PHOTO-FENTON DEGRADATION OF 2,2',4,4'-TETRABROMODIPHENYL ETHER IN AQUEOUS SOLUTION

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Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used as additive brominated flame retardants (BFRs) since the 1970s in various consumer products, which are known as ubiquitous contaminants in the environment [1]. Due to their persistence, great bioaccumulation potential and toxicity [2], the penta- and octa- BDE commercial mixtures have been listed into the Annex of the Stockholm Convention [3]. Nevertheless, the concentrations of PBDEs were still very high in the sewerage treatment plant effluents and the estuarine region [4].

The disposal techniques for reducing the PBDEs in water include the physical [5], chemical [6] and biological [7] methods. Among these methods, the photo-Fenton oxidation is one kind of advanced oxidation processes (AOPs), which can produce the hydroxyl radical ($\cdot$OH) [8], an effective oxidant to degrade PBDEs.

This work investigated the degradation of PBDEs by photo-Fenton reaction (Fe (III)/hydrogen peroxide (H_2O_2) system) under visible irradiation, using 2,2',4,4'-tetrabromodiphenyl ether (BDE 47) as the probe compound.

Materials and methods

4-bromodiphenyl ether (BDE 3), 4,4'-dibromodiphenyl ether (BDE 15), 2,4,4'-tetrabromodiphenyl ether (BDE 28) and BDE 47 were obtained from Accustandard (New Haven, CT, USA). The photochemical experiments were carried out using a SGY-I photochemical reactor (Nanjing stonetech electric equipment Co., Ltd., China) equipped with 350W Xenon lamps and 290 nm cutoff filters to simulate sunlight. BDE 47 was introduced into a quartz tube (35 mm i.d. × 20 cm), then evaporated to dryness under a gentle stream of nitrogen. Subsequently, the solution (pure water, iron ions, H_2O_2, or Fe(III)/H_2O_2) was added into the quartz tubes following a strong mixing before irradiation. The photolysis products were extracted by dichloromethane with hydrochloric acid (1 M). The extracts were concentrated prior to analysis by GC-MS (6890/5973, Agilent, USA) equipped with the DB-5MS (30 m × 0.25 mm i.d. × 0.25 μm film, J&W Scientific, Folsom, CA).

Results and discussion

As shown in Fig. 1, the degradation of BDE 47 was studied under simulated solar light in pure water, the BDE 47 concentration decreased by 17.6 % and 8.2 % in irradiation and dark control experiment, respectively. In blank experiments, the PBDEs congeners were not detected. And in photochemical reactor, the quartz tube with

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BDE 47 was covered with the aluminium foil avoiding irradiation to simulate dark condition. However, the ambient temperature is increased under the xenon radiation causing the volatilization of BDE 47. Compared with the degradation of BDE 47 in dark, the photodegradation of BDE 47 was slowly in pure water.
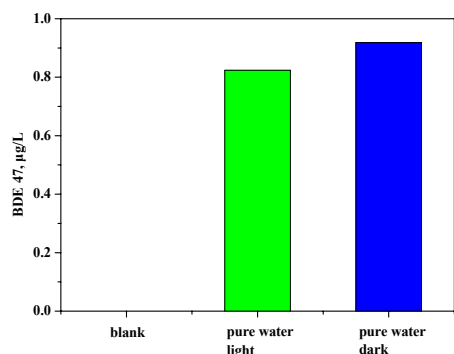

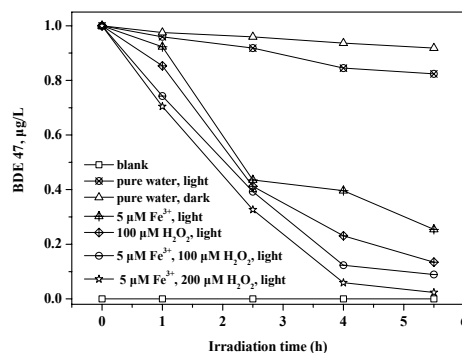Fig. 1 The concentrations of BDE 47 (1 μg L^{-1}) photodegraded for 5.5 h in pure water

Fig. 2 Photodegradation of BDE 47 (1 μg L^{-1}) under the different conditions

Simultaneously, the irradiation of BDE 47 was also studied under simulated solar light in ferric chloride (FeCl$_3$) - H$_2$O$_2$ solution. Fig. 2 shows BDE 47 degradation under the different conditions with the presence of Fe(III), H$_2$O$_2$ and Fe(III)/H$_2$O$_2$. It is obvious that the photodegradation of BDE 47 was increased in presence of Fe(III) or H$_2$O$_2$ alone, and increased significantly with the coexistence of Fe(III) and H$_2$O$_2$. At the end of irradiation experiments, BDE 47 was degraded more than 90 % in the coexistence of Fe(III) and H$_2$O$_2$. According to researches of Wu [9] and Duesterberg [10], the •OH was mainly generated during the cycle of Fe(III)/Fe(II) (reaction 1~2), which causes the degradation of BDEs.
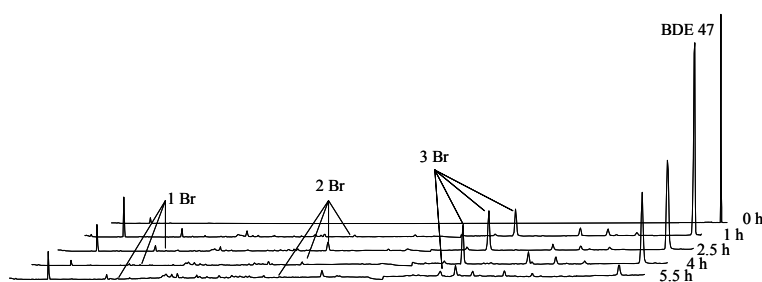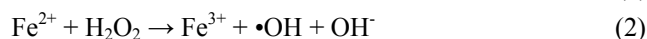
$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH \qquad (1)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (2)$$

Fig. 3 GC-MS chromatograms of PBDE congeners after simulated solar light irradiation of BDE 47 (1 μg L^{-1}) in Fe(III)- H$_2$O$_2$ solution at different times

Fig. 3 shows the GC-MS chromatograms of PBDE congeners after simulated solar light irradiation of BDE 47 in Fe(III)- H$_2$O$_2$ solution at different times. BDE 28, BDE 15, and BDE 3 were confirmed to be the photoproducts of BDE 47 under photodegradation with the coexistence of Fe(III) and H$_2$O$_2$. Moreover, with the

increasing time of irradiation, the amount of BDE 47 in the aqueous solution was decreased and lower brominated PBDEs were found. The main identified compounds were BDE 28 and BDE 15. These main photoproducts were agreement with the results reported by Fang et al. [11] in researching the photolysis of six PBDEs in hexane. Therefore, it could be concluded that the main degradation mechanism about photooxidation of BDE 47 were stepwise debromination. Among these PBDE congeners, bromines at the ortho positions are much more photo-reactivity than those at the para positions.

As can be seen in Fig. 4, compared with other conditions, the coexistence of Fe(III) and H_2O_2 can increase the yield of BDE 28 and BDE 15 in the early time of irradiation, then these lower brominated degradation products were quickly degraded causing the accumulation amount of BDE 28 and BDE 15 in Fe(III)/H_2O_2 solution to be lowered.
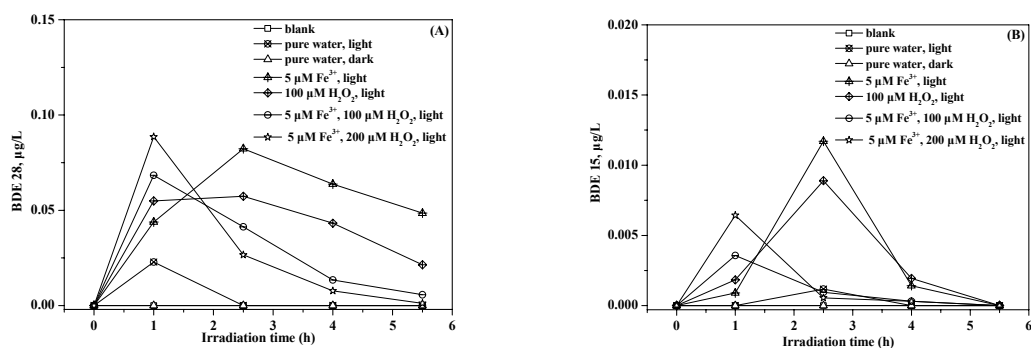

Fig. 4 The formation of BDE 28 (A) and BDE 15 (B) in different solutions

This work investigated the photodegradation of BDE 47 in photo-Fenton (Fe(III)/H_2O_2 system) under simulated solar light. The existence of Fe(III)/H_2O_2 can effectively degrade BDE 47 following a stepwise debromination process. The reported experimental results are helpful for PBDEs control in the environment.

References

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