Study on photodegradation of typical new brominated flame retardants on soil minerals and actual soil

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Abstract: The photodegradation process of hexabromobenzene (HBB) adsorbed on four soil minerals and actual soil was studied under simulated sunlight irradiation. The results showed that the photodegradation of HBB on all soils was in accordance with the pseudo-first-order kinetic process. In different soil types, the order of photodegradation rate from fast to slow was silica gel (simulated soil mineral system) > montmorillonite > kaolinite > Sanya soil > quartz sand > Haikou soil. The higher the thickness of soil laying, the lower the photodegradation efficiency of HBB. The photodegradation rate in the system with humic acid (HA) decreased significantly, and the higher the HA concentration, the more obvious the inhibition effect. The photodegradation products of HBB were identified by GC-MS, mainly the formation of debromination products, and the degradation pathway was reduction debromination.

1 Introduction

Brominated flame retardants (BFRs) are widely used as chemical additives in electronic equipment, building materials and textiles, and have attracted much attention in the past decades due to their excellent flame retardancy properties. However, traditional BFRs have been classified as persistent organic pollutants by the Stockholm Convention, and their production and use are severely restricted. Therefore, new brominated flame retardants (NBFRs) have been widely used as substitutes. As a substitute for NBFRs of PBDEs, HBB is widely used in flame retardant treatment of polymer materials, electronic equipment and household furniture. However, due to its persistence in the environment and potential toxicity, HBB has become one of the most widely concerned pollutants. As a persistent organic pollutant, HBB has low biodegradability, so it is easy to accumulate in the atmosphere, water and soil, posing a potential threat to the ecosystem and human health [1].

Soil is the main reservoir of organic pollutants, and the higher octanol-water partition coefficient makes HBB more inclined to accumulate in soil [2], and the presence of HBB has been detected in soil in different regions. For example, An et al. observed HBB in agricultural soils in eastern China during 2011-2021, with a concentration of nd-0.15 ng/g dw [3]. The concentrations of HBB in the soils of Fildes Peninsula, Antarctica [4] and Tianjin, China [5] are nd-11.13 pg/g dw and nd-15.4 ng/g dw. Direct photolysis of NBFRs usually occurs on the soil surface due to the strong light shielding effect of soil particles. Some studies have found that soil minerals and organic matter have an important impact on the photodegradation rate of flame retardants. Clay minerals in soil can catalyze the photolysis of flame retardants. For example, Ahn et al. [6] studied the photodegradation process of BDE-209 on six solid substrates (including clay minerals and metal oxides), and found that the photolytic rate of BDE-209 on clay minerals was faster and more debrominated products were generated, while the photolytic rate on metal oxides was slow. Li [7] et al. studied the photodegradation of DBDPE adsorbed on silica gel (as a simulated soil system) and found that the removal rate of DBDPE was as high as 98.4% after 18 h of exposure to simulated sunlight at high pH.

At present, the degradation of NBFRs is mostly carried out in organic solvents or simulated soil systems, while there are few studies on the photodegradation behavior of HBB in soil environment. Therefore, this study intends to select montmorillonite, kaolinite, quartz sand and silica gel as well as the actual soil collected in Haikou and Sanya to study the photodegradation process of HBB on soil minerals and actual soil. It has important theoretical value and practical environmental significance to elucidate the photodegradation mechanism of HBB on soil minerals and actual soil.

2 Experimental materials and methods

2.1 Chemicals and reagents

HBB (purity≥99%), quartz sand (QS, 200-250 mesh), kaolinite (GLS) purchased from Shanghai Yien Chemical Technology Company. Silica gel (SG, 200-300 mesh) purchased from Qingdao Ocean Chemical Company. Montmorillonite (MTS) was acquired from Shanghai Bider Medical Technology Company. HPLC grade solvent n-hexane was purchased from Shanghai Anpu Experimental Technology Company. In order to keep its

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particle size consistent, MTS, GLS, QS, SG are all over 200 mesh screen. In addition, Sanya actual soil (SYT) and Haikou actual soil (HKT) are collected from 0 to 20 cm above the surface, then air dried, ground, dried and stored for use after passing through a 200-mesh screen.

2.2 Preparation of HBB samples adsorbed to soil surface and photodegradation experiment

Weigh 5 g solids into a round-bottomed flask, add 10 mL HBB (0.05 mg) reserve solution, and then slowly evaporate the solvent through a rotary evaporator to prepare a solid sample loaded with HBB with a surface load of 10 μg/g. All light experiments were performed in the modified photochemical reacter (Figure 1). The light source uses 500 W Xe lamp. The 0.1g supported sample was evenly spread in a petri dish (6 cm in diameter) and placed on the base of the photochemical reaction instrument to conduct the corresponding photodegradation experiment. The control group was performed in dark conditions. All experiments were set up in three parallel sets.

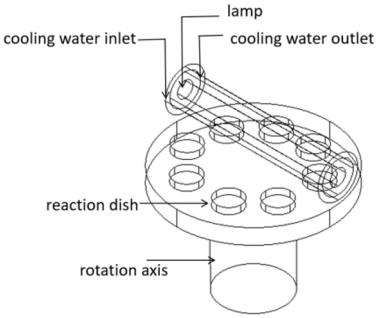

Figure 1. Schematic diagram of the modified photochemical reactor.

2.3 Sample preparation and analysis method

After the reaction began, samples were taken at 0, 15, 30, 60, 120 and 240 min respectively, and each sample was put into a centrifuge tube, 2 mL n-hexane was added, and then the sample was extracted by ultrasound. Finally, 1 mL supernatant was taken for GC analysis. The extraction efficiency was 89.7%. The HBB in the sample was quantified by a Thermo Scientific TRACE 1300 gas chromatograph equipped with ECD. 2 μL samples were absorbed and injected into TG-5SILMS column (30 m× 0.32 mm, 0.25 μm) with high purity N_2 carrier gas at a flow rate of 3.0 mL/min through an automatic sampler in a non-diverging mode. The temperature of the gasification chamber and the detector are set at 280 ℃ and 320 ℃ respectively. The heating procedure is as follows: first, the temperature is kept at 80 ℃ for 2 min, then it is heated at 30 ℃/min to 290 ℃, and then it is heated at 10 ℃/min to 320 ℃ for 10 min. The intermediate product of HBB degradation was determined by Agilent 8890-7250 GC/QTOF gas chromatography and mass spectrometry. The separation column was DB-5ht (15 m×0.25 mm, 0.1 μm), the sample was injected 1 μL by automatic injector in non-shitter mode, the inlet temperature was 280 ℃, and the carrier gas was high purity He. The column flow rate is 1.0 mL/min (constant current). The temperature procedure is as follows: first, 80 ℃ is maintained for 2 min, then it is increased to 280 ℃ at 12 ℃/min and maintained for 3 min. The mass spectrometry conditions are as follows: ion source is EI source, temperature is 230 ℃, ionization energy is 70 eV, solvent delay is 5 min, and the mass spectrometry range is m/z=60-600.

3 Results and discussion

3.1 Photodegradation kinetics of HBB on soil minerals and actual soil

The experimental results show that HBB can significantly degrade on SG, QS, GLS, MTS, SYT and HKT under Xe lamp irradiation. With the extension of light time, the degradation rate of HBB in the six soils increased gradually. The degradation of soil minerals and HBB in actual soil was not observed in the dark. The photodegradation process of HBB in soil minerals can be fitted using a pseudo-first-order kinetic model, and its photodegradation kinetic curve and pseudo-first-order kinetic model are shown in Figure 2. The degradation rate constants were 0.02617 min^{-1} (SG) > 0.00659 min^{-1} (MTS) > 0.00285 min^{-1} (GLS) > 0.00252 min^{-1} (SYT) > 0.00177 min^{-1} (QS) > 0.00039 min^{-1} (HKT); The degradation half-life was 4.34 min (SG) < 5.72 min (MTS) < 6.55 min (GLS) < 6.68 min (SYT) < 7.03 min (QS) < 8.54 min (HKT). In the study of BFRs, the photodegradation rate of BFRs adsorbed on the surface of different solid substrates is also different, which is related to the chemical composition, surface structure and optical properties of different solid substrates [8]. For example, SG and QS have the same composition, but they show different removal efficiencies due to different crystal structures [9].

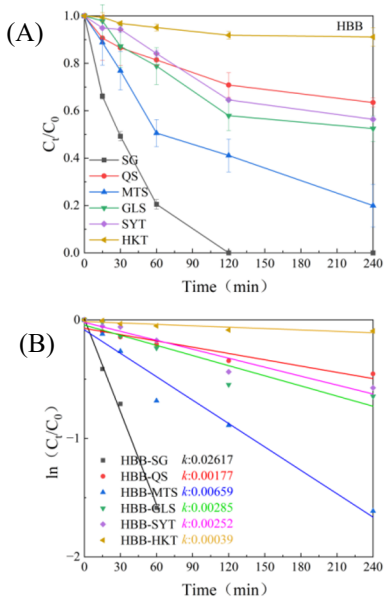

Figure 2. (A) Photodegradation kinetics of HBB on SG, QS, MTS, GLS, SYT and HKT; (B) Pseudo-first-order kinetic model of photodegradation of HBB on SG, QS, MTS, GLS, SYT and HKT.

3.2 Study on the dynamic influencing factors of HBB on soil minerals and actual soil

The effect of soil thickness. Due to the obvious photodegradation process of HBB on the soil surface, the influences of different factors on its photodegradation were investigated. The first is the influence of soil thickness. HBB on SG, QS, GLS, MTS, SYT and HKT all follow the rule that the thicker the soil laying thickness, the lower the photodegradation efficiency. Compared with 0.1 mm HBB/ soil minerals, the reaction rate of HBB was greatly reduced when the laying thickness was increased to 0.2 mm, especially 0.4 mm (Figure 3). The reason for this result may be that the increased thickness of the soil will lead to a stronger shading effect. The increase in the thickness of soil minerals leads to an increase in the amount of solid samples, thus obstructing the penetration of light [10], resulting in the inability of some light to effectively shine on HBB molecules.

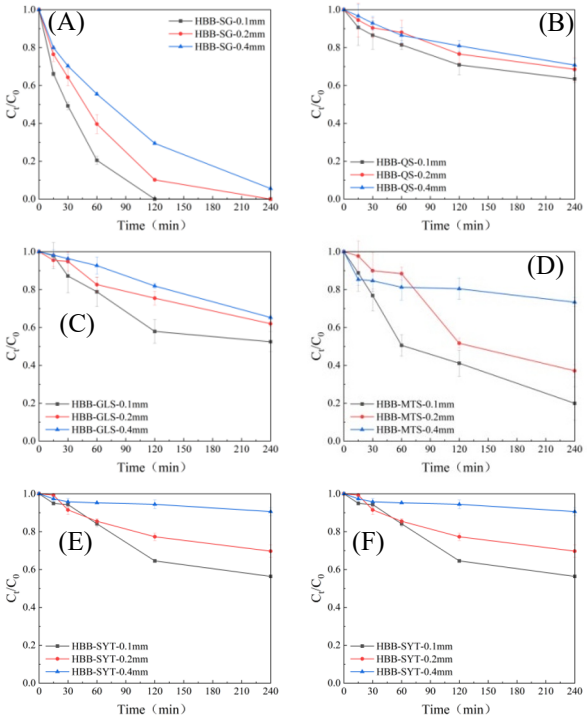

Figure 3. Effect of different layings thickness on surface photodegradation of HBB in (A) SG, (B) QS, (C) GLS, (D) MTS and (E) SYT, (F) HKT.

Effects of different concentrations of HA. HA is a widely distributed natural organic macromolecule, which accounts for about 60%-90% of soil organic matter [11]. Therefore, this study explored the effect of different concentrations of HA on the photodegradation rate of HBB on the SG surface. The photodegradation rate of HBB significantly decreased in the system with HA presence, and the degradation efficiency also decreased at 240 min, as shown in Figure 4. With the increase of HA concentration, the k value of HBB decreased from 0.02617 min^{-1} to 0.00489 min^{-1}, and the degradation efficiency of 240 min also decreased from 100% to 72.85%, and the higher the HA concentration, the slower the degradation rate of HBB. Previous studies have shown that HA, as a light-absorbing substance, reduces the light absorption efficiency of pollutants by competitively absorbing light and photon energy, thus reducing the photodegradation rate [12]. At the same time, the adsorption of HA on SG may cover the surface active site, which may also lead to inhibition of photodegradation of HBB.

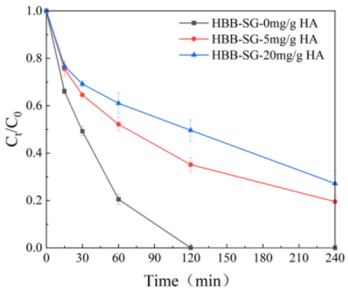

Figure 4. Effect of HA concentration on photodegradation of HBB on SG.

3.3 Intermediate product analysis and reaction pathway

When photodegradation of HBB occurred on SG, QS, GLS and MTS, the degradation products were detected by GC-MS system, and the degradation products were all step-debromination products. Pentabromide, tetrabromide and tribromobenzene were detected in each of the four systems, and their MS/MS were shown in Figure 5. The degradation path (Figure 6) is a step-by-step debromination process after C-Br bond break, from hexabromobenzene to tribromobenzene.

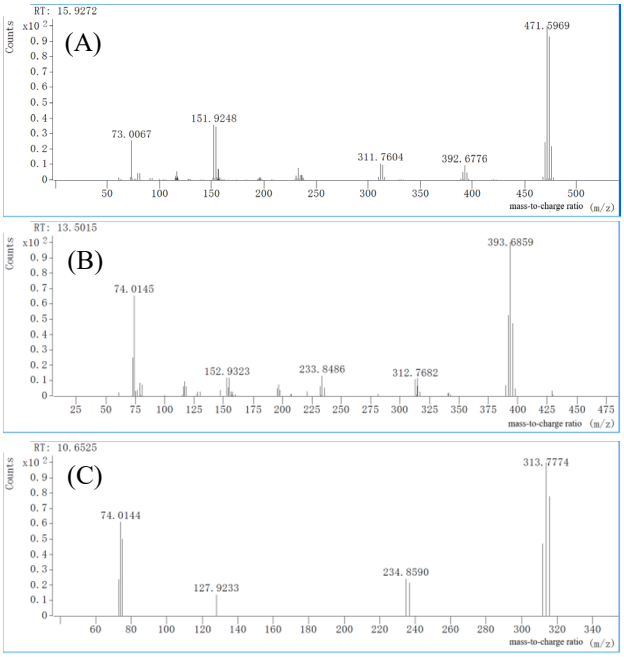

Figure 5. Product ion spectra of transformation products (A)C_6HBr_5, (B)$C_6H_2Br_4$ and (C)$C_6H_3Br_3$ of HBB.

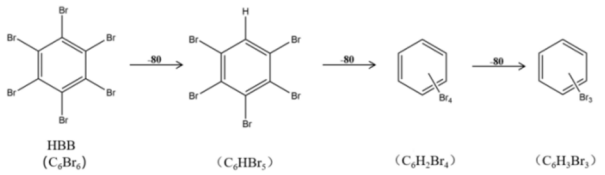

Figure 6. Reaction pathway of HBB in surface photodegradation of soil minerals.

4 Conclusion

Under the irradiation of 500W Xe lamp, HBB can photodegrade in SG, QS, GLS, MTS, SYT and HKT soil systems, and the degradation process follows a pseudo-first-order kinetic model. HBB in these six soil systems followed the rule that the thicker the soil laying thickness, the lower the photodegradation efficiency. The photodegradation rate of HBB on the surface of four soil minerals was significantly slowed down by the addition of HA due to the presence of photoshielding effect. The degradation products of HBB were detected by GC-MS system. The degradation products of HBB on the surface of four soil minerals were all step debromination products.

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