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Effect of three kinds of surfactants and β-cyclodextrin on the phytoremediation of BDE-209 contaminated sediment

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Abstract. Plant-accelerated removal of BDE-209 from sediment by aquatic macrophyte *Scirpus validus* Vahl in the presence of a cationic-surfactant (CTAB), an anionic-surfactant (SDS), a nonionic-surfactant (Tween 80) and β-cyclodextrin (β-CD) at the concentrations ranged from 300 mg/kg to 1000 mg/kg were investigated. Significantly negative effect were not observed for the growth of *S. validus* in terms of plant height and stem diatemeter, which indicated that it is preferable for CTAB, SDS, Tween 80 and β-cyclodextrin to be utilized as the BDE-209 phytoremediation amendment. Furthermore, CTAB, SDS and Tween 80 in the certain concentrations significantly enhanced the phytoremediation efficiencies and 11.78-19.33% of increase in BDE-209 removal rates was obtained. Significantly enhance of BDE-209 phytoremediation efficiency was not observed in the added β-CD concentration ranges. Results obtained from this study provided some insight with regard to the feasibility of phytoremediation for BDE-209 contaminated sediments with addition of suitable solubilizers, especially Tween 80.

1. Introduction

Soil or sediment contamination with organic pollutants(OPs) has increasingly become a serious global environmental issue in recent years[1]. A large number of studies have shown that the slow release of OPs such as polycyclic aromatic hydrocarbons(PAHs), polychlorinated biphenyl s(PCBs) and polybrominated diphenyl ethers (PBDEs) in the aqueous phase resulted in their limited bioavailability, thereby reducing the degradation rate of these pollutants in the soil[2]. The use of solubilizers capable of increasing the solubility of OPs for contaminated soil or sediment is a very promising remediation technique that increases the apparent solubility of OPs in soil or sedimentary facies[3].

The technology of solubilizer enhanced phytoremediation is widely used in phytoremediation of OPs contaminated soil or sediment, and the two kinds of solubilizers, surfactants and cyclodextrins, are widely used in the OPs remediation application [4]. The main principle of this technique is that surfactant can desorb the OPs adsorbed on the soil, solubilize it in the soil solution, improve the plant and rhizosphere microbial availability of OPs and promote the OPs degradation through the rhizosphere microorganisms, thereby improving the bioremediation efficiency[5]. Cyclodextrins are cyclic, no reducing malt oligosaccharides produced from the enzymatic degradation of starch and related compounds by certain bacteria that contain the cyclodextrin glycosyltransferases [6].

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Cyclodextrins have been used in environmental applications to improve the remediation of contaminated soil and groundwater[7].

Decabromodiphenyl ether (BDE-209) is a member of polybrominated diphenyl ethers (PBDEs), which are becoming increasingly prevalent in the environment[8]. The ubiquitous distribution of PBDEs in the environment as well as their potential risk to animals and humans has become an increasing concern [9]. Therefore, it is necessary to remove this pollutant from the environment.

In the present research, the potential and effectiveness of solubilizers-enhanced phytoremediation of BDE-209 contaminated sediment in the presence of three typical kinds of surfactants, cationic-surfactant (cetyltrimethyl ammonium bromide, CTAB), anionic-surfactant (sodium dodecyl sulfate,SDS), nonionic-surfactant (Tween80) and β-cyclodextrin(β-CD), was investigated. Results obtained from this study are expected to provide some insight with regard to the feasibility of phytoremediation for PBDEs contaminated sediment with solubilizers and to provide a theoretical basis for the development of practical techniques for efficient phytoremediation of PBDEs contaminated sediment.

2. Materials and methods

2.1. Chemicals

Decabromodiphenyl ether (BDE-209, $C_{12}OBr_{10}$) was purchased from Alfa Aesar (Johnson Matthey, USA) with 99% chemical purity (GC). Dichloromethane and n-hexane of HPLC grade were used in the extraction and cleanup. CTAB, SDS, Tween80 and β-cyclodextrin used were of analytical grade.

2.2. Plant materials

Scirpus validus Vahl (*S. validus*) used in the experiment were collected from the Tangxun Lake in Wuhan, Hubei Province, China (30°29′04.61″ N, 114°21′30.33″ E). Plants with initial height of about 60 cm were cultured in the artificial pond for 10 days before experiments.

2.3. Sediments

Sediments without detectable BDE-209 were collected from the 0-20 cm surface sediments at a local lake in Wuhan, Hubei province, China. Physical and chemical properties of sediment were: organic matter, 10.23%; pH, 5.88; total nitrogen, 0.48mg/g; total phosphorus, 0.27 mg/g.

2.4. Phytoremediation treatments setup

15 kg of contaminated dry sediments (BDE-209 at approximately 2 mg kg^{-1}) were loosely packed into cultivation box and then equilibrated for 7 days before the addition of water. The top of each pot was covered to minimize the evaporation and photolysis of BDE-209 in sediments. Each treatment had triplicates and *S. validus* with initial plant height of about 60 cm were transplanted into each box. Tap water was then added and kept at the level 4 cm above the sediment surface. The exposure experiment was carried out in natural conditions for 180 days. Five treatments were established and displayed in Fig.1.

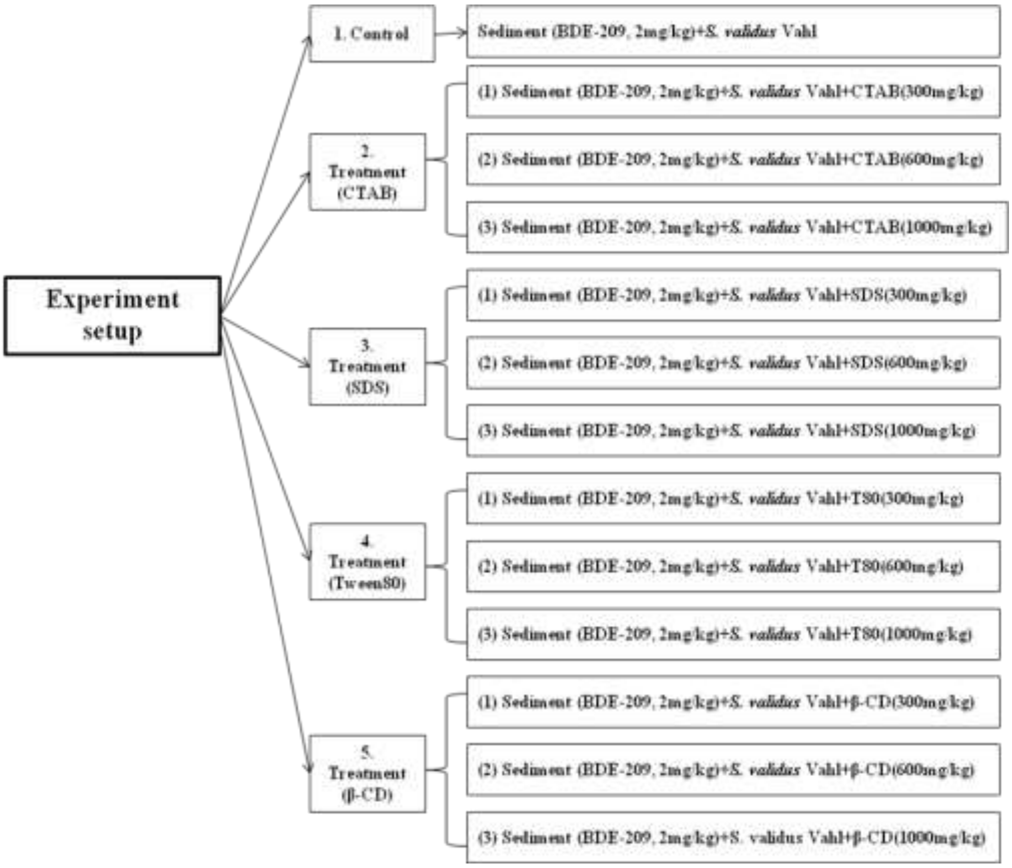

Fig.1 Phytoremediation experiment setup

2.5. Sample preparation

Sediments were collected using a sampling spade. Rhizosphere sediment samples were collected by vigorously shaking and rolling the roots to remove residual sediments. After collection, the sediment samples were oven-dried, ground, homogenized, passed through a 80-mm standard sieve, and then stored in glass containers at -20 °C until analysis.

2.6. BDE-209 analysis

2.6.1. BDE-209 extraction and cleanup. Three replicate sediment samples (dw, 3 g) were extracted with 30 mL of n-hexane/dichloromethane (1:1, v: v) for 30 min by ultrasonic extraction. This extraction was performed for three times. The combined 90 mL of extract was deeply filtrated by glass microfiber Filters (GF/C, whatman) and then concentrated to 3 mL by rotary evaporation. The extracts were then partitioned with concentrated H_2SO_4 to remove proteins, lipids, and atrace water. After centrifugation (3000 rpm, 5 min), the organic phase was collected and transferred. The acidic phase was re-extracted with 1 mL of n-hexane and the extracts were also collected and combined with the former collection.

2.6.2. BDE-209 analysis. Quantitative analysis of BDE-209 was performed by an Agilent 6890 gas chromatograph (GC) equipped with a ^{63}Ni-electron capture detector (GC-μECD). DB-5 HT column (15 m Length × 0.25 mm I.D. × 0.10 μm Film, J & W Scientific, Folsom, CA) was selected as the analytical column. The GC-ECD was operated as follows: injection port, 280°C with splitless mode; Ultrahigh nitrogen (99.99%) at a constant flow rate of 1.5 mL min^{-1} was used as carrier gas. Detector temperature was 320 °C. The flow rate of make-up gas was 60 mL min^{-1}. The oven program was set for: 2 min at 110 °C, ramp at 15 °C/min to 315°C (10-min hold). The extracted sample (1 μL) was injected into the DB-5 HT column.

2.7. Statistical analysis.
One-way analysis of variance (ANOVA) was used to examine the significance in plant growth (plant height and stem diameter) and BDE-209 dissipation rates among different treatment. Differences between two parameters were compared by independent-samples t-test (two-tailed). All data was presented as mean± SD (n≥3) and statistical analyses were performed by using GraphPad Prism 5.0.

3. Results and discussions

3.1. Effect of Surfactants and β-cyclodextrin on the growth of S. validus
As for the growth, *S. validus* grew well in the process of entire experiment. Compared to the control, *S. validus* in the treatments of CTAB, SDS, Tween80 and β-cyclodextrin in the range of 300-1000 mg/kg showed no significant poisoning symptom in terms of plant height (p>0.05) and stem diameter (p>0.05) (Table 1). The result of growth indicated that the concentration range of CATB, SDS, Tween 80 and β-CD is suitable for use as a synergist for phytoremediation.

Table 1. The growth of *S. validus* Vahl in the presence of CATB, SDS, Tween80 and β-cyclodextrin

Treatment	Concentration	Plant height (cm)	Stem diameter (mm)
Control	-	205.1±11.2	13.3±0.1
CTAB	300 mg/kg	194.2±12.2	13.0±0.8
	600 mg/kg	191.5±12.5	13.2±0.9
	1000 mg/kg	187.1±10.9	12.3±0.6
SDS	300 mg/kg	196.1±12.9	13.5±0.5
	600 mg/kg	196.5±7.9	12.8±0.8
	1000 mg/kg	198.7±6.2	12.9±0.7
Tween 80	300 mg/kg	204.2±7.9	12.9±1.2
	600 mg/kg	208.5±5.5	13.5±0.8
	1000 mg/kg	202.0±8.0	12.8±0.6
β-CD	300 mg/kg	201.8±7.7	13.4±0.6
	600 mg/kg	205.4±8.1	13.0±0.8
	1000 mg/kg	208.2±7.0	13.8±0.4

3.2. Effect of surfactants and β-cyclodextrin on the phytoremediation
Surfactants have the ability to increase aqueous concentrations of low solubility compounds enhancing their availability to microorganisms[8]. Effect of different concentrations of CTAB on the phytoremediation rate of BDE-209 was displayed in Fig.2a. With the increase of CTAB concentration in sediments, the phytoremediation effiency increased. After 180 days, the concentration of BDE-209 in the control sediments was reduced by 34.93% and CTAB of 300mg/kg slightly increased the degradation rate of BDE-209(2.85%), but the enhanced efficiency was not significant(p>0.05). CTAB with concentration of 600-1000mg/kg significantly enhanced the phytoremediation rate of BDE-209 in sediment, which were respectively 6.93% and 11.78% higher than the control sediments (p<0.05). The above results indicated that cationic-surfactant (CTAB) in the suitable concentration of 600 to 1000 mg/kg can significantly promoted the removal of BDE-209 in the phytoremediation.
The effect of different concentrations of SDS on the removal rate of BDE-209 was displayed in Fig.2b. The phytoremediation effiency increased as the increase of SDS concentration added. The BDE-209 degradation rate was increased by 4.52% in the presence of SDS with concentration of 300mg/kg, but the enhanced efficiency was not significant (p>0.05). CTAB with concentration of 600-1000mg/kg significantly enhanced the phytoremediation rate of BDE-209 in sediment, which were respectively

11.03% and 14.25% higher than the control sediments. This indicated that anionic-surfactant (SDS) in the suitable concentration of 600 to 1000 mg/kg can significantly promoted the removal of BDE-209 in the phytoremediation.

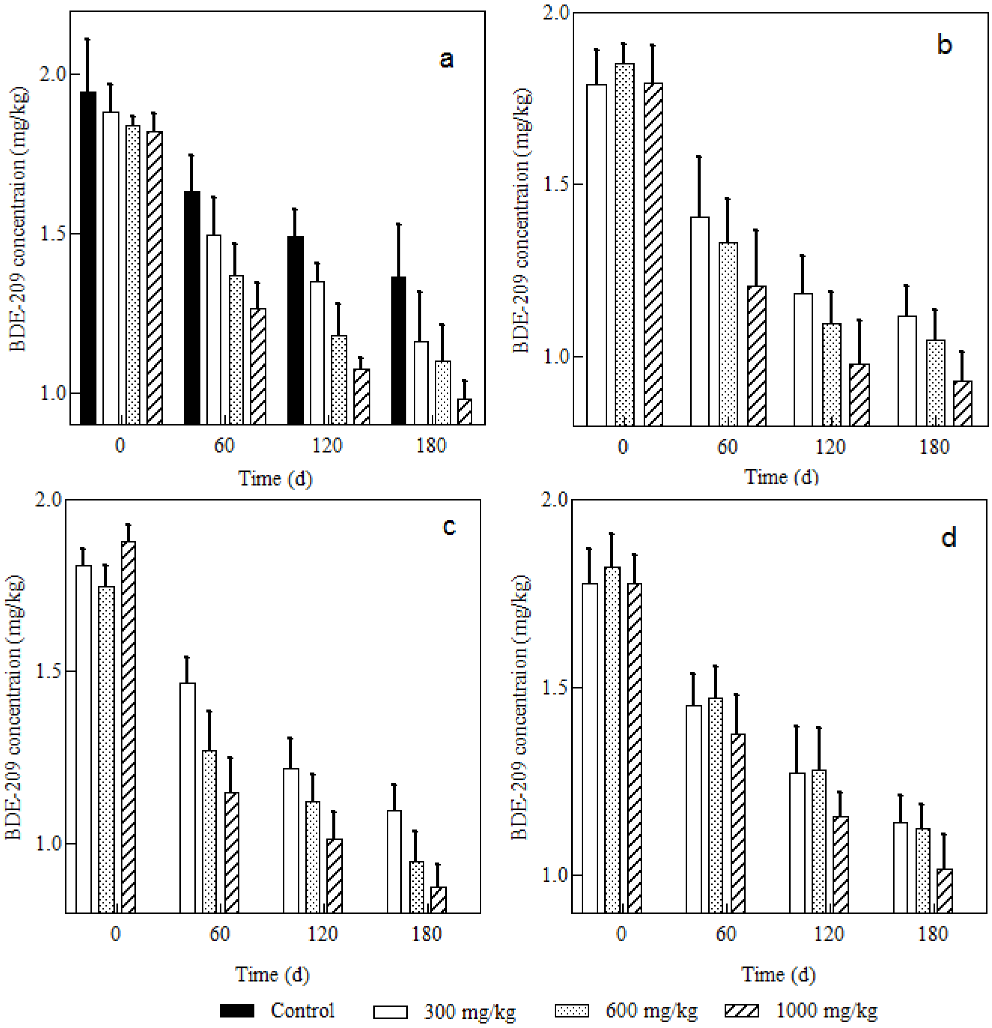

Fig.2 Changs of residual BDE-209 concentrations in sediment as a function of the added CTAB(a), SDS(b), Tween80(c) and β-cyclodextrin (d) concentrations(Mean±SD)

In the three typical kinds of surfactants, nonionic-surfactant (Tween 80) had the greatest enhanced effect on the removal of BDE-209 in the phytoremediation and was displayed in Fig.2c. With the increase of Tween 80 concentration in sediments, the phytoremediation effiency increased. When the concentration of Tween 80 was 300mg/kg, the degradation rate of BDE-209 increased by 7.37%, the enhanced efficiency was significant (p>0.05). Tween 80 with concentration of 600-1000mg/kg significantly enhanced the phytoremediation rate of BDE-209 in sediment, which were respectively 14.81% and 19.33% higher than the control sediments. Nonionic surfactant(Tween 80) can increase the solubility of hydrophobic organic compounds such as BDE-209 may due to the formation of micelles in the solution[8].The above results indicated that nonionic-surfactant (Tween 80) in the suitable concentration of 600 to 1000 mg/kg can significantly promoted the removal of BDE-209 in the phytoremediation.

Effects of different concentrations of β-CD on the removal rate of BDE-209 were presented in Fig.2d. When the concentration of β-CD was 300mg/kg, the degradation rate of BDE-209 was increased by 1.03%-7.78% in the presence of β-CD with concentration of 300-1000mg/kg, although the removal rate was further improved, but there was no significant difference ($p > 0.05$). The above results indicated that β-cyclodextrin 300-1000 mg/kg did not improve the efficiency of BDE-209 in sediments.

4. Conclusion

The present study demonstrated the use of surfactants and β-cyclodextrin for enhanced phytoremediation of BDE-209 contaminated sediment. Growth results indicated that CTAB, SDS, Tween 80 and β-cyclodextrin can be utilized as the BDE-209 phytoremediation amendment. Among all, CTAB, SDS, Tween 80 significantly enhanced the phytoremediation efficiencies, especially Tween 80, 11.78-19.33% of increase in BDE-209 removal rates was obtained. β-cyclodextrin at the concentration range of 300-1000mg/kg did not significantly enhance the BDE-209 phytoremediation efficiency in the added concentration ranges and was not the suitable solubilizers for phytoremediation.

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