RESEARCH ARTICLE

Photocatalytic degradation of polybrominated diphenyl ethers in pure water system

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Abstract Due to the low water solubility of polybrominated diphenyl ethers, organic solvent is usually added into the oxidation system to enhance the removal efficiency. In this study the photocatalytic degradation of decabromodiphenyl ether (BDE209), a type of polybrominated diphenyl ether used throughout the world, in pure water without the addition of organic solvent was investigated. In the pure water system, BDE209 was not dissolved but dispersed as nano-scale particles with a mean diameter of 166 nm. Most of BDE209 ($> 98\%$) were removed within 4 h and the final debromination ratio was greater than 80%. Although the addition of organic solvent (tetrahydrofuran, THF) could lead to a relatively high BDE209 degradation rate, the final debromination ratio ($< 50\%$) was much lower than that in pure water system. Major oxidation intermediates of tetrahydrofuran, including tetrahydro-2-furanol and γ-butyrolactone, were detected indicating the engagement of THF in the BDE209 degradation process. The photocatalytic degradation of BDE209 in the pure water system followed first-order kinetics. The BDE209 degradation rate constant increased from 0.0011 to 0.0023 min^{-1} as the pH increased from 3 to 9.

Keywords polybrominated diphenyl ethers, photocatalytic degradation, solvent

1 Introduction

Polybrominated diphenyl ethers (PBDEs) have been produced as flame-retardants worldwide and are found in paints, textiles, and electric and electronic equipment [1].

The market demand for PBDEs has sharply increased and about 86% of the PBDEs were distributed in the Americas and Asia [2]. Known as a kind of persistent organic pollutants, PBDEs tend to accumulate in various environmental compartments [3–6]. PBDEs have also been detected in food samples [7]. Concentrations of PBDEs in the environment and food have increased over time [8]. A recent study reported that PBDEs may cause neurodevelopmental and endocrine disruption toxic effects [9].

There are three types of PBDE technical mixtures that are commercially available, among them decabromodiphenyl ether (BDE209) is the only one produced in large quantities worldwide [10]. Since biodegradation is not the primary pathway for removal of PBDEs due to their high lipophilicity and persistence [3,4], advanced oxidation techniques have been developed for efficient removal of them [11–14].

PBDEs are sparingly soluble in water [15] but readily dissolve in organic solvents such as tetrahydrofuran (THF) and methanol [11–14]. For this reason, these organic solvents (and others) have been added to various oxidation systems to increase the solubility of PBDEs [11–14]. Rare information was available on the oxidation of PBDE in pure water systems. Additionally, the usage of organic solvents can jeopardize real-world application of these techniques in the water industry due to toxicity considerations. In this study, a novel, environmentally friendly method for removal of PBDEs from pure water without the addition of organic solvent was first developed. Titanium dioxide (TiO$_2$) was added into the water solution while ultraviolet (UV) was applied to catalyze the degradation of PBDEs. The final goal was to obtain initial information on the photocatalytic degradation of PBDEs in pure water. The findings have significant implications in the terms of the rapid removal of PBDEs in water.

2   Materials and methods

2.1   Experiment set-up

To prepare the pure water system for BDE209 (purity > 98%, TCI, Tokyo, Japan) removal by oxidation, a solvent exchange protocol was conducted. BDE209 was first dissolved in THF, then dripped into water drop by drop. Vigorous stirring was applied to ensure that PBDE209 was well dispersed. THF was subsequently removed quickly via distillation and then 80 mL of the BDE209-water solution was transferred into a stirred cell (Model 8200, Millipore, USA) with an ultrafiltration membrane (YM10, molecular weight cut-off = 10000, Millipore, USA). Forty mL of ultrapure water was added when the volume of aqueous BDE209 reached 40 mL. This washing process was repeated 12 times. Finally, the aqueous BDE209 were filtered using microporous filtering films (d = 0.22 μm). The particle size of BDE209 in water was characterized using a dynamic light scattering (DLS) technique and residual THF was quantified using high-performance liquid chromatography (HPLC) (described later). For comparison, a BDE209/THF/water system was also included as a control. The final THF/water ratio was 1:1 according to Zhao et al. [12].

Photocatalytic degradation of BDE209 was conducted in a cylindrical quartz reactor (150 mL) with a double walled thermostating jacket to keep the solution temperature constant throughout all experiments. Six mercury lamps were attached around the reactor to serve as an irradiation source. The maximum light intensity of the lamps occurred at 365 nm (ca. 3080 μW·cm^{-2}·nm^{-1}). One hundred mL of BDE209 solution was added into the cylindrical vessel. The photocatalyst [16], TiO$_2$ Degussa P25 (75% anatase and 25% rutile form, surface area ca. 50 m^2·g^{-1}, Degussa Company, Germany), was also added into the BDE209 oxidation systems at a dose of 2 g·L^{-1}. Reaction suspensions were magnetically stirred during the irradiation. Before performing the oxidation experiments, reaction suspensions were stirred in darkness for 60 min to achieve air saturation.

To investigate the removal potential of BDE209, the initial concentrations of BDE209 for both controls (THF/ water system) and treatments (pure water system) were 2 mg·L^{-1}. To determine how much BDE209 was removed by other processes such as adsorption or evaporation, blank experiment without light irradiation (pure water system without UV) was performed. Blank experiment without photocatalyst (pure water system without TiO$_2$) was also performed to determining the potential photodegradation of BDE209 without photocatalyst. Photoirradiation of BDE209 was carried out for 11 h at an initial pH of 5. The pH was adjusted with sodium hydroxide or hydrochloric acid (2 mol·L^{-1}). Water samples (5 mL) were collected for analysis at different time intervals. The degradation kinetics and debromination ratio of BDE209 in the pure water (treatment) and THF/water (control) systems were investigated at different pHs (3, 5, 7, and 9) to gain further information on the oxidation behaviors of PBDE in the pure water oxidation system. All the experiments were repeated twice.

2.2   Analytical methods

The particle size distribution of BDE209 in water was characterized using a DLS particle size analyzer (model S4700, Malvern Instrument, UK). THF was analyzed using an LC-2010 series HPLC equipped with a Shimadzu C18 column (4.6 m × 250 mm) and an isocratic eluent (95% Acetonitrile and 5% water) at a flow rate of 1.0 mL·min^{-1}.

After photocatalytic degradation, 5 mL of reaction solution was removed from the cylindrical vessel and subjected to a liquid–liquid extraction with an equal volume of dichloromethane in a 15 mL glass tube. The mixture was vortexed vigorously for 3 min and shaken for 1 h at 200 r·min^{-1}. The organic phase was transferred to a gas chromatography (GC) vial for analysis. The inorganic phase was subjected to Br$^-$ analysis. The intermediates of BDE209 were not analyzed because of the lack of chemical standards during the experiments. Alternatively, Br$^-$ was analyzed to obtain further information on the debromination of PBDE during photocatalytic degradation. Br$^-$ concentrations were measured using a Metrohm ion chromatography system (Metrohm, Switzerland), equipped with a 818 IC pump, 819 IC detector, 833 IC liquid handling unit, and Metrosep A Supp 5-250 anion separation column (250 × 4 mm). The eluent, 4.2 mmol ·L^{-1} NaHCO$_3$-Na$_2$CO$_3$, was pumped at 0.7 mL·min^{-1}.

BED209 was analyzed using a GCMS-QP2010 gas chromatograph mass spectrometer with a mass spectrometer operated in negative chemical ionization (NCI) mode. A DB-5HT (15 m × 0.25 mm × 0.1 mm) capillary column was used with helium as the carrier gas at a constant flow rate of 1.5 mL·min^{-1}. A sample volume of 1 μL was injected in splitless mode. The inlet temperature was held at 320°C. The oven temperature program was as follows: initial temperature, 100°C hold for 3.5 min, increase to 320°C at 20°C·min^{-1}; hold at 320°C for 6 min. The ion source temperature was held at 250°C. Methane was used as the chemical ionization source. The mass spectrometer was operated in selected ion monitoring (SIM) mode. The quantitative ions were m/z 79 + 81 [17]. The MDL was 0.01 μg·L^{-1} while the method recovery was greater than 80%.

Oxidation products of THF were analyzed using the previously described GCMS-QP2010 gas chromatograph and mass spectrometer under similar conditions, except for the following modifications. In this case the carrier gas was held at a constant flow rate of 1.78 mL·min^{-1}. The column oven temperature program started at 40°C (2 min hold), increasing at 8°C·min^{-1} to 200°C (5 min hold), and

increasing at 10°C·min⁻¹ to 220°C (5 min hold), and increasing at 10°C·min⁻¹ to 345°C. This analysis was run in electron impact ionization mode (EI) with a mass scan range of m/z 19–800. The identification of the oxidation products was performed according to Henry et al. [18]. Tetrahydro-2-furanol was confirmed by comparison with mass spectra within the NIST Mass Spectral Library since an authentic standard was not available. γ-butyrolactone was determined by comparison with an authentic standard (purity > 98%, Sigma-Aldrich, St Louis, MO, USA).

2.3 Data analysis

The data collected were evaluated to determine whether the degradation of BDE209 fit first-order or second-order reaction kinetics. The degradation rate constant (k) for BDE209 in the exponential phase was calculated according to the following expressions:

$$\ln\frac{[A]_0}{[A]_t} = kt, (\text{first order reaction}) \tag{1}$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt, (\text{second order reaction}) \tag{2}$$

where $[A]_0$ and $[A]_t$ refer to BDE209 concentrations at the beginning and end time t when samples were collected, respectively.

3 Results

3.1 Characterization of the BDE209 water oxidation system

HPLC analysis showed that THF could not be detected in the BDE209/water system (Fig. 1), suggesting that THF was removed from the BDE209/water system during the preparation procedures. BDE209 particles were formed in water due to the low solubility of PBDEs in water [15]. The DLS characterization confirmed that BDE209 formed nano-scale particles in water (Fig. 2). The particle size distribution of BDE209 ranged from 100 nm to 300 nm,
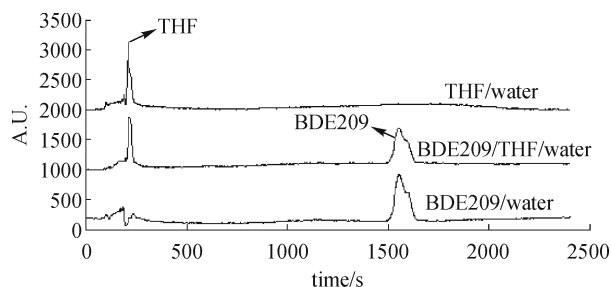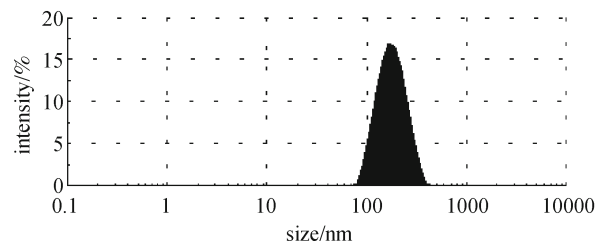

Fig. 2 Particle size distribution of BDE209 in pure water oxidation system

with a mean diameter of 166 nm. The nano-scale particles were the primary form of BDE209 in the pure water oxidation system.

3.2 Photocatalytic degradation of BDE209

Photocatalytic degradation experiment was performed to evaluate the removal potential of BDE209 in the pure water system. Results indicate that BDE209 can be removed efficiently in the pure water system through photocatalytic degradation (Fig. 3). Most of BDE209 (> 98%) were removed within 4 h in both pure water (treatment) and THF/water (control) systems. Although the removal efficiency of BDE209 in the pure water system was lower than that in the water/TFH system at the beginning, high removal efficiency was observed in both systems after 4 h. Slight amount of BDE209 (1.6%) was removed in the blank experiment without light irradiation, indicating that BDE209 was mainly removed through photocatalytic degradation but not other processes such as adsorption or evaporation. Slight removal of BDE209 (4.9%) in blank experiments without TiO₂ was observed, indicating that photocatalyst (TiO₂) is essential for the rapid removal of BDE209.
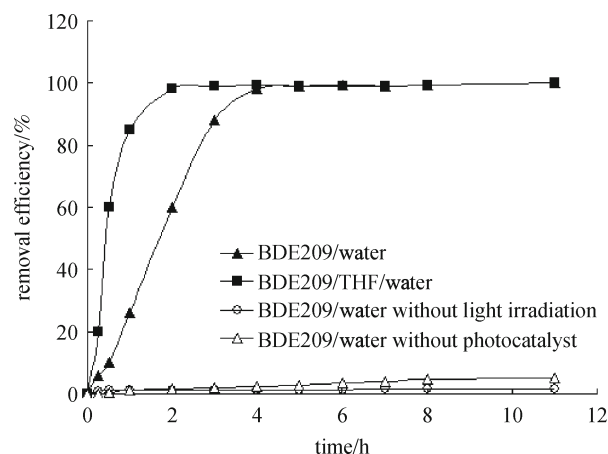

Fig. 1 HPLC chromatographs of THF/water, BDE209/THF/water, and BDE209/water systems. The peak at 3.6 min refers to THF

Fig. 3 Removal efficiency of BDE209 *vs.* time. The initial pH was 5.0

3.3 Debromination of BDE209 during photocatalytic degradation

The debromination ratio of BDE209 in the pure water and THF/water systems was investigated to gain further information on the oxidation removal potential of PBDE in the pure water oxidation system. Results from these studies are shown in Fig. 4. The results indicate a debromination ratio of greater than 80% in the pure water system following irradiation; while that of the THF/water system was only 47.7%. Although the debromination ratio in the pure water system was lower than that in the THF/water system in the early stage, the debromination ratio of BDE209 in pure water system became much higher than that in the THF/water system as irradiation continued.

3.4 Photocatalytic degradation kinetics of BDE209

The photocatalysis rate constant (k) and correlation coefficient (R^2) for BDE209 are shown in Table 1. Kinetic analysis indicates that the photocatalytic degradation of BDE209 in pure water system fit first-order kinetics; while the photocatalytic degradation of BDE209 in the THF/water system (control) fit second-order kinetics. The R^2 ranged from 0.9512 to 0.9873. Additionally, the influence of pH on the degradation rate constant in the pure water system was different from that in the water/THF system. The oxidation rate constant in the pure water system increased as pH increased; while the degradation rate constant for the water/THF system reached its maximum when the pH increased from 2 to 5, and began to decrease
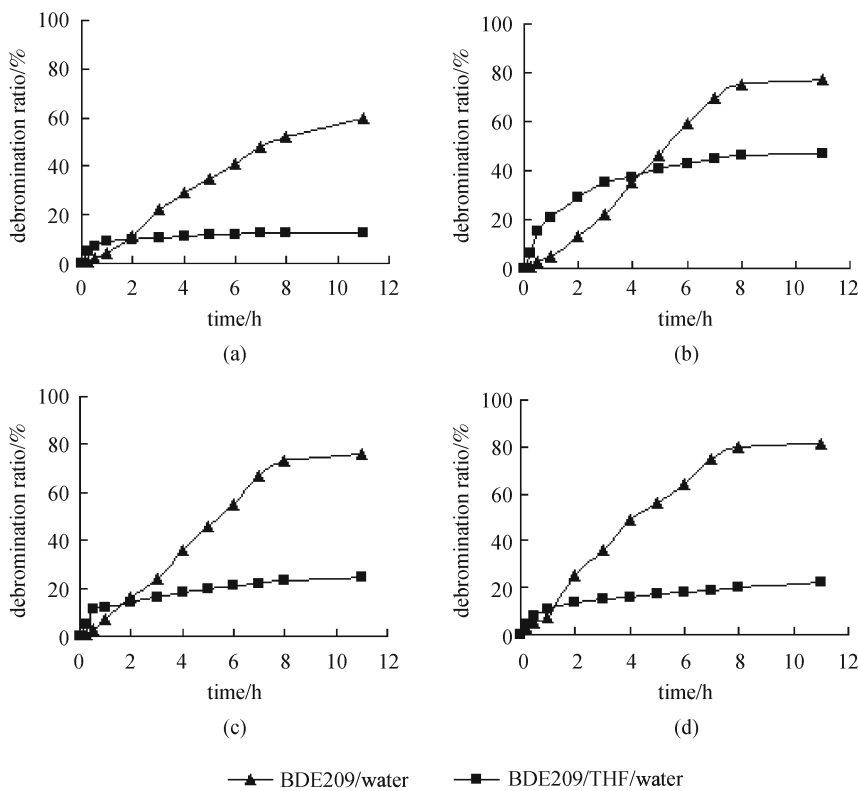

Fig. 4 Changes in debromination ratio during BDE209 degradation. Degradation experiments were conducted at pH 3 (a), 5 (b), 7 (c), and 9 (d)

Table 1 Photocatalytic degradation rate constants (k) and correlation coefficient (R^2) of BDE209 in different degradation systems

pH	second order kinetics in THF/water system		first order kinetics reaction in pure water system	
	k /(L·mg^{-1}·min^{-1})	R^2	k /min^{-1}	R^2
3	0.0019	0.9762	0.0011	0.9512
5	0.0059	0.9842	0.0013	0.9526
7	0.0029	0.9873	0.0015	0.9862
9	0.0025	0.9869	0.0023	0.9604

at pHs above 5. In the pure water system, the BDE209 oxidation rate constant increased from 0.0011 to 0.0023 min^{-1} as the pH increased from 3 to 9.

3.5 Oxidation of THF in water/THF system during BDE209 degradation

THF could be oxidized during the BDE209 degradation, leading to the formation of major oxidation products including tetrahydro-2-furanol and γ-butyrolactone [19,20]. For this reason, tetrahydro-2-furanol and γ-butyrolactone were monitored to obtain the information on the engagement of THF in the BDE209 degradation process. The GC chromatogram and mass spectra of THF degradation products in the BDE209/THF/water system during photocatalytic degradation of BDE209 is shown in Fig. 5. Major oxidation products of THF were observed. Tetrahydro-2-furanol eluted out at 3.5 min; while γ-butyrolactone eluted out at 5.19 min.

4 Discussion

Organic solvents (including THF and methanol) have been added to dissolve PBDEs [15] in water before subjecting them to oxidative removal processes [11–14]. Results showed that BDE209 could be removed efficiently in the pure water system without the addition organic solvent (THF). Additionally, the final debromination ratio was much higher than that of the control with THF. Since the wide occurrence of PBDEs in various environments has been observed [2,5], results from this study have significant potential to provide an alternative option for their efficient removal from water.

The BDE209 removal rate in the pure water system was lower than in the THF system while the final debromination ratio was much higher, indicating that significantly different mechanisms for the photocatalytic degradation of PBDEs in the two systems. According to Sun et al. [21], solvent has important role in the photocatalytic degradation process of BDE209 because solvent-derived radials were formed in different solvents. In the BDE209/water system, ·OH is the primary free radical that contributes to the debromination of BDE209; while both THF· and ·OH are the primary free radicals for the degradation of BDE209 in water/THF system. Previous studies have showed that ·OH is the primary free radical that contributes to photocatalytic degradation of contaminants in the pure water system [22] while both THF· and ·OH are the primary free radicals for the degradation of organic pollutants in water/THF system [12]. A previous investigation reported that when THF amounts greatly exceeded BDE209 in the THF/water system, abundant THF· could be formed, which when combined with ·OH resulted in relatively high degradation rates [12]. This is likely why a much higher debromination ratio was observed in the early
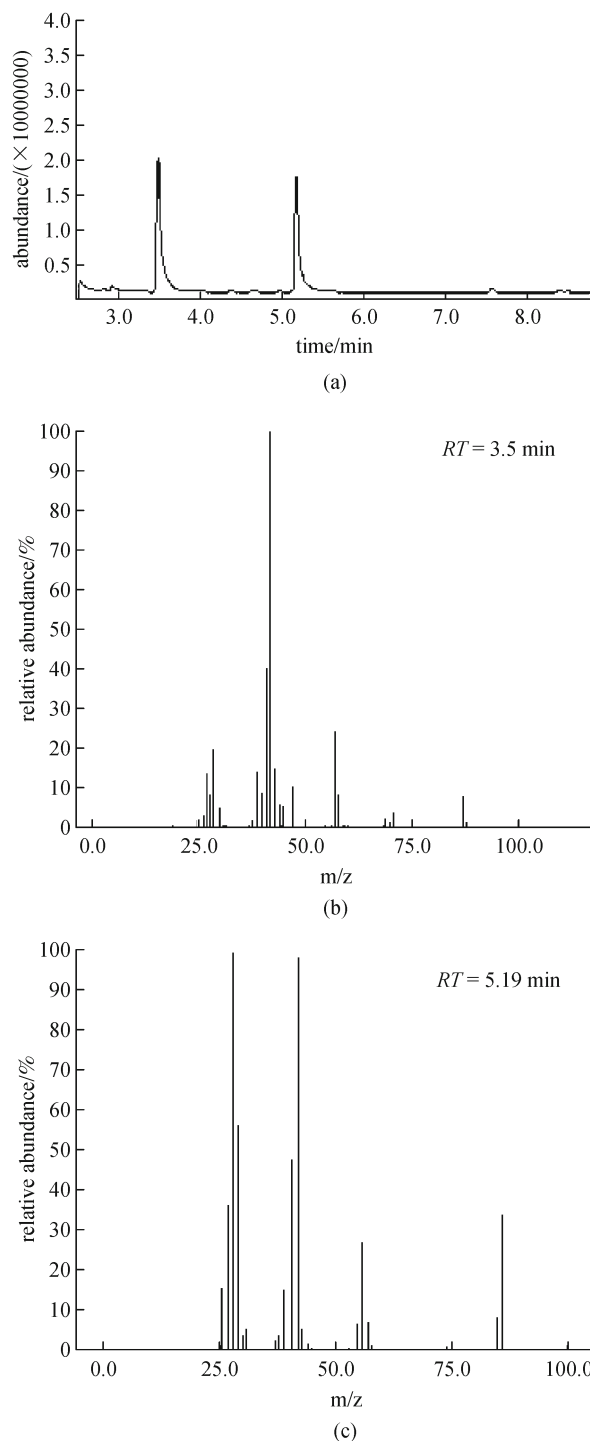

Fig. 5 Total ion chromatogram (a) and mass spectra of tetrahydro-2-furanol (b) and γ-butyrolactone (c). Reaction conditions: pH = 5; reaction time was 2 h

degradation stages of the BDE209/THF/water system relative to the pure water system. However, the accumulated tetrahydro-2-furanol could compete with BDE209 for ·OH, which subsequently led to the decrease in the debromination ratio of BDE209 later. This process was confirmed by the further oxidation of tetrahydro-2-furanol

into GBL [19,20].

The pH might have great influence on the formation of free radicals, which subsequently led to the differences in BDE 209 degradation under different pH conditions. The ·OH was easily be formed under neutral and alkaline conditions [22,23]. For this reason, the increase in pH led to the increase in removal efficiency in the pure water system. However, the influence of pH on the formation of free radicals in the THF/H$_2$O system might be more complicated. Although ·OH was easily be formed under alkaline conditions, higher pH may lead to the accumulation of free radical scavenger intermediates (e.g., tetrahydro-2-furanol) that could compete with BDE209 for ·OH, which subsequently led to the decrease in the degradation of BDE209. Further study is needed to know these processes better.

5 Conclusions

The efficient degradation of BDE209 in a pure water system where BDE209 was dispersed as nano-scale particles was observed. The results illustrated that BDE209 can be removed efficiently through photocatalytic degradation in pure water, indicating that no additional organic solvent was needed to enhance removal. The mechanism for photocatalytic oxidation of BDE209 in pure water is different from that in THF/water system, which led to differences between the degradation behaviors. Although the removal rate of BDE209 in the pure water system was lower than that in the water/THF system in the early degradation stage, the final debromination ratio in pure water system was much higher than that in the presence of THF. Additionally, the photocatalytic degradation of BDE209 in the pure water system followed first-order kinetics; while that in the presence of THF followed second-order kinetics.

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