

Degradation of Polybrominated Aiphenyl Ethers in a UV Advanced Reduction Process with Different Reducing Agents

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Abstract. Polybrominated diphenyl ethers (PBDEs) are toxic and persistent, and their efficient degradation is currently a challenge. In this study, decabromodiphenyl ether (BDE-209) was selected as the target compound and was degraded by a UV photochemical system with different reducing agent. The result showed that the optimal BDE-209 removal in 1 hour by UV/sodium sulphite (Na_2SO_3) was 86.87%. With the same concentration of BDE-209 and reaction time, the optimal removal rate by UV/sodium borohydride (NaBH_4) was 89.25%. Kinetic analysis revealed that the degradation of BDE-209 conformed to the first-order kinetic model. The order of rate constant of different UV photochemical processes is $k_{\text{UV}} < k_{\text{UV}/\text{Na}_2\text{SO}_3} < k_{\text{UV}/\text{NaBH}_4}$. Debromination rate indicated that reducing agents can promote the removal of bromine during the degradation of BDE-209. As a reducing agent, sodium borohydride showed a better enhanced effect for the removal of bromines.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used in the fields of electronic products, building materials, textiles, adhesives, sealants, coatings and inks as a kind of brominated flame retardants (BFRS). Due to highly persistent, a high potential for bioaccumulation and food-web biomagnification, as well as for long-range transport. Adverse effects are reported for soil organisms, birds, fish, frog, rat, mice and humans [1]. In 2009, parts of PBDEs were listed as persistent organic pollutants at the Stockholm Convention by the United Nations Environment Programme (Persistent Organic Pollutants Review Committee, POPRC, 2009)[2].

So far, the researches on PBDEs were mainly focused on environmental distribution, pollution characteristics, environmental behavior and human exposure etc[3-5]. Studies on the degradation of PBDEs are rather few. Several studies on the treatment of PBDEs have been reported mainly using biological method, photochemical method, hydrothermal method, zero-valent iron reduction method and electrochemical method [6-12]. Among them, photodegradation is one of the most popular methods for the destruction of PBDEs. With fluorescent lamps from 295 to 390 nm as light source, Eriksson et al. studied the photolysis behavior of PBDEs in methanol/water and tetrahydrofuran solution respectively. The results showed that the photodynamic of PBDEs followed the first order reaction kinetics. And the reaction rate has a very close relation with the number of bromine



substitution [13]. At the same time, some studies have shown that the photodegradation rate and quantum yield of PBDEs are also affected by the bromine substitution position in a certain extent [14]. Based on the lipophilic and hydrophobic characteristic of PBDEs, Rayne et al. investigated the degradation of PBDEs in acetonitrile solution with UV light irradiation of 302 nm. It was found that during the degradation of PBDEs pentabromodiphenyl ether was produced first, then tetrabromodiphenyl ether was converted followed by a small amount of other low bromide generation [15]. Recently, Wei et al studied the photodegradation of 13 kinds of PBDEs, and investigated the photodegradation pathways of PBDEs with different structures [16]. In general, the degradation of halogenated organic compounds is limited due to the limitations of existing photochemicals, hydroxyl radicals ($\text{HO}\cdot$) [17]. Besides, low reaction rate and production of highly toxic byproducts such as polybrominated dibenzofurans and dioxins still are the main problem need to solve today [18].

Recently, hydrated electrons (e_{aq}^-) have been considered as the degradation of halogenated organic compounds due to the special reducibility. The reduction potential of e_{aq}^- is -2.9V, which can promote the dehalogenation of halogenated organics faster than other reactive groups such as hydroxyl radicals ($\cdot\text{OH}$) and hydrogen atoms ($\cdot\text{H}$) [19-20]. Fischer and Warneck in their study have reported that some reducing agents such as sulfurous acid or sulfite with quantum irradiation can produce active electrons such as $\cdot\text{H}$ and e_{aq}^- , which is more conducive to the degradation of certain refractory organic matter [21]. The combination of activating methods like UV irradiation and reducing agents, in some studies, also known as advanced reduction processes (ARPs) [22]. Each of different reagents (dithionite, sulfite, sulfide, and ferrous iron) were used as the reducing agents and combined with ultraviolet light produced by two types of lamps (medium pressure mercury UV and narrow-banded UV) as the activating methods [23-25]. Especially, studies on UV/sulfite ARPs indicate their potential to degrade chlorinated organics like vinyl chloride, mono-chloro acetic acid and 1,2-DCA [26]. However, few studies using this method to perform the degradation of PBDEs.

The objective of the current research is to apply the UV photochemical technology with two different reducing agents (sodium sulfite (Na_2SO_3) and sodium borohydride (NaBH_4)) to degrade the decabromodiphenyl ether (BDE-209) and investigate the process efficiency. Debromination rate, which is a measure of efficiency of a photochemical process was calculated for the removal of bromine atoms to analyze the mechanism and effect of different experimental conditions on the ARP efficiency.

2. Experiment

2.1. Preparation of BDE-209

A certain concentration solutions of the BDE-209 were prepared by dissolving the pure solid in tetrahydrofuran. A portion of the prepared solution was taken out and diluted with a mixture of pure deionized water at different pH using a dilute sulfuric acid or sodium hydroxide solution when using.

2.2. UV Experiment

The experiment was conducted in the apparatus developed by Environmental Science and Engineering Research Center, Harbin Institute of Technology. The light source was a high pressure Hg lamp. The prepared solution of BDE-209 was placed in the reactor. At the same time, a certain amount of reducing agent was added as soon as possible. 10 mL of the irradiated sample was taken out and analyzed samples after a period of time.

2.3. Analytical methods

2.3.1. Determination of BDE-209 concentration. For all experiments, samples were taken directly from the reaction vessel and extracted with n-hexane. The pretreated samples were analyzed with a high performance liquid chromatography (HPLC, Agilent 1100). The reaction programs were as follows: injection sample of 10 μL , X Terra MS 4.6 \times 250 mm column, methanol/ pure deionized water

(8:2) as mobile phase, column temperature keep at 25 °C, a flow rate of 1 mL / min, retention time for 15 min, and detection wavelength of 230 nm.

2.3.2. Determination of Bromide Ion Concentration. The water samples were filtered through a 0.45 µm filter and the concentration of bromide ions in the samples was analyzed by ion chromatography (IC, DIONEX ICS-3000). The working conditions were as follows: injection volume of 10 µL, Ion Pac AG19 2×50 mm Guard column, mobile phase with volume ratio of 9 of deionized water to 0.1mol/L NaOH solution, temperature hold at 25 °C, flow rate of 0.25 mL/min, and retention time for 4 min/6 min.

3. Result and discussion

3.1. Degradation of BDE-209 by UV/Na₂SO₃ advanced reduction process

Some text. Sulfite usually was used as reducing agent in an ARP because it can form the sulfite radical anion and hydrated anion, or hydrogen radical. In this study, sodium sulfite (Na₂SO₃) was chosen in the UV process to degrade the BDE-209 first. With the BDE-209 initial concentration of 40 mg/L, initial pH of 10, ultraviolet light intensity of 350uW/cm², the effect of Na₂SO₃ dose on BDE-209 removal was obtained in Fig. 1.

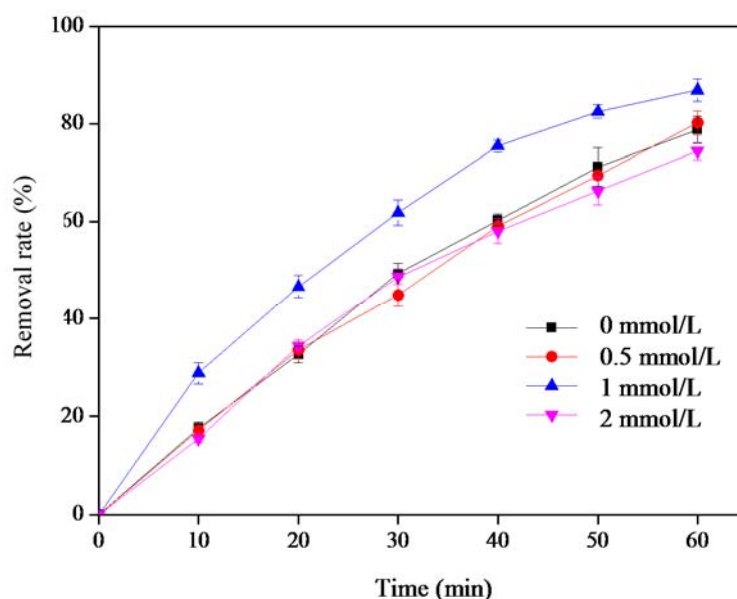


Fig. 1 The effect of Na₂SO₃ dose on BDE-209 removal

Results showed that there was a certain removal of BDE-209 by UV photochemical system only (Na₂SO₃ dose is zero). The removal effect of BDE-209 was improved after adding Na₂SO₃. The highest removal efficiency of BDE-209 was obtained when the concentration of Na₂SO₃ was 1 ppm. But the effect was limited if the dose of Na₂SO₃ continues to increase. The optimal removal rate of BDE-209 was 86.87% after 60 min. It was proved that the addition of reducing agent Na₂SO₃ has a promotion to a certain extent on the removal of BDE-209.

3.2. Degradation of BDE-209 by UV/NaBH₄ advanced reduction process

Sodium borohydride (NaBH₄) is widely used as a reducing agent to prepare various catalysts. With the BDE-209 initial concentration of 40 mg/L, initial pH of 12, ultraviolet light intensity of 350uW/cm², the effect of NaBH₄ dose on BDE-209 removal was obtained in Fig 2. Compared with using UV degradation only (NaBH₄ dose is zero), the removal effect of BDE-209 was improved after adding NaBH₄ in the UV process. The highest removal efficiency of BDE-209 was obtained when the

concentration of NaBH_4 was 2 ppm. But the effect was limited if the dose of Na_2SO_3 continues to increase. The removal rate of BDE-209 was 89.25% after 60 min. It was proved that the addition of reducing agent NaBH_4 has a certain promotion on the removal of BDE-209. Meantime, there was a better removal of BDE-209 by UV/ NaBH_4 process than that of UV/ Na_2SO_3 process.

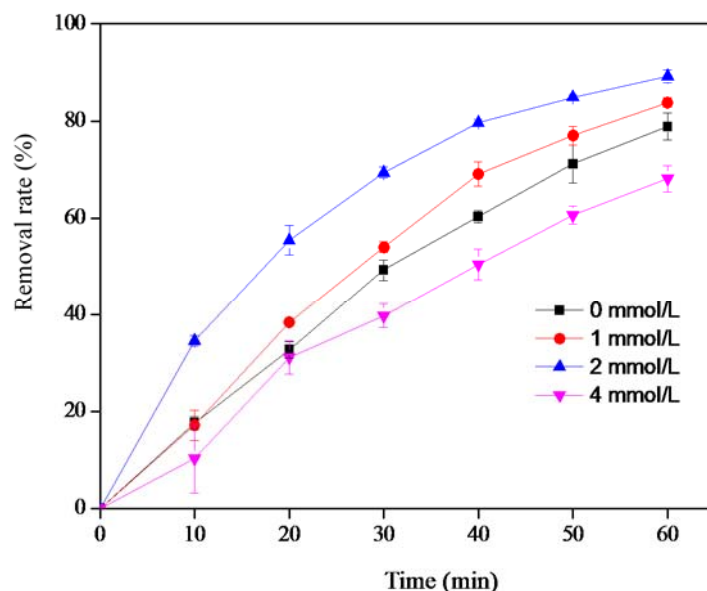


Fig. 2 The effect of NaBH_4 dose on BDE-209 removal

3.3. Kinetic analysis of different UV photochemical processes

Kinetic analysis of different UV photochemical processes was conducted in the following conditions. In one process with Na_2SO_3 as reducing agent, the initial concentration of BDE-209 is 40 mg/L, the dosage of Na_2SO_3 is 1 mmol/L, and the pH value of the solution is 10. In another process with NaBH_4 as reducing agent, the dosage of NaBH_4 is 2 mmol/L, the pH value of the solution is 12. Moreover, there is still a third process, UV only without any reducing agent. All the light intensity is 350 $\mu\text{W}/\text{cm}^2$ and the reaction time is 60 min. In all these cases, reaction kinetics of BDE-209 degradation was shown in Figure 3 and Table 1.

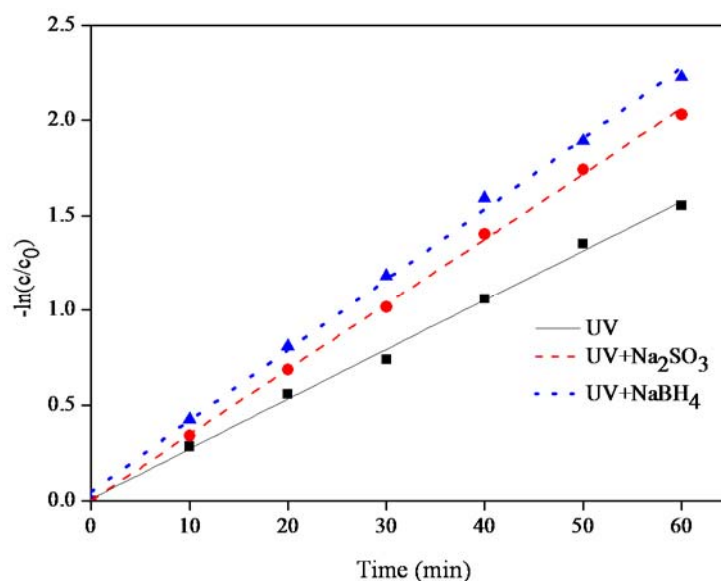


Fig 3 Reaction kinetics analysis of different UV photochemical process

Table 1. Kinetic parameters of BDE-209 degradation with different reducing agents

Reaction process	Kinetic equations	R^2	$k \times 10^{-2} \text{min}^{-1}$
UV	$y = 0.0261t + 0.0096$	0.9965	2.61
UV+Na ₂ SO ₃	$y = 0.0344t + 0.0011$	0.9990	3.44
UV+NaBH ₄	$y = 0.0372t + 0.0464$	0.9971	3.72

Fig. 3 showed that the degradation of BDE-209 was appreciably improved by adding reducing agent. Under the each optimum reaction conditions, the reduction of UV/NaBH₄ was slightly better than UV/Na₂SO₃. The kinetic equations and constant of BDE-209 degradation in different reaction processes were summarized in Table 1. The results indicated that the degradation of BDE-209 conformed to the first-order kinetic model. The order of rate constant of three different UV photochemical processes is $k_{\text{UV}} < k_{\text{UV+Na}_2\text{SO}_3} < k_{\text{UV+NaBH}_4}$. This further revealed that UV/NaBH₄ was more effective to remove BDE-209 than UV/Na₂SO₃.

3.4. Comparison of debromination rate of different UV reaction system

The degree of dehalogenation of organic matter in the system can be obtained by the determination of bromide ions, which can further proved the ability of degradation of halogenated organic compounds by UV assisted chemical methods. The change of bromine ions in BDE-209 solution was determined during the different reaction system (UV only, UV/Na₂SO₃, UV/NaBH₄). Fig. 4 showed the results of debromination of different UV photochemical processes.

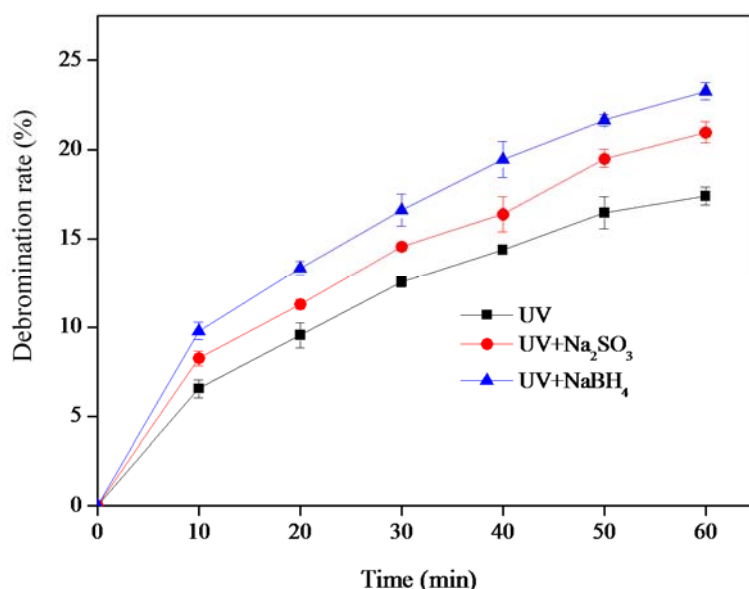


Fig. 4 Debromination analysis of different UV photochemical processes

It can be seen from Figure 4, three kind of UV photochemical system have a certain effect on the removal of bromide ions. After 60 minutes, the bromination rate with Na₂SO₃ and NaBH₄ were 20.98% and 23.25% respectively. That was higher than 17.41% of by using only UV photochemical processes. It indicated that adding reducing agents can improve the bromide removal rate significantly compared with that of UV only. But the overall debromination rates were less than 25%. The reason for this phenomenon is that the bromine atoms of decabromodiphenyl ether are too much, even if the removal rate of BDE-209 is more than 80%, which is mainly due to the change of molecular structure or partial removal of bromide ions. The total amount of free bromine ions ratio is still low.

4. Conclusion

This study investigated the ability of UV/sulfite ARP and UV/sodium borohydride ARP to remove BDE-209. About 75% of bromate was removed by the UV photochemical system only. At the same condition, the removal rate could reach about 86%~90% by adding reducing agents of suitable doses. The results indicate that although the effect of degradation of BDE-209 could be enhanced with ARP, direct photolysis is the dominant bromate removal mechanism in the UV ARP under the experimental conditions studied. UV/NaBH₄ ARP showed better degradation than that of UV/Na₂SO₃ ARP. The bromine atom of the BDE-209 was partly converted to bromide ions by direct photolysis with irradiation. Adding reducing agents has limited improvement in the debromination rate of BDE-209.

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