



Oxidation and mechanism of decabromodiphenyl ether (BDE209) by thermally activated persulfate (TAP) in a soil system

Hongjiang Peng^a, Wei Zhang^{a,*}, Liya Xu^a, Rongbing Fu^{b,*}, Kuangfei Lin^a

^aState Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, School of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China

^bShanghai Academy of Environmental Sciences, Shanghai 200233, China

HIGHLIGHTS

- Effective oxidation of BDE209 was achieved at pH 5 in a TAP system.
- The BDE209 destruction followed a pseudo-first-order kinetics pattern in the tests.
- High temperature and PS content, as well as low level of chloride facilitated the BDE209 removal.

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ABSTRACT

Decabromodiphenyl ether (BDE209) poses a significant threat to human health. Most research so far has focused on BDE209 debromination by the reduction, which will produce more toxic products and further cause more serious environmental problems. In this study, we focused on thermally activated persulfate oxidation of BDE209. Various factors have been investigated, such as initial persulfate (0.05, 0.1, 0.2 and 0.5 M) or BDE209 content, temperature, pH and inorganic ion. The results show the of BDE209 removal rate constants (k_1) indicated quadratic curve relationship with initial persulfate concentrations ($k_1 = -0.293 \times [PS]_0^2 + 0.267 \times [PS]_0 + 0.046$, $R^2 = 0.917$, $[PS]_0 = 0.05\text{--}0.5$ M) and a good linear relationship with initial BDE209 contents ($k_1 = -0.004 \times [BDE209]_0 + 0.312$, $R^2 = 0.994$). At the test pH range of 3–9, the highest degradation efficiency occurred at pH 5. However, inhibitory effects were observed in the presence of bicarbonate (HCO_3^-), and chloride (Cl^-) exhibited either positive or inhibitive effect on the BDE209 degradation. The addition of an appropriate level of Cl^- (e.g., $[Cl^-]_0/[PS]_0 = 0.1/1$) could significantly enhance the BDE209 decomposition, while higher contents of Cl^- (e.g., $[Cl^-]_0/[PS]_0 = 2/1$) resulted in totally inhibitory effect.

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1. Introduction

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) have been widely used in electronic products, furnitures, and building materials, etc. Because they are not chemically bonded but directly added to the products, which makes PBDEs easily migrate out of these products, and release into the environment, causing a series of environmental problems [1]. Among the typical commercial PBDEs products (such as penta-, octa-, and deca-bromodiphenyl ether), the demand of decabromodiphenyl ether (BDE209) is the greatest of all [2]. The

destruction of PBDEs arouses high environmental concern because of their persistence, bioaccumulation, and high toxicity [3].

Different methods to degrade BDE209 have been conducted, such as chemical reductions with sodium borohydride [4] and zero-valent iron [5]. By these methods, the BDE209 degradation followed a stepwise debromination manner, because the low brominated intermediates are rather difficult to be further reduced, the debromination is often incomplete [6]. In addition, the low brominated intermediates, such as hexa-BDE, hepta-BDE, tetra-BDE and penta-BDE, which show more toxic than BDE209 and have been added to the Stockholm Convention list of persistent organic pollutants (POPs) in 2009 because of their persistence and tendency to bioaccumulation [7]. The above mentioned strategies were required to be carried out in a liquid media, except the use of (photo-) catalysts. However, in many cases involving the pollution of PBDEs, the pollutants exist in complex solid matrices.

* Corresponding authors.

E-mail addresses: wzhang@ecust.edu.cn (W. Zhang), rongermmfu@163.com (R. Fu).

So, it is high time to develop efficient technologies for degrading PBDEs in solid phases.

In situ chemical oxidation (ISCO) has gained more and more attentions due to its effective and environmental friendly trait for the treatment of organic contaminated soil and ground-water. ISCO involves the introduction of chemical agents with a strong ability of oxidation into the subsurface, aiming to transform organic contaminants into harmless or less harmful chemical species [8]. Persulfate is a new but increasingly used oxidant for in situ chemical oxidation due to its stability under normal conditions and high redox potential ($E_0 \sim 2.01$ V). Furthermore, persulfate can be further activated by different ways transforming to much stronger sulfate radical, $\text{SO}_4^{\cdot-}$ ($E_0 \sim 2.60$ V) [9]. In addition, persulfate anion could persist more than five months in a soil system [10], giving this oxidant several advantages over other oxidant candidates used in ISCO. The $\text{SO}_4^{\cdot-}$ can be effectively generated by activating the $\text{S}_2\text{O}_8^{2-}$ by using heat [11], alkaline pH [12], and transition metals (Me^{n+}) [13]. Among the above mentioned methods, the use of thermally activated persulfate (TAP) is considered as a highly effective and clean method for the treatment of hazardous organic [14]. However, to the best of our knowledge, TAP has never been conducted on BDE209 removal in soil.

This study aimed to: (1) evaluate the technical feasibility of BDE209 removal by TAP in soil; (2) determine the effects of basic constituents of soil matrix system, such as Cl^- and HCO_3^- with respect to the degradation efficiency; (3) explore the impacts of oxidant dosage, initial chemical concentration, and initial soil pH on the removal of BDE209.

2. Materials and methods

2.1. Chemicals

Decabromodiphenyl ether (BDE209; >98.0%; the selected physicochemical properties of BDE209 are shown in Table 1) was obtained from J&K Scientific Ltd., Shanghai, China. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, PS; $\geq 99.5\%$) was used as source of $\text{SO}_4^{\cdot-}$; Sodium chloride (NaCl ; $\geq 99.9\%$), potassium bicarbonate (KHCO_3 ; $\geq 99.5\%$), toluene, dichloromethane and *n*-hexane were obtained from Lingfeng Chemical Co., Ltd., Shanghai, China. All organic solvents used in the experiments were at least of analytical grade and used as received without further purification. The required amount of PS was freshly prepared immediately prior to the experiments. All solutions were prepared using deionized water before each run.

2.2. Soil samples

Clean soil was collected from East China University of Science and Technology in Shanghai, China. The soil was air-dried at room temperature for 2 weeks, stones and large plant residues were removed, and then grinded to pass a 2 mm sieve. The soil was characterized as follows: silty clay loam, pH 7.3, 6.5% organic matter. BDE209-spiked soil samples were prepared as follows: 300 g

uncontaminated soil was placed in a 600-mL beaker and spiked with 1000 mg kg^{-1} of BDE209 stock solution 3 mL, 6 mL or 15 mL diluted with 300 mL *n*-hexane, followed by the addition of excessive *n*-hexane to thoroughly submerge the soil. The soil was then stirred vigorously for 15 min with a glass rod to promote homogeneous distribution of BDE209. And then the spiked soil was placed in a fume hood to eliminate the solvents. To make sure that the entire quantity of *n*-hexane solvent had been eliminated, the weight of the mixture was monitored at intervals until it remained unchanged. After thoroughly mixed and aged for more than one month, the final concentration of BDE209 was determined to be 10, 20 or 50 mg kg^{-1} in the spiked soil.

2.3. Oxidation experiments

The degradation experiments were conducted in 50-mL polypropylene tubes. Prior to each experiment, 2.0 g spiked soil was added to the tubes, followed by the addition of 2.5 mL PS with desired concentrations, respectively. The tubes were kept in a water bath oscillator maintained at different temperature (50, 60 and 70°C) in the dark and were shaken at 200 rpm for reaction with different time. Control samples were prepared in the same way except no PS stock solution addition. Initial pH was adjusted by 1 M of H_2SO_4 or NaOH to desired values, and the pH was measured with a Mettler Toledo pH meter. No buffer was introduced in the present study to avoid potential reactions between buffer and radicals [15]. At each sampling point, all the soil in the tubes was sampled. At pre-specified time intervals, the sample vials were immediately put into an ice-water bath for 10 min to quench the reaction. Then frozen at -70°C for 2 h and then transferred in a freeze-dryer for additional 24 h. All experiments were conducted in duplicates.

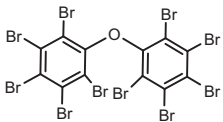
2.4. Samples pretreatment

After freeze dried for 24 h, the soil samples were broken into soil particles with a glass rod, then were conducted by the ultrasonic assisted extraction for 2 times with 50 mL high purity dichloromethane/*n*-hexane (2:3, v/v) for 40 min. The extracts were concentrated to approximate 5–6 mL by a rotary evaporator (Buchi R-210, Switzerland), and then passed through a PTFE membrane and diluted to 10 mL with *n*-hexane. BDE209 analysis was performed by a gas chromatograph (GC) equipped with an electron-capture detector (ECD).

2.5. Analysis of samples

BDE209 content was determined using an Agilent GC/ECD (GC7890A and 7693A auto-sampler) equipped with a HP-5 capillary column (30-m length, 0.32-mm i.d., 0.25- μm thickness). The temperature of the injector and detector were both 280°C , respectively, and the oven temperature was programmed starting at 110°C for 1 min, then increased to 260°C at a rate of $40^\circ\text{C min}^{-1}$, and then raised to 320°C at a rate of $10^\circ\text{C min}^{-1}$ where it was held for 10 min. The injection was in a splitless mode with exact $1 \mu\text{L}$ solution. High purity nitrogen was used as the carrier gas and ECD makeup gas with a constant of 3 and 20 mL min^{-1} , respectively. Agilent GC/MS (7890A/5975C) equipped with a capillary column (J&W, Scientific, $15 \text{ m} \times 0.25 \text{ mm} \times 0.1 \mu\text{m}$, DB-5HT). The MSD spectrometer equipped with an electron impact (EI) or chemical ionization (CI) source was used to determine the potential debrominated intermediates of BDE209. When MS used a CI mode, the quadrupole and source temperature were both kept at 150°C . The injection was in a splitless mode with exactly $1 \mu\text{L}$ solution, and the high purity Helium (99.999%) was the carrier gas at a constant flow of 1.0 mL min^{-1} . The temperature conditions during the

Table 1
Selected physicochemical properties of BDE209.

Chemical formula	Chemical structure	Molecular weight (g mol^{-1})	Water solubility (g mL^{-1} , 20°C)
$\text{C}_{12}\text{Br}_{10}\text{O}$		959.17	<0.001

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