBDEs by nanoscale Fe⁰ and palladized nanoscale Fe⁰ are promising techniques due to their fast kinetics and full debromination potential for a wide-range of PBDEs. The commercially available N25 slurry was found to debrominate PBDE effectively to mono- and di-BDEs in one week. A biological oxidation process might be introduced to further mineralize those lower-brominated BDEs. For example, an nZVI-biological sequential treatment method can degrade PBDE to bromophenols and other prospective metabolites in one month (Kim et al., 2012). PBDE debromination by nZVI/Pd is advantageous because of its faster kinetics, concerted debromination, and preferred elimination of para-bromines. Work presented in this study shows that nZVI/Pd can debrominate selected environmentally-abundant PBDEs to diphenyl ether in one week. The palladium loading should be optimized, and proper drying and stabilization processes should be developed to facilitate the handling and deployment of nanoscale Fe⁰ particles while still preserving their activity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- Both commercially-available and laboratory-synthesized nZVI can fully debrominate PBDEs.
- nZVI/Pd is effective in debrominating environmentally-abundant PBDEs to diphenyl ether.
- There is an optimum palladium loading to maximize PBDE debromination kinetics.
- The freeze-drying and stabilization processes slow PBDE debromination.
- Step-wise debromination pathways for environmentally-abundant PBDEs by unamended and palladized nZVI are elucidated.

Figure 1.

The effect of palladized loading on BDE 1 debromination conversion fraction and unit hydrogen production rate in 1 hr by palladized laboratory-synthesized nanoscale zero-valent iron particles (nZVI/Pd). The conversion fraction was calculated by Equation S1.

Figure 2. Debromination reaction pathways of selected PBDEs, including BDE 209, 183, 153, 99, 47 by (a) nanoscale Fe⁰, N25, and (b) palladized nanoscale Fe⁰, nZVI/Pd (0.3 Pd/Fe wt%). The numbers represent the BDE congeners. The capital letters next to the numbers represent the major intermediates of respective parent compounds BDE-209 (A), 183 (B), 153(C), 99 (D), 47 (E) in each congener group. The thick arrows represent the major pathways inferred from major intermediates by debrominating different parent compounds. The specific position of a bromine debrominated in each pathway is shown in the box: P for para-Br, M for meta-Br, O for ortho-Br. An asterisk (*) indicates a congener that is presumptively identified due to lack of available standards.

Table 1

Physical, chemical and debromination properties of laboratory-synthesized and commercially-available nanoscale zero-valent iron.

Composition (wt % or g/L) ^a		N ₂ BET surface area (m ² /g)	BDE 47 debromination kinetics			
Fe ^b	Fe ^c		k _{obs} (h)	k _{Fe} ^c (L/h/g)	2 days conversion % ^d	
nZVI	76±2	60±3	24±1	0.09	1.50E-03	2.7
N25S	131±7	119±5	-	0.37	1.87E-02	8.6
N25	129±6	120±5	-	1.25	6.24E-02	44
DN25S	90±2	78±3	22±2			2.5
DN25	90±2	80±2	25±1			3.1

Note:

^aThe composition has a unit of wt % for dried particles (nZVI, DN25S, DN25), the composition has a unit of g/L for wet slurries (N25S, N25).

^bTotal iron content.

^cThe observed rate constants (k_{obs}) were normalized by the mass concentration of ZVI in the system.

^dThe conversion fraction was calculated by Equation S1.

Table 2

Physical, chemical and debromination properties of palladized laboratory-synthesized and commercially-available nanoscale zero-valent iron.

	Pd loading (Pd/Fe wt %)	Composition (wt % or g/L) ^a		N ₂ BET surface area (m ² /g)	BDE 1 debromination kinetics		
		Fe _t	Fe ⁰		k _{obs} (h)	k _{Fe} ^b (L/h/g)	15 min conversion % ^c
nZVI/Pd	0.3	76±2	60±3	25±1	0.48	0.08	31
N25S/Pd	0.3	66±2	59±4	-	1.98	0.73	62
N25/Pd	0.3	65±3	60±4	-	7.02	2.58	87

Note:

^aThe composition has a unit of wt % for dried particles (nZVI/Pd), the composition has a unit of g/L for wet slurries (N25S/Pd, N25/Pd).

^bThe observed rate constants (k_{obs}) were normalized by the mass concentration of ZVI in the system.

^cThe conversion fraction was calculated by Equation S1.