



Nonionic surfactant greatly enhances the reductive debromination of polybrominated diphenyl ethers by nanoscale zero-valent iron: Mechanism and kinetics



Da-wei Liang, Yu-han Yang, Wei-wei Xu, Si-kan Peng, Shan-fu Lu, Yan Xiang*

School of Chemistry & Environment, Beihang University (BUAA), 37 Xueyuan Rd, Beijing 100191, China

HIGHLIGHTS

- Surfactants can improve the efficiency of PBDE debromination by nZVI.
- Nonionic surfactant TX greatly promotes PBDE reductive debromination.
- The effect of surfactant on PBDE debromination is concentration dependent.
- Debromination of PBDE and its byproducts can be described as a consecutive reaction.

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ABSTRACT

Nanoscale zero-valent iron (nZVI) has been considered as an effective agent for reductive debromination of polybrominated diphenyl ethers (PBDEs). But the high lipophilicity of PBDEs will hinder their debromination owing to the inefficient contact of PBDEs with nZVI. In this study, different ionic forms of surfactants were investigated aiming to promote PBDE debromination, and the beneficial effects of surfactant were found to be: nonionic polyethylene glycol octylphenol ether (Triton X-100, TX) > cationic cetylpyridinium chloride (CPC) > anionic sodium dodecyl benzenesulfonate (SDDBS). Except for with SDDBS, the promotion effect for PBDE debromination was positively related to the surfactant concentrations until a critical micelle concentration (CMC). The debromination process of octa-BDE and its intermediates could be described as a consecutive reaction. The corresponding rate constants (k) for the debromination of parent octa-BDE (including nona- to hepta-BDEs), the intermediates hexa-, penta-, and tetra-BDEs are $1.24 \times 10^{-1} \text{ h}^{-1}$, $8.97 \times 10^{-2} \text{ h}^{-1}$, $6.50 \times 10^{-2} \text{ h}^{-1}$ and $2.37 \times 10^{-3} \text{ h}^{-1}$, respectively.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame-retardants (BFRs) extensively used over the past several decades in various industrial and consumer products. Among all the PBDE congeners, three major PBDEs, deca-, octa-, and penta-BDEs, are most commonly used [1,2]. Although penta- and octa-BDEs have been banned in Europe and the United States since 2006 because of their persistence and high toxicity [3–5], the bio-accumulation of PBDEs in the environment has continued to increase [6–8]. PBDEs are listed as persistent organic pollutants (POPs), thus it is important to develop effective and feasible technologies for eliminating PBDE contamination in the environment.

Recent studies demonstrate that zero-valent iron, a strong reducing reagent, can degrade an array of halogenated aliphatic and aromatic compounds, including PBDEs [9]. Due to its larger specific surface area, nanoscale zero-valent iron (nZVI) can greatly increase reaction rates [10]. However the reductive dehalogenation by nZVI is a surface-mediated reaction [11]. Nevertheless, the high lipophilicity of PBDEs will hinder their debromination owing to the inefficient contact with nZVI. This situation could be resolved by using supplementing surfactants, which can increase the concentration of sparingly soluble organics on non-reactive surfaces, such as soil and sediment particles [12–14]. For an instance, a non-ionic surfactant, TX-114, can increase the reduction rate of dichlorodiphenyl trichloroethane (DDT) with ZVI by a factor of two compared to that without the surfactant [15]. The chemical properties of the aqueous solution containing surfactant is largely dependent on its critical micelle concentration (CMC), the concentration at which surfactant monomers aggregate to form micelles, and consequently, change

* Corresponding author. Tel.: +86 10 82339163; fax: +86 10 82339539.
E-mail address: xiangy@buaa.edu.cn (Y. Xiang).

the surface tension and the thickness of the electric double layer of the particles in the solutions. Thus the effect of surfactant on the debromination of PBDEs by ZVI could also be concentration dependent, on which is still limited so far.

During debromination, PBDEs yield lower brominated congeners [16,17], which have much higher toxicity than their parent congeners, depending on the bromine numbers and positions [18,19]. Understanding debromination kinetics of parent PBDE and its intermediates is crucial to elucidate the PBDE degradation mechanism. Keum and Li [29] proposed that the debromination of deca-BDE by ZVI could be described with a pseudo-first-order kinetic model, which was also found in the debromination of BDE 21 and BDE 209 with nZVI [9,20]. Recently, the debromination of BDE 21 and its specific intermediate by nZVI has been discussed, and eight differential equations were set up to model the debromination kinetics and pathways of BDE 21 [20]. For highly brominated PBDEs debromination, there will be more intermediates produced, making the analysis of the reactions more complex. Therefore, a simpler method is necessary to elucidate the debromination kinetics of the highly brominated PBDE congeners and their intermediates.

In this study, the reductive debromination of a commercial highly brominated octa-BDE mixture with nZVI was conducted. To promote the PBDE debromination, different ionic forms of surfactants, and their concentration effects, were investigated to probe the interaction of reactants with PBDEs and their intermediates in the solution. Additionally, simplified kinetics models were set up to shed further light on the reductive debromination mechanism of PBDEs by nZVI.

2. Materials and methods

2.1. Synthesis and characterization of nZVI

nZVI particles were synthesized by using a liquid-phase reduction method. A NaBH_4 solution was added into a vigorously stirred FeSO_4 solution with a peristaltic pump at a rate of 1 mL min^{-1} , with a reactant molar ratio of 1:2 for $\text{Fe}^{2+}/\text{BH}_4^-$. The mixed liquor was then filtrated and the solid residue was washed by deionized water three times to obtain nZVI. The synthesized nZVI was transferred into a tightly sealed bottle purged with nitrogen. Deoxygenated water was added to the bottle to make a concentration of 100 g L^{-1} nZVI aqueous stock solution. The morphology of the nanoparticles was investigated using the BET (Brunauer, Emmett and Teller) method [21]. The ζ -potential of the particles in the aqueous solution was determined using the dynamic light scattering approach (Zetasizer Nano ZSP, Malvern) [22].

2.2. Debromination experiments

The dispersed nZVI was diluted to 10 g L^{-1} with deionized water and was distributed to 4 mL amber vials. Different surfactants, including SDDBS, TX and CPC, were separately added into the vials to the desired concentrations. As recorded in the literature, the CMC for SDDBS and TX are 0.55 g L^{-1} and 1.5 g L^{-1} [23,24]. The CMC of CPC was determined by measuring the solution conductivity to be 0.5 g L^{-1} . An octa-BDE stock solution was prepared by dissolving an octa-BDE technical mixture (containing six PBDE congeners, BDE153, BDE183, BDE196, BDE197, BDE203, BDE207) in HPLC grade iso-octane with a concentration of 0.5 g L^{-1} . Then a 10- μL octa-BDE stock solution was injected into the 4-mL amber vial to make the final octa-BDE concentration at 1 mg L^{-1} . The total volume of the reaction system was 1 mL, and the amber vial was sealed with a Teflon/silica septum. The prepared solutions were placed on a horizontal shaker at 150 rpm. At different time intervals, samples were

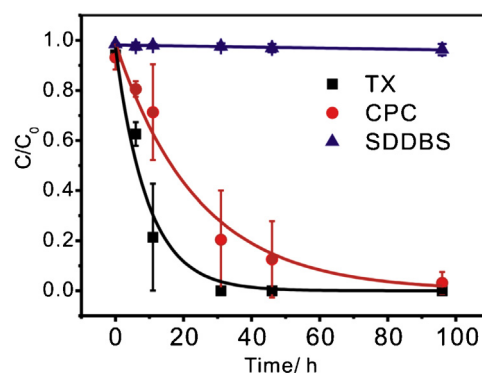


Fig. 1. The debromination of octa-BDE by nZVI with various ionic forms of surfactants. The debromination curves were well fitted with a pseudo-first-order kinetics model. Error bars indicate standard deviations of two measurements.

extracted with iso-octane (1:1, v/v) to measure the concentrations of the parent and the reaction products. No apparent change of PBDE concentration was observed for the control without nZVI but dosed with three different surfactants, indicating that the extract efficiencies were high enough and consistent for sample analysis.

2.3. Chemical analysis

The congeners of octa-BDEs and their debromination products were analyzed using a gas chromatograph with an electron capture detector (GC-ECD; Shimadzu-2014C) system equipped with a DB-5 column ($15 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm}$). One μL of the sample was injected in split mode with the inlet maintained at 280°C . Nitrogen was used as carrier gas at 60 kPa. The oven temperature program began at 110°C , and increased at the rate of $15^\circ\text{C min}^{-1}$ to the temperature of 250°C , held for 20 min, then immediately ramped at $10^\circ\text{C min}^{-1}$ to 310°C , and held for 15 min, for a total time of 48 min. First, mixed PBDE standard solution (1 mg L^{-1} in iso-octane, AccuStandard, EO5113) containing 39 congeners from mono- to hepta-BDEs was analyzed with GC-ECD. Since there is no standard for all of the PBDE congeners, the debromination products were determined by using GC-MS (Agilent-6890N) with selected ionization mode. Helium was used as the carrier gas at a flow rate of 1.2 mL min^{-1} , the detector temperature was set at 330°C . For quantification of product peaks, five-point calibration curves were constructed by using the average peak areas of congeners in the same homolog group in the above mentioned analytical standard, the same procedure as in a previous study [25]. Currently, averaged calibration curves are the most feasible way to quantify unknown debromination products.

3. Results and discussion

3.1. Effects of surfactant on PBDE debromination

In this study, the synthesized nZVI particles had a BET surface area of $29 \text{ m}^2 \text{ g}^{-1}$, which agrees with the result reported by Liu et al. [26]. Assuming nZVI to be spherical, the synthesized nZVI particles are calculated at an average diameter of 15 nm.

Different surfactants (at 1 g L^{-1}) lead to different debromination efficiencies, as shown in Fig. 1. The results show that in the presence of the nonionic TX and the cationic CPC, the concentration of octa-BDE was close to zero after 96 h. The debromination rate is much greater with TX than with CPC. In comparison, octa-BDE was hardly debrominated in the presence of the anionic SDDBS, ever after 100 h. In a control test without surfactant, the concentration of octa-BDE slightly decreases although no distinct debromination product was found after 96 h, as the product is too low to detect.

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