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Application of Low-Cost Sponge Iron for Complete Debromination of Polybrominated Diphenyl Ethers

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ABSTRACT

Although penta- and octa-BDE congeners were included in the Stockholm Convention recently, decabromodiphenyl ether (BDE 209) is currently exempted from regulation and continues to be used heavily. Thus a large amount of environmental samples has been seriously contaminated, which calls for proper economic remediation technologies. In this study, debromination of BDE 209 with sponge iron, also called direct-reduced iron, was studied to investigate the degradation process and reaction kinetics. The reaction was described well by the pseudo-first-order kinetic model. With increasing reaction time, sponge iron particles could debrominate BDE 209 into lower environmental dominant brominated compounds, such as BDE-153, BDE-100, BDE-99, BDE-47 and diphenyl ether, the complete debromination product. This is the first report of complete debromination of BDE 209 using sponge iron. Influenced by iron dosage, PBDEs concentration, solvent condition and other parameters, the reaction rates were comparable with nanoscale zerovalent iron and other Fe-based materials. From an engineering point of view, sponge iron would spawn low-cost remediation technologies for complete detoxification of PBDEs and benefit practical halogenated organic compounds remediation.

KEYWORDS: Debromination, Kinetics, Pathway, Polybrominated Diphenyl Ethers, Sponge Iron.

1. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of organobromine compounds that are widely used as flame retardants in a wide range of products, including building materials, electronic equipment, furnishings, plastics and textiles.¹ Sharing some features or commonalities with polychlorinated biphenyls (PCBs),² PBDEs are found in sediments, freshwater, birds, plants and human tissues, even in remote area because of their unlimited consumption in the past.^{3,4} Recent evidence suggested that PBDEs concentrations in the environment have increased exponentially in the past 30 years.⁵ Due to their potential toxicity, bioaccumulation, and persistence, the European Union has initiated regulations to phase out the production and usage of penta- and octa-BDE technical mixtures in the RoHS Directive in August 2004, and the United States voluntarily phased out the production of penta- and octa-PBDE formulations. In May 2009 certain congeners contained in commercial penta- and octa-BDEs were added to Annex

A of the Stockholm Convention on Persistent Organic Pollutants (POPs) by the fourth Conference of the Parties in Geneva.

However, till now the decabromodiphenyl ether (BDE 209), which is currently exempted from regulation, continues to be heavily used, accounting for ~83% of all PBDEs used (mass basis).⁶ From a chemical point of view, BDE 209 is a labile molecule, which can be reduced by hydride reagents,⁷ and be photolyzed under UV irradiation and natural sunlight.^{8,9} Literature review indicated that BDE 209 usually underwent reductive debromination to form lower PBDE congeners, such as those in the penta-BDE formulation,^{10,11} potentially increasing the environmental burden of PBDEs. It is of importance to develop potential sustainable remediation technologies for BDE 209 decomposition. Several elementary metals have been applied to remediate organic pollutants with dramatic results. Zerovalent iron (ZVI) is one such metal and can reduce highly oxidized halogenated organic compounds, such as PCBs and PCDDs.^{12,13} Recently, remediation of PBDEs contamination in aquatic system using ZVI has also been carried out.^{4,14,15} The decrease of ZVI particle size can greatly improve reaction rate due to the higher surface reactivity on larger specific surface area (SSA).¹⁶ However, due to the difficulty of assembling, the

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application of the nano-sized particles can be problematic with a view to engineering practice.¹⁴ Moreover, the economic cost of nano-ZVI (nZVI) will be another important factor when to determine whether it can be applied to environment or not. Occupational safety and health are also important concerns towards nanoparticles in combination with the risks of fire or explosion during the storage and handling.¹⁷ Sponge iron, also called direct-reduced iron, is produced from direct reduction of iron ore by a reducing gas produced from natural gas or coal. As an effective oxygen scavenger, sponge iron is easy to produce, transport and install. The primary reason for this selection is the abundant local supply and relatively low cost (~\$0.5/kg) in combination with a fairly large SSA (~1.0 m²/g) and comparatively high ZVI content. If applied, sponge iron can conquer the drawbacks of nZVI without sacrifice the efficiency.

Recent studies indicated that during the reductive dehalogenation of BDE 209 as low as di-BDE and tri-BDE were produced.^{4,14} The complete debromination of BDE 209 has not been demonstrated. Previous study has shown that parent diphenyl ether underwent hydroxylation or methoxylation prior to, or in conjunction, with aromatic ring cleavage treated by bacteria or fungi.¹⁸ Chemical remediation can be used as a pre-treatment of microbial process for completely non-toxicity of BDE 209. Although nZVI has proved to be a powerful reducing agent for PBDEs remediation, the high cost and other disadvantages hamper its engineering application seriously. To find an alternative, this study was initiated to investigate the degradation reactivity of BDE 209 toward cost-effective sponge iron, to examine the kinetics of PBDEs transformation, and to propose the degradation pathway.

2. EXPERIMENTAL DETAILS

2.1. Sponge Iron Preparation and Characterization

Sponge iron was purchased from Lida Material Company (Gongyi, China) with a density of 1.7 g/cm³. For debromination experiments, sponge iron was prepared in a centrifugal ball mill (QM-3SP2, Nanjing Nanda Instrument, Nanjing, China), equipped with four 100 mL steel grinding jars (inner dimensions 5.0 cm by 5.5 cm) each containing 40 steel ball bearings (0.5 cm diameter, at a total mass of 36.58 g). After milled for 30 minutes, the material was sieved by using a 325 mesh sieve.

The morphology of the prepared particles was investigated using a scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) and the surface elemental composition of the particles was determined by energy dispersive X-ray detector (EDS, INCAx-sight, Oxford Instruments, UK). Particles were dispersed in ethanol by sonication and dripped onto a carbon-coated Cu-grid for later observation in a transmission electron microscopy (TEM, JEM-1011, JEOL, Japan). The X-ray diffraction

(XRD) analysis with Cu K α edge ($\lambda = 1.5418 \text{ \AA}$) radiation was performed on a powder Bruker AXS D8 Advance X-ray diffractometer (Karlsruhe, Germany). XPS investigations were performed with a PHI 5300 spectrometer (USA), using a monochromatized focused Al K α X-ray source (1486.6 eV). The Brunnaer-Emmett-Teller (BET) SSA of triplicate prepared particles was performed using a QUADRASORBTM SI surface area and pore size analyzer (Quantachrome Instruments, USA), employing the nitrogen adsorption method. The element contents of the particles were determined from atomic absorption spectrophotometry (AAS, 3510, Anjielun Technologies, Shanghai, China) by following EPA Method 7010.

2.2. Debromination Experiments

Designed gram of sponge iron was added to a serum vial, in which different concentrations of BDE 209 stock solution were mixed with an equal volume of ultrapure water to form a 10 mL solution containing desired concentration of BDE 209. As PBDEs with high hydrophobicity is difficultly soluble in water, the PBDEs stock solution was prepared by dissolving BDE 209 (TCI Development Co., Ltd., Shanghai, China) in tetrahydrofuran (THF, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).¹⁹ The THF/water ratio used in the experiments was 1:1. The sample bottle was sealed, and sonicated in a water bath for 2 min to disperse the particles. The prepared samples were placed on a shaker incubator at 200 rpm at room temperature and covered to avoid photodegradation. At preselected time intervals, samples were taken to measure the parent compound and the reaction products. All samples were prepared in triplicate.

2.3. Instrumental Analysis

A mixture of 8 PBDE congeners (Code BDE-CSM) each having from three to seven bromine atoms and BDE 209, was obtained from Accustandard Inc. (New Haven, CT, USA). Gas chromatograph thermal decomposition issues are avoided in PBDE analysis using liquid chromatography.²⁰ High performance liquid chromatography (HPLC) was well applied to analysis PBDEs, especially BDE 209 in samples.^{19,21,22} In this study, samples were directly analyzed by a HPLC (P1201, Elite Analytical Instruments, Dalian, China) with a UV detector (UV 1201) and a Sinochrom ODS-BP C18 column (200 mm $\times$ 4.6 mm). HPLC-grade methanol was used as mobile phase at a rate of 1.0 mL/min. Quantification was done with a calibration curve of the BDE 209 standard. Aqueous samples were liquid/liquid extracted in dichloromethane and the collected extract was dried using anhydrous Na₂SO₄ (granular, 10–60 mesh, Fisher), and further concentrated down to 1 mL under a gentle N₂ stream. Reaction products in the extracts were analyzed using a 7890A gas

chromatography (GC) with a 5975C mass spectrometric (MS) detector (Agilent Technologies) equipped with a DB-5MS capillary column (15.0 m $\times$ 250 μ m $\times$ 0.25 μ m). One μ L of the sample was injected in splitless mode with the inlet maintained at 320 $^{\circ}$ C. The oven was held initially at 90 $^{\circ}$ C for 1 min, and increased at the rate of 20 $^{\circ}$ C/min to the final temperature of 320 $^{\circ}$ C, which was held for 15 min. Helium was used as carrier gas at 1.5 mL/min. The interface temperature for MSD and ion source temperature were both set at 230 $^{\circ}$ C. The mass spectrometer was in the selective ion monitoring (SIM) mode at the electron impact energy of 70 eV. To further analyze the reaction products, sample chromatograms were compared with the standard solution of PBDEs (BDE-CSM).

3. RESULTS AND DISCUSSION

3.1. Characterization of Sponge Iron

As shown in the XRD pattern of Figure 1(a), the characteristic peaks of Fe metal were Fe-110 and Fe-200 diffraction peaks, which appeared at 44.82 $^{\circ}$ and 65.20 $^{\circ}$, respectively. The peaks were strikingly consistent with commercial reduced iron. The diffraction peaks which characterized iron oxides and/or hydroxides were not detected, indicating the crystal structure of the sponge iron was α -Fe 0 .¹⁹ It's also estimated from XRD patterns that the mean crystallite iron grain size (from the Scherrer equation) of sponge iron was $\sim$ 30 nm. Peaks identified on the XRD patterns confirmed that the particles prepared from ball mill are composed mainly of ZVI. The Fe 2p XPS data (Fig. 1(b)) show a strong signal of oxidized iron on the surface besides ZVI, indicating that the surface of ZVI is covered by a layer of iron oxide film. As XPS is sensitive to analyze the outer 3–5 nm of the particles,^{5,23} the presence of the peaks for Fe 0 confirms that the oxide shell was couple nanometers thick. XPS showed that the sponge iron surfaces are comprised of mostly Fe, O, and C. AAS analysis revealed that the prepared sponge iron comprised approximately 78.5% iron in any form by weight, 0.5% Mn by weight, 0.05% Ni by weight and small amount of carbon, silicon and calcium ($\sim$ 0.05% by weight), with the remaining $\sim$ 20% considered mostly to be oxygen.

The morphological observation of the as-received sponge iron and fine particles prepared from ball mill was carried out by both scanning and transmission electron microscopy. Figure 2(a) and b show the SEM images of the received sponge iron. The raw sponge iron is composed of aggregates facets and irregular particles. Higher magnification image further confirms the rough surface, small fractal-like shapes of particles are intensely convoluted and display various kinds of porosity. After ball milling, the diameters of the grains were about $\sim$ 1 μ m (Fig. 2(c)). The grains were comprised of $\sim$ 30 nm crystals that were aggregated into approximately spherical 400–1000 nm diameter

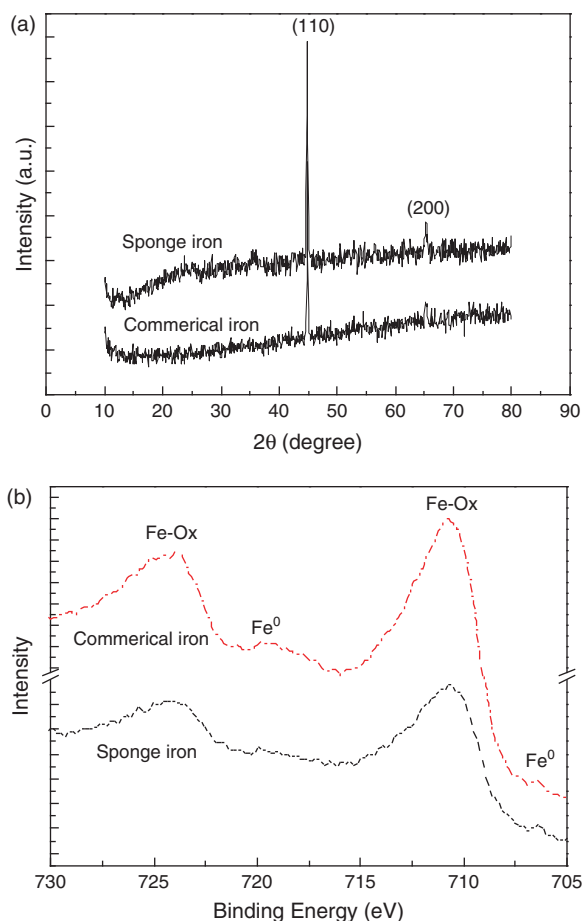


Fig. 1. (a) X-ray diffraction pattern of prepared sponge iron particles and commercial iron powder. (b) Fe 2p spectra from X-ray photoemission spectroscopy for sponge iron particles and commercial iron powder.

particles, and these spheroidal submicro-size granules were easy to further cluster together to form aggregates due to magnetic interaction. The EDS spectrum indicated a small amount of Ni, Si and Mn metals was detected from the surface detection of randomly chosen regions (Fig. 3). Fe and O were the main surface elements and accounted for 90 wt% based on EDS analysis.

The as-received sponge iron particles had a BET surface area of $\sim$ 1.0 m 2 /g. After ball milling, the prepared sponge iron particles had a BET surface area of $\sim$ 2.3 m 2 /g, which agrees with data reported in the literature.²⁴ This value was much lower than these of nZVI.^{5,19,25} Assuming ZVI to be spherical, calculation from Eq. (1) reveals that the ZVI particles would have a SSA of $\sim$ 1.9 m 2 /g with an average diameter of 400 nm, so the calculated and measured surface areas show reasonable agreement.

$$SSA = (6\pi d^2)/(\pi d^3 \rho) = 6/d\rho \quad (1)$$

where SSA represents specific surface area (m 2 /g); d means diameter of ZVI particle; ρ denotes density of ZVI (7800 kg/m 3 for iron).

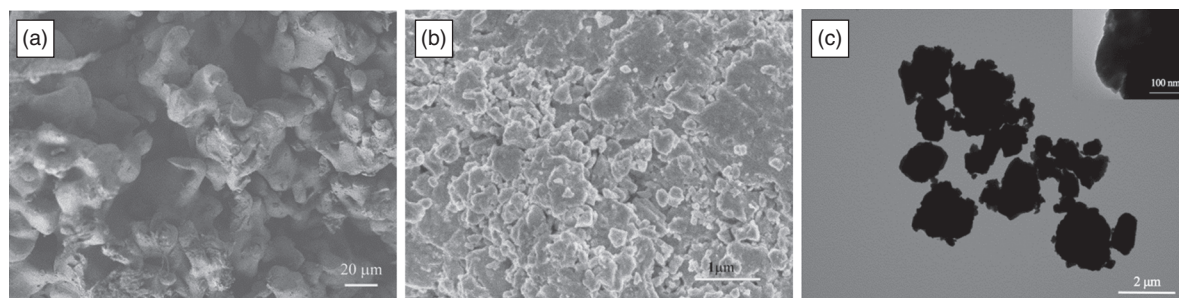


Fig. 2. SEM and TEM images of sponge iron. (a–b) SEM images showing the as-received sponge iron. (c) TEM images of ball mill prepared sponge iron particles.

3.2. Debromination of BDE 209 by Sponge Iron

3.2.1. Effect of Sponge Iron Dosage

Figure 4(a) illustrates the BDE 209 degradation at different sponge iron addition. Along with the contact time, all the samples with different dosage exhibited a decrease in BDE 209 concentrations. After reaction of 120 hours, only 8.1% and 13.2% BDE 209 were remained in the solution under the addition of 12 and 8 g/L sponge iron. Then, the removal efficiency slowed down to reach 62.4%, 80.9%, 87.8%, and 93.2% for 2, 4, 8, 12 g/L sponge iron dosage after 7 days. The dosage for further study was selected to be 4 g/L, as no significant improvement of PBDEs removal exhibited with further increase of iron dose and economic cost is an important aspect for the application. Other researchers observed the same trend when treating pollutants with ZVI particles.^{13,26} It was explained that the remediation of Fe-based nanoparticles is an interface reaction.⁴ As the reduction occurs on the iron particle surface, its surface property changes govern its reactivity. Initially, the process fast proceeded and as reaction going on, oxides produced on the surface.¹⁹ The Fe 2p XPS data show a stronger signal of oxidized iron on the surface, indicating the formation iron oxide film as the passivation layer. Iron oxide or hydroxide, which is usually formed during the zerovalent iron mediated reduction of contaminants, is not as reactive as elementary iron,¹² resulting in slow reaction after 120 hours (Fig. 4). However, some researchers suggested that contaminants may adsorb on or

co-precipitate with iron oxides/ hydroxides and contaminant reduction through primary corrosion products indeed occurred.²⁷ This may explain that longer treatment lead to more PBDEs removed. With more ZVI particles added, there will be more surface sites for reaction with PBDE to accelerate the debromination process. This was evidenced in Figure 4(a) that the increase of iron dose enhanced the debromination rates of BDE 209. Furthermore, analysis of the first-order rate constant of BDE 209 removal confirmed this relationship.

3.2.2. Effect of Initial BDE 209 Concentration

To evaluate the effect of initial BDE 209 concentration, 4 g/L sponge iron was added into 2, 4, 6 and 8 mg/L BDE 209 solutions, respectively. Variation of BDE 209 concentrations significantly affected the sponge iron performance (Fig. 4(b)). As the increase of solution loading, the removal efficiencies dropped from over 90% to lower than 75%. At the same time the observed rate constants decreased. When fixing sponge iron amount, the active sites were limited. The competitive contact/adsorption may affect the degradation of subjects on the particle surface. The contact opportunity for PBDEs at low concentration was higher, resulting in higher removal efficiency. If we define removal rate (mg/g) as the BDE 209 removal amount (mg) of one gram iron particles, trends of removal rates at different BDE 209 concentrations presented a striking contrast to removal efficiency. As illustrated in Figure 4(b) inset, removal rate increased from 0.45 mg/g at 2 mg/L BDE 209 to 1.47 mg/g at 8 mg/L BDE 209. By using nZVI, 6.44 mg/g BDE 209 was removed at a concentration of 4 mg/L,¹⁹ which is ~8-fold higher than that of this study. This is because the SSA of nZVI was much higher than micro-ZVI (mZVI) (more than 10-fold higher). High activity of nano-particles mainly comes from its larger SAA. Accordingly, normalizing reaction rates with respect to SAA may be a good choice to compare different-sized ZVI materials.²³ The surface area normalized rate constant in this study ($0.96 - 1.96 \times 10^{-3} \text{ L/h} \cdot \text{m}^2$) is similar to that of nZVI ($1.3 \times 10^{-3} \text{ L/h} \cdot \text{m}^2$),¹⁶ indicating that the higher removal rate of the nZVI is mainly attributed to the higher surface area.

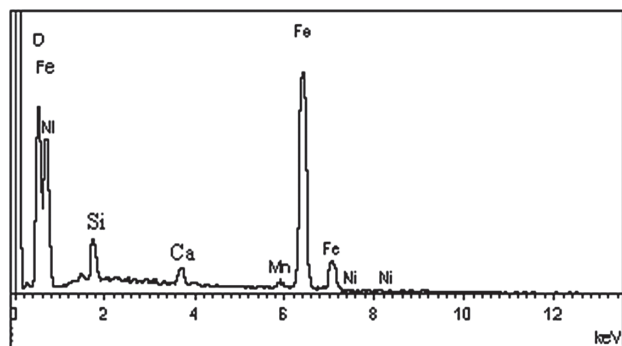


Fig. 3. EDS pattern of prepared sponge iron.

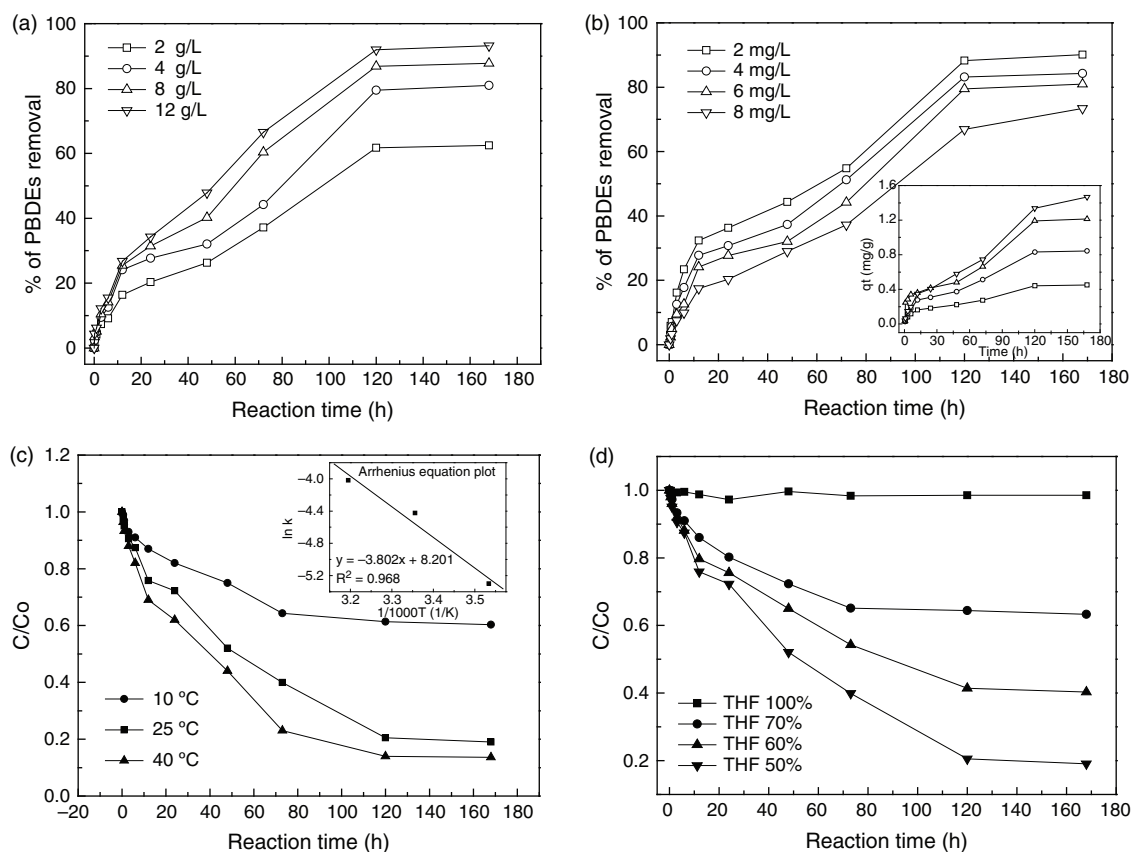


Fig. 4. Factors influencing the debromination of BDE-209 by sponge iron. (a) Sponge iron dosage, (b) Initial BDE 209 concentration, (c) Reaction temperature, and (d) Solvent composition.

3.2.3. Effect of Reaction Temperature

At different temperatures (10, 25 and 40 °C), 4 g/L sponge iron was added into 6 mg/L BDE 209 solutions. The degradation of BDE 209 was promoted as the increase of reaction temperature (Fig. 4(c)). At 10 °C, only approximately 40% of BDE 209 was reacted, while about 80% of BDE 209 was degraded at 25 °C and 40 °C. The little degradation variation between 25 and 40 °C illustrated that environmental temperature has limited impact on the degradation equilibrium of brominated compounds. Using nZVI to remediate hexachlorobenzene contamination, Shih et al. found that temperature effect was quite small with dramatic degradation at the end of the experiments achieved with increasing temperature.²⁶ The regression lines by plotting $\ln C/C_0$ against time possess high correlation coefficients, indicating that the degradation of BDE 209 follows the pseudo first-order kinetics model at different reaction temperatures. Based on Arrhenius equation, the relationship between temperature and rate constant can be illustrated as:

$$\ln k = -E_a/RT \quad (2)$$

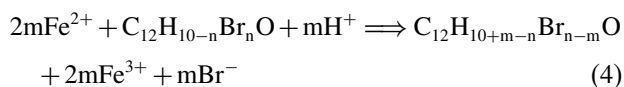
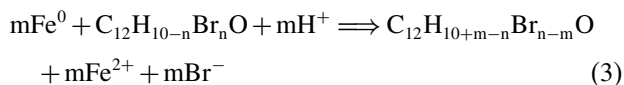
where k (1/h) is the first-order rate constant, which can be replaced by the observed rate constant (k_{obs}); E_a (kJ/mol)

denotes the activation energy; A represents the pre-exponential factor. Based on Eq. (2), a strong linear relationship was obtained by plotting $\ln k$ against $1/T$ (Fig. 4(c) inset). The activation energy (E_a) was calculated as 31.6 kJ/mol through the slope. Literature review indicated that the activation energy varied significantly when using nZVI or bimetallic particles to degrade pollutants.^{26,28}

3.2.4. Effect of Solvent Composition

Due to the high hydrophobicity ($\log K_{ow} = 8.7$), BDE 209 is difficult to dissolve in aqueous solutions. To make high free concentrations of BDE 209 in aqueous solutions, many efforts were made using organic solvent, for example, ethyl acetate, acetone, and THF.^{4,5,29} To make clear the cosolvent effect on BDE 209 degradation, the stock solution was mixed with different fractions of ultrapure water. As illustrated in Figure 4(d), for pure THF, almost no BDE209 was removed within the set time of the experiment, indicating that adsorption or precipitation played minimal role in the system. The decrease of THF fraction from 100% to 50% enhanced BDE 209 removal notably. Debromination efficiency increased remarkably from 37% to 81% when the water content increased from 30% to

50%. Obviously, the fraction of water in the solution plays an important role in the debromination process, influencing removal efficiency and degradation kinetics.²⁶ This was because catalytic hydrogenation was proposed as the major pathway for the debromination process by ZVI.^{14, 19} Possible reaction pathways for PBDEs removal from the aqueous phase in a $\text{Fe}^0\text{-H}_2\text{O}$ system could be depicted by Eqs. (3–4):^{19, 27}



Reaction (1) depicts the direct reduction that is currently considered as the major reaction path (Fe^0 reduction).²⁷ During this process, hydrogen ions play the most significant roles. It's known that THF is an aprotic solvent with a dielectric constant of 7.6, whereas the ionization constant of water is 1×10^{-14} . No protons were provided when THF was the only solvent. Thus, in THF system the debromination reaction was limited and as higher proportion of water was introduced to the system more BDE 209 was degraded.

3.3. Debromination Pathways of PBDEs by Sponge Iron

In the pure organic solution and control samples, no debromination products of BDE 209 were observed. Due to the lack of standard solution, nona- and octa-BDEs were not evaluated. A mixture of 8 PBDE congeners each having from three to seven bromine atoms and BDE-209 was used as the standard solution to confirm the debromination products. The information of PBDE standards and their retention times was listed in Table I. During this study, hepta-BDEs (BDE-183) were detected after 6 hours of BDE 209 degradation. And 24 hours later hexa-BDEs (BDE-153) were determined. Eventually, tri- to penta-BDEs (BDE-28, BDE-47, BDE-99, and BDE-100) were produced in 120 hours. Another hexa-BDE (BDE-154) was also detected. Confirmed by GC-MS, the

completely debrominated form of BDE 209, diphenyl ether (DE) was formed during the late period of long-term operation. This indicated that the complete debromination of BDE 209 can be realized by sponge iron, as observed in the literature using other types of ZVI.^{5, 15} It is noted that the environmental dominant congeners, such as BDE-153, BDE-100, BDE-99, BDE-47, were produced in sequence during the treatment. Two major decomposition pathways for BDE-183 were proposed: 1) BDE-183 $\rightarrow$ BDE-153 $\rightarrow$ BDE-99 $\rightarrow$ BDE-47 $\rightarrow$ BDE-28 and 2) BDE-183 $\rightarrow$ BDE-154 $\rightarrow$ BDE-100 (99) $\rightarrow$ BDE-47 $\rightarrow$ BDE-28. Tetra- to hexa-BDEs are probably the principal congeners to which humans are exposed via food and they are more inclined to accumulate in biota.^{4, 11} From the point of view of ecotoxicity, the production of lower brominated PBDEs increased the toxicity of PBDEs involuntarily. Herein, further degradation to fulfil complete debromination is of significance for detoxification and opens the possibility for mineralization of PBDEs.

In all, the debromination pathways in the reductive transformation of BDE 209 can be summarized as follows (Fig. 5). The first step is a loss of one bromine atom. Over time, the replacement of Br atom by H atom was continued and higher BDEs continued debromination to form lower PBDE congeners. The Br atom at ortho and meta positions were easier to be replaced by H atom than that at para position.¹⁴ Eventually, the extent of dehalogenation became significant as indicated by the increasing concentration and number of lower BDEs. And finally, BDE 209 was reduced to the complete debromination product, DE. These results were in accordance with the observation that debromination of BDE 209 is stepwise with bromines being substituted sequentially.^{4, 14}

3.4. Debromination Kinetics of Sponge Iron

A pseudo-first-order kinetic model (Eq. 5) was applied for the description of reductive debromination of BDE 209:

$$C/C_0 = e^{-kt} \quad (5)$$

with C and C_0 as concentrations of BDE 209 at any sampling and initial time, respectively; k as a first-order rate constant (1/h); and t as reaction time. The debromination

Table I. Information for PBDE standards and their relative retention time.

Peak #	Component	IUPAC #	Purity (%)	Manufacturer	Relative retention time (min)
I	2,4,4'-Tribromodiphenyl ether	BDE-28	99.3	AccuStandard Inc.	5.0
II	2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	100	AccuStandard Inc.	5.7
III	2,2',4,4',6-Pentabromodiphenyl ether	BDE-100	100	AccuStandard Inc.	6.1
IV	2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	99.2	AccuStandard Inc.	6.8
V	2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	100	AccuStandard Inc.	7.2
VI	2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE-153	100	AccuStandard Inc.	7.8
VII	2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE-183	100	AccuStandard Inc.	8.3
VIII	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether	BDE-209	98.3	AccuStandard Inc.	12.7

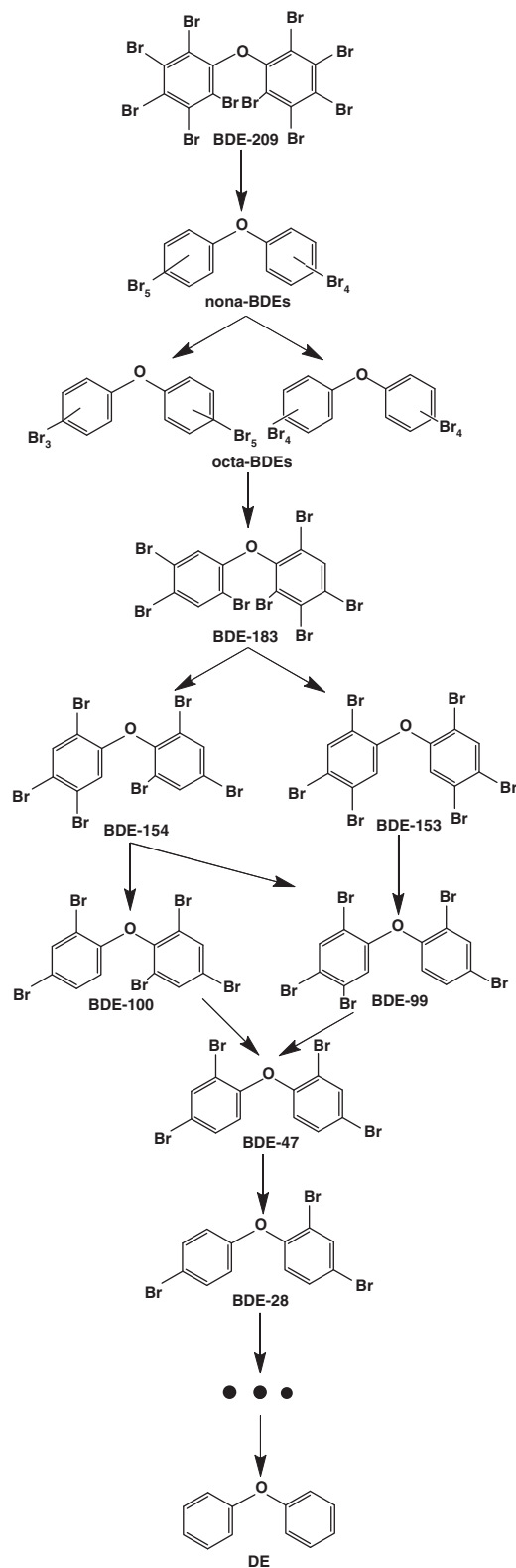


Fig. 5. Proposed debromination pathways of BDE 209 by sponge iron. of BDE 209 by sponge iron is described well by the pseudo-first-order kinetic model (Fig. 6). The rate constants increased with the increase of iron dosage, which is in accord with findings from PBDEs reduction by nZVI.¹⁹

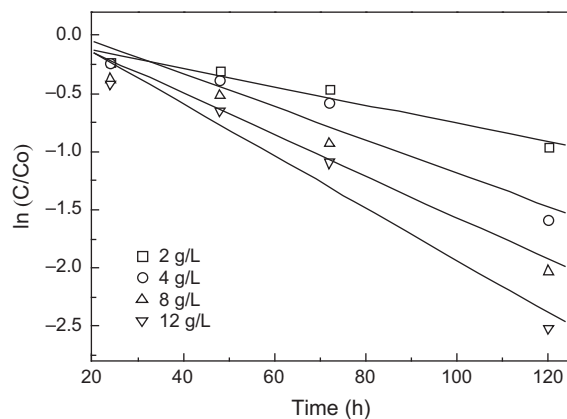


Fig. 6. Relationship between logarithmic plots of concentration versus time.

For long-term operation, 1 g sponge iron was added into 5 mL BDE 209 stock solution at 10 mg/L, which was mixed with equal volume of ultrapure water later. Rapid debromination was observed in the initial 3 days followed by a gradual decrease during further treatment (Fig. 7(a)). As the reduction occurs on the iron particle surface, its

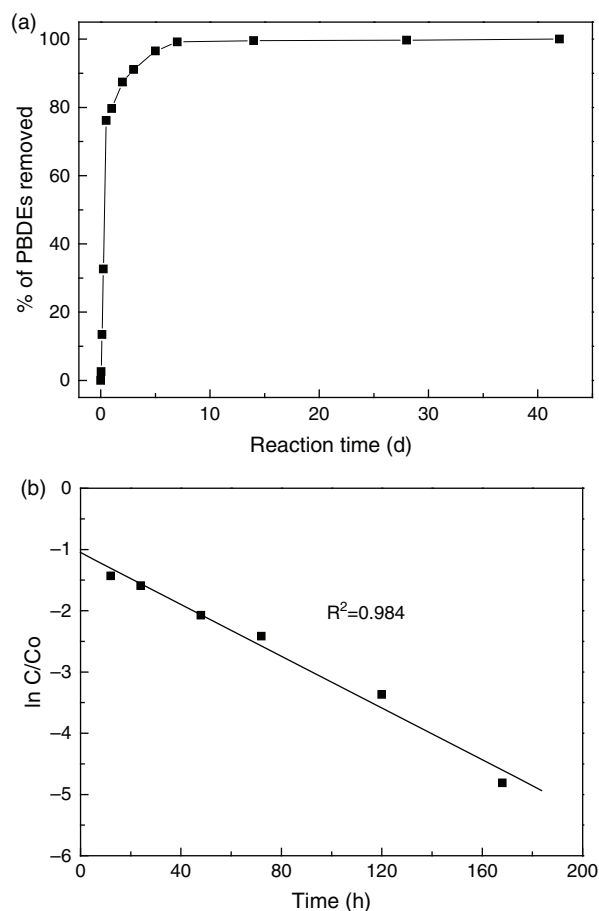


Fig. 7. Long-term treatment of BDE 209 by sponge iron. (a) Removal efficiency. (b) First-order kinetic plot.

Table II. Comparison of estimated debromination rate constants for BDE 209.

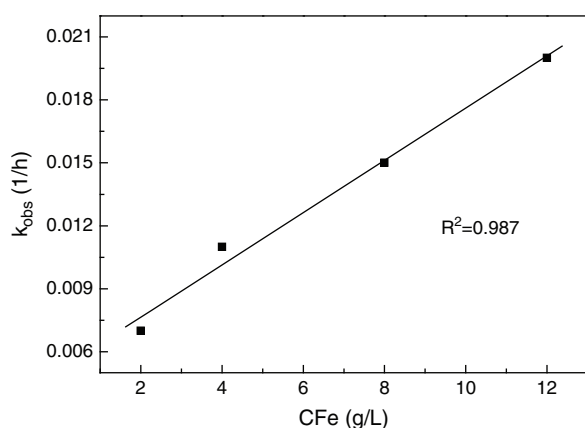
Materials	Dose (g/L)	Solvent composition	k_{obs} (1/h)	k_m (10^{-3} L/h · g)	k_{SA} (10^{-3} L/h · m ²)	$t_{1/2}$ (h)	Reference
mZVI	2	THF and H ₂ O	0.009	4.5	1.96	77.0	This study
mZVI	4		0.017	4.3	1.87	40.8	
mZVI	8		0.021	2.6	1.13	33.0	
mZVI	12		0.026	2.2	0.96	26.7	
mZVI	500	H ₂ O with trace ethyl acetate	0.006	0.283	5.51	115.5	
nZVI	14	acetone and H ₂ O	0.28	20	—	2.5	14
nZVI	20	H ₂ O with trace toluene	1.32	66	1.3	0.5	16
mZVI	480		0.204	0.43	2.5	3.4	19
S-NZVI ^a	4	THF and H ₂ O	0.132	33	0.94	5.2	
nZVI	4		0.031	7.8	0.22	22.4	
Fe powder	4		0.002	0.5	0.17	346.6	

^aS-NZVI: Nanoscale zerovalent iron prepared from steel pickling waste liquor.

surface property influences its reactivity significantly.¹² Oxidation of the iron surface and formation of inert layer lead to lower reactivity than elementary iron and decreases the reduction rate eventually (Fig. 7(a)). Iron corrosion and reduction reactions contribute to an increase of pH and the debromination rate decreased with increasing pH values,^{15, 16} similar to what we found that low solution pH enhanced the debromination reaction (data not shown). This also explained the slower reaction rate at the later stage. After 42 days of treatment, all the BDE 209 introduced was degraded which fits well to the above pseudo-first-order kinetics (Fig. 7(b)).

It is concluded that SSA determine the reactivity of ZVI. Herein normalized reaction rates with regard to SSA make different-sized ZVI materials comparable.²³ Another alternative is mass concentration normalized rate constant when SSA is not drastic different among different materials.⁵ To compare reaction rates among different materials, rate constants normalized with ZVI mass concentration and SSA were calculated using Eq. (6):

$$\begin{aligned} dC_{PBDE}/dt &= -k_{obs} \cdot C_{PBDE} = -k_m \cdot C_{Fe}^0 \cdot C_{PBDE} \\ &= -k_{SA} \cdot SSA \cdot C_{Fe}^0 \cdot C_{PBDE} \end{aligned} \quad (6)$$

**Fig. 8.** Relationship among observed rate constants and ZVI dosage.

where k_{obs} means the observed rate constant (1/h), k_m represents ZVI mass concentration normalized rate constant (L/d · g), C_{Fe}^0 stands for ZVI mass concentration, k_{SA} denotes ZVI surface area normalized rate constant (L/d · m²), and SSA represents the calculated specific surface area. The results are summarized in Table II. The differences in experimental conditions such as iron dose may also cause differences in reaction kinetics besides ZVI particle characteristics. In this work, we found that the rate constants correlated highly with ZVI dosage (Fig. 8, $R^2 = 0.987$). At the same dose, observed rate constant in this study are much higher than commercial Fe powder and mZVI,^{4, 16, 19} while they are comparable with nZVI.¹⁹ Also, the micro-sized iron normalized rate constants, k_m were 1 order of magnitude greater for sponge iron. When k_m values were compared with k_{SA} values, it suggested that the high surface area of ZVI plays a more important role than its mass. One and two orders of magnitude difference in the mass normalized rate constants, k_m , between nZVI and sponge iron were decreased to a factor of 1.4 when the rates were normalized with SSA.¹⁶ The data collected in a shorter period of time might contribute to greater k_{SA} values considering the oxidation and aging of nZVI over the course of the reaction.⁵ The data in this study were collected up to 42 days. Though Fang et al., Keum and Li, and Shih and Tai used data collected from less than 24 hours, 3 days and 2 hours, respectively, the SSA normalized rate constants are comparable with current study,^{4, 16, 19} without considering other contributions such as the environmental conditions. Zhuang et al. found that the addition of catalytic metal, i.e., Pd, into ZVI would contribute directly to catalytic reduction of halogenated compounds and increase the rate of debromination of the PBDEs greatly.¹⁵ In the current study, a small amount of Mn and Ni was detected in the sponge iron particles. Galvanic coupling between the iron and Mn and Ni metals enhanced BDE 209 reduction by electron transfer and it also contribute water reduction and the formation of activated H-species.³⁰

Table III. Economic evaluation of sponge iron and other Fe-based materials.

Materials	Production cost of 1 kg (dollar)	Cost to remove 1 kg BDE 209 (dollar)	Reference
S-NZVI ^a	534	115 534	19
nZVI	550	217 357	
Nano Ni/Fe	727	146 606	
Fe powder	8.3	38 409	
Sponge iron	0.5~0.8	346~518	This study

^aS-NZVI: Nanoscale zerovalent iron prepared from steel pickling waste liquor.

From the point of view of engineering application, economic cost is an important index to evaluate whether a technology is applicable. The debromination of 1 kg BDE 209 by using environment-friendly sponge iron particles only cost ~500 dollars which was ~2 to 3 orders of magnitude more economic efficient than S-NZVI, nZVI, Ni/Fe nano-bimetallic and Fe power (Table III). For the practical application, the nano-sized materials are difficult to install/assemble in an engineered facility. And nanotoxicity is another concern for public safety and health. In contrast, already used as oxygen scavenger, sponge iron can be easily assembled in the wastewater treatment plants without any acute toxicity. Furthermore, produced iron ions during the treatment process are trace elements for microorganisms.

4. CONCLUSION

As a new category of POPs added to the Stockholm Convention, PBDEs are detected even in remote areas, which need economic engineering remediation technologies. In this study, sponge iron was adopted to debrominate the fully-brominated BDE 209. Following the pseudo-first-order kinetics, stepwise reductive debromination was the dominant reaction and complete debromination of BDE 209 to DE can be realized. The low debromination cost, in combination of its engineering aspects, indicated that sponge iron was as an efficient remediation tool both economically and practically. This study can elucidate further information for the remediation of halogenated organic compounds, besides PBDEs.

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