DOCTORAL THESIS

Combined photocatalysis and phytoremediation for efficient treatment of polybromodiphenyl ethers (PBDES)

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ABSTRACT

Brominated flame retardants have been widely used in industry. There is a rapidly growing public concern about their ubiquity in the environment. This project investigated the possible removal treatments of polybrominated diphenyl ethers (PBDEs) using two treatment methods: (I) photocatalysis by TiO_2 and (II) phytoremediation by *Oryza sativa* and *Phragmites australis*, and a combined system involving these two technologies. Advanced oxidation process (AOP) is a promising technology for removing emerging chemicals. In this case, nano-scaled titanium (IV) oxide was applied to evaluate its capability in the degradation of BDE-209 under visible light. The residual PBDE congeners after reaction were analyzed by gas chromatography-mass spectrometry (GC-MS). The half-life for removing BDE-209 by TiO_2 was 3.05 days under visible light. Tetra- and penta-BDEs were the major degraded products of BDE-209. Optimum conditions for photocatalytical degradation of BDE-209 was found to be pH 12 (93% ± 1%), at least 5 mg/L (93 ± 1.70%) of humic acid and in the form of anatase/rutile TiO_2 (82% ± 3%). Incomplete removal of PBDEs by water treatment plants and point-source contamination may lead to their discharge into water bodies and ultimately into soils. Consequently, the second part of the project was phytoremediation of PBDEs. Uptake of BDE-209 by rice cultivars, namely Fengmeizhan, Hefengzhan and Guangyinzhan, and common reed were examined by 60-day cultivation in sterilized BDE-209 spiked soil. Hefengzhan possessed the greatest ability in the removal and accumulation of BDE-209 among the three cultivars, especially when associated with *Glomus intraradices*, at pH 7. A series of plant-contamination sorption analyses were also employed for pathway studies of PBDEs uptake by rice. A partition-limited model was applied for describing and estimating the uptake of BDE-209 by rice roots. The average quasi-equilibrium factors (α_{pt}) of BDE-47, -99 and -209 in root uptake were 1.44×10^{-3}, 0.966×10^{-3} and 0.115×10^{-3} in sand (< 1), implying a non-equilibrium state of the movement of molecules and a dominant passive transport uptake. From the result of sorption analysis of dead and fresh roots, the apoplastic pathway likely dominated the transport of PBDEs into root cells. These results provide essential information on the uptake mechanism of PBDEs into plants. Based on the results from photocatalysis and phytoremediation, a combined photocatalysis (TiO_2 and visible light) and constructed wetland system (*Oryza sativa* (Hefengzhan) and *Phragmites australis* (common reed) was set up for comparing PBDEs removal efficiencies. The removal percentages of BDE-209 in the combined system were

found to be promoted when compared to the individual systems, which could be explained by enhanced biodegradability of PBDEs in photocatalysis. Therefore, the proposed advanced wastewater treatment technology (combined photocatalysis and constructed wetland systems) might help to degrade and eliminate BDE-209 in the wastewater, and thus reduce the risks of marine contamination by discharging these incompletely or partially treated wastewaters containing PBDEs.

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