

Assessment of PCB-contaminated soil pretreatment remediation by hydroxypropyl- β -cyclodextrin (HP- β -CD)

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Abstract: The present study thoroughly evaluated the effect of hydroxypropyl- β -cyclodextrin (HP- β -CD) on eluting of Aroclor1242 (one kind of PCBs (polychlorinated biphenyls)) from contaminated soil. The factors that might affect eluting efficiency including HP- β -CD concentration, contact time, eluting cycles, temperature, pH, salt content, humic acid, and ultrasonic were all tested to evaluate the PCBs eluting efficiency by HP- β -CD. Results indicated that Aroclor1242 can be eluted effectively from soil by HP- β -CD solution, 81% of Aroclor1242 was eluted from soil by 50 g/L of HP- β -CD solution after three cycles eluting, and the eluting efficiency was improved by increasing temperature and with ultrasonic. Furthermore, it was shown that the humic acid and extreme acidic/alkaline condition both decreased the eluting efficiency. In addition, column eluting experiment was conducted to simulate the practical HP- β -CD eluting of Aroclor1242 from contaminated soil, 18% of the PCBs was eluted from the soil column by 10 g/L of HP- β -CD. Overall, the results indicated the high extract power of HP- β -CD toward PCBs polluted soil and potential use of HP- β -CD for in situ remediation of PCBs contaminated soils.

Introduction

Soil contamination is posing major challenges to our environment. China environmental research centers found that 16.1% of land is contaminated with various organic and inorganic contaminants and is considered more extensive than USA and UK (Fava et al. 2015, Fijałkowski et al. 2011, Mackay et al. 1992). An indication shows that about 36 million hectares of agricultural land have been polluted by organics such as petrochemicals, pesticides, and polycyclic aromatic hydrocarbons (PAHs), more than 20 million hectares of soils are potentially contaminated by heavy metals such as cadmium and lead (Mackay et al. 2008, Tong 2001). Relevant organizations have initiated actions to control land pollution. Specifically, polychlorinated biphenyl (PCB), one kind of typical persistent organic pollutants (POPs), is a commercial admixture based on biphenyl ring and is a mixture system of chlorine biphenyl homogenchloridized by metallic catalysis in high temperature. Due to its stable physical and chemical characteristics, PCB is widely used in industrial production, in transformer oil, anti-friction material, plastic, and resin fields (Billingsley et al. 2002, Burke et al. 1978, Tajik et al. 2014, Zheng et al. 2004). On the other hand, the large quantity plant use and unconscious release of POPs led to their wide distribution around the world, which brought pollution to our environment. Soil environment can continuously accept any

potential released PCBs (Hutzinger 1974, Macherzyński et al. 2012, Sawhney 1988). Although the use of PCBs is banned worldwide under the Stockholm Convention, these chemicals are still commonly found in soil due to their long persistence and can still pose long term ecological risk (Szymański et al. 2016). Thus, research on how to remove PCBs from soil has great significance.

There are emerging technologies to treat PCBs polluted soils, including physical, chemical, biological techniques or combination. For example, process efficiency of soil eluting technique has a dependency on bioavailability and contaminants contents; while traditional “Pump and Treat” technique (Palmer et al. 1992, Truex 2017) is used to treat the soil that contaminated with semi-volatile organic compounds (SVOCs) (Kimbrough et al. 2010), petroleum and fuel residuals, heavy metals, PCBs, PAHs, and pesticides (Rosińska et al. 2011). For example, surfactants solution was applied in washing contaminated soil (West 1992), however, the potential impact of residual flushing agents on microbial processes is a question of concern, and it has been well known that surfactant itself might bring in secondary pollution and result in subsequent difficulties in soil remediation (Cserhádi et al. 2002, Zhou et al. 1998). Thus, a more environmental friendly and more effective pretreatment method is needed to remediate PCBs contaminated soil. An interesting alternative are cyclodextrins. The most notable feature of cyclodextrins is their

ability to form inclusion complexes (host–guest complexes) with a very wide range of compounds by a phenomenon of molecular complexation. Inclusion in cyclodextrins exerts a profound effect on the solubility enhancement of highly insoluble guests. However, underivatized β -CD has a very low solubility of 18 g/L. To enhance its solubility, the -OH group of the cyclodextrin molecule is usually modified, and hydroxypropyl- β -cyclodextrin (HP- β -CD) in particular, is known to be less toxic to soil microorganisms compared to other chemical agents such as strong acids, chelating agents and surfactants (Jiradecha 2000). Toxicological studies by Gould indicate that HP- β -CD is toxicologically safe, with clear no effect dose levels and reversible histopathological and biochemical changes (Gould 2005). HP- β -CD is a derivative of CDs ($(C_9H_{16}O_6)_n$), which is extremely soluble in water with a solubility of $4.55 \cdot 10^{-1}$ mol/L, it has a doughnut-shaped structure with a relatively hydrophilic exterior and relatively hydrophobic interior hole, so low-polarity organic substances with a proper size and shape can form inclusion complexes with CDs (Fenyvesi et al. 1996), improving its solubility in a significant way. The lower surface activity of HP- β -CD makes it a promising “sugar flushing” method for the pretreatment of PCBs contaminated soil remediation (Fava et al. 2002). Most work performed so far has been focused on PAHs, and there are several reports on PCBs washing by cyclodextrin solution for soil remediation (Fenyvesi et al. 2011, 2015, Leitgib et al. 2008, Liu et al. 2017, McCray et al. 2010, Molnár et al. 2009). For example, McCray et al. (2010) investigated the potential of HP- β -CD to reduce the sorption and to enhance the transport of several low-polarity organic compounds (McCray et al. 2010). The retardation of organic compounds such as anthracene, naphthalene, and trichlorobiphenyl was significantly reduced in the presence of cyclodextrin (Cserháti et al. 2002, West et al. 1992). Wang et al. (1993) studied the promotion of HP- β -CD on the transport of weakly polar organic pollutants in soil (Wang et al. 1993). Cyclodextrin solution was used to repair soil contaminated with multi-component organic compounds. It was shown that the solubility of cyclodextrin solution in water increased 100 to 20,000 times for all pollutants in the soil (McCray et al. 2015). HP- β -CD aqueous solution can significantly promote the transport of weakly polar organic pollutants in soils (Brusseu et al. 1994). Some other experiments showed that the elution efficiency of HP- β -CD to pentachlorophenol in soil is 3.5 times that of water elution (Hanna et al. 2005, Peng et al. 2014). Although many works have indicated that cyclodextrins could be used as alternatives to surfactants in enhancing the desorption and degradation of recalcitrant organic contaminants in soil, there are few reports

on a comprehensive and further understanding of HP- β -CD eluting on PCBs remediation. In our earlier fundamental research (Liu et al. 2008), we have found out that the efficiency of washing could be increased by increasing the concentration of HP- β -CD and the number of washing respectively, but a thorough research considering all potential influencing factors needs to be clarified.

Therefore, the aim of this work was to investigate the effect of HP- β -CD on PCBs desorption from soil, and to evaluate influencing factors including HP- β -CD concentrations, contact time, repeated washing, pH, temperature, humid acid concentration, salt substance, and ultrasound aided mixing. Columns washing experiments were also conducted to simulate the practical washing process. Results will provide a comprehensive understanding of the pretreatment of PCBs from soil by HP- β -CD for further practical remediation guidance.

Material and methods

Soil sampling preparation

The PCBs contaminated soil was collected from a transformer oil contaminated site in the city of Hangzhou, Zhejiang Province, China (120.2E, 30.3N). The soil sample was collected from the 0–20 cm layer and air-dried to grind through a 2 mm screen to remove coarse fragments. Selected properties of the soil are summarized in Table 1. About 40% is clay soil and the soil type was categorized into typical clay loam. Soil pH was measured in a mixture of soil and water (1:1 by weight) with a glass pH electrode.

Experimental design

In the present study batch scale experiments and column eluting experiment were conducted:

Batch scale experiments

Experiments were performed under different conditions, including different HP- β -CD concentrations at 1 g/L, 5 g/L, 10 g/L, 20 g/L and 50 g/L, different contact time at 15 min, 1 h, 2 h, 5 h, and 8 h, different salt type (calcium chloride and sodium acetate), humid acid addition, ultrasound, and different temperature at 20°C and 40°C.

Under each eluting condition, exactly 1 g of soil powder was placed into each of the 40 mL Pyrex glass tubes, then filled with 20 mL of HP- β -CD solution to form different concentrations (1 g/L, 5 g/L, 10 g/L, 20 g/L and 50 g/L, distilled water was used as blank sample), and then sealed with Teflon-lined caps and placed in a mechanical rotary mixer at 20°C and mixed thoroughly. The samples were then centrifuged

Table 1. Soil Characteristics

Soil sieving mm	0.5–0.05 mm (sand)	0.05–0.01 mm (coarse silt)	0.01–0.005 mm (fine silt)	0.005–0.001 mm (course clay)	<0.001 mm (clay)
Mass percent (%)	11.87	33.10	13.71	20.56	20.76
Mass (g/kg)	118.7	331.0	137.1	205.6	207.6
pH	6.5–7.2				
Moisture content (%)	12				

for 30 min at 10000 rpm/min to separate the soil and liquid phase. 2 mL of solution from the liquid phase was withdrawn from each tube and placed into another clean Pytex glass tube, followed by the addition of 4 mL of hexane on the top. Next, the sample tubes were sealed with Teflon-lined caps to prevent any volatilization, and then the tubes were shaken in the mechanical rotary mixer at 20°C for 10 min and the samples were let sit for a while until a clear divided layer could be seen. The extracted phase was diluted properly to 0.5 mL immediately and 3 μL internal standard of 1,2,4-trichlorobenzene was added in preparation for GC detection.

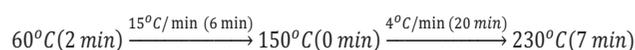
Column washing experiment

Three stainless steel columns with 38 mm outside diameter, 35 mm inside diameter, and 30 cm height were designed. The bottom of the column was placed with Teflon gasket with openings, and a layer of cotton wool pads was placed on the top to prevent soil leaking, then the glass beads (3mm diameter), and mixture of quartz sand and soil were sequentially put on the top of the cotton wool pads, forming the filter layer, while on the most top layer, relatively larger size stone and glass bead were placed in order to prevent the soil from floating.

In column eluting experiment, different washing solutions with 0 g/L, 5 g/L, 10 g/L HP-β-CD were pumped into the three columns, at a flow rate of 6 mL/min. Under each condition, 8 ml eluent was collected every 10 min in centrifugal tube, for further n-hexane extraction, centrifugation, and gas chromatography detection. Similarly, the extracted phase was diluted properly to 0.5 mL immediately and 3 μL internal standard 1,2,4-trichlorobenzene was added, samples were prepared for GC analyzation.

GC analysis and calculations

The extracted aqueous samples were analyzed by GC with ECD detector. Analysis and calculation method of Aroclor1242 was based on the previous report (Frame et al. 1996). The chromatogram column used in the study was DB-1 glass capillary column, the temperatures for both detector and injector were kept at 300°C. The carrier gas for ECD was nitrogen, and the flows were set as 2.2 mL/min and 25 mL/min for carrier gas and supplemental gas, respectively. The running procedure was as follows:



The concentration of each peak (PCBs homology) of Aroclor 1242 was determined by the weight fraction of each peak (PCBs homology) in the standard Aroclor 1242 reported by Frame (Frame et al. 1996). The sum of the concentration of each peak (PCBs homology) became the total concentration of Aroclor 1242 in the sample.

The formula is as follows (Frame et al. 1996):

$$\sum[X]_s = \sum[X]_{std} \frac{[IS]_s A_{ISstd} A_{Xs}}{[IS]_{std} A_{ISs} A_{Xstd}}$$

In the experiment, the concentration of the internal standard and the sample is the same:

$$[IS]_s = [IS]_{std}$$

$$[X]_{std} = [total\ PCB]_{std} \times wt\%$$

Therefore, the equation can be simplified to:

$$\sum[X]_s = [total\ PCB]_{std} \sum wt\% \frac{A_{ISstd} A_{Xs}}{A_{ISs} A_{Xstd}}$$

- [X]_s – Concentration of single PCB chromatographic peak of Aroclor1242 to be measured;
- [X]_{std} – The concentration of a single PCB peak in the standard sample;
- [IS]_s – Concentration of internal standard in Aroclor1242 to be measured;
- [IS]_{std} – Concentration of internal standard in standard samples;
- A_{Xs} – Single PCB chromatographic peak area to be measured in Aroclor1242;
- A_{Xstd} – Corresponding to a single PCB peak area in the standard;
- AIS_s – Chromatographic peak area of internal standard for Aroclor1242;
- AIS_{std} – Area of internal standard of standard sample;
- [total PCB]_{std} – Total concentration of certified reference material;
- wt% – The weight fraction of peak X in Aroclor1242 is here, using the data reported by Frame;

Results and discussion

Characteristics of original soil

The background PCBs concentration in soil was determined by Soxhlet Extraction method (U.S. EPA method 3541). In Soxhlet extraction method, 200 mL of acetone/hexane (1:1) solution was added into 10 g polluted soil, heating and extracting lasted for 2 hours, then cupric sulfate anhydrous was added into the extracted liquid to remove any water. The supernatant was extracted and diluted for GC-ECD detection.

The results of chromatographic analysis showed that the gas chromatogram peak of original sample is corresponding to that of Aroclor1242 standard sample (Figure 1). Thus, the soil was confirmed to be polluted with Aroclor 1242. The background concentration of the soil was 6.60 mg PCBs/g soil.

Factors that affect PCBs eluting

Effect of HP-β-CD concentration

In order to examine the optimal concentration of HP-β-CD on PCBs eluting, we selected 1 g/L, 5 g/L, 10 g/L, 20 g/L, and 50 g/L as concentration series. The experimental results are shown in Figure 2a. The results show that removal of PCBs was increased along with the increase of the HP-β-CD concentration, the GC peak profiles for Aroclor1242 in Figure 3 also showed the same trend. After desorption from the soil, Aroclor1242 entered the cavity of HP-β-CD and achieved a stable condition. The complexes were extremely soluble in water due to the high solubility characteristic of HP-β-CD in water, thus the mobility of PCBs from soil was promoted and it was transferred into liquid phase for further disposal. There were 0.8%, 10%, 15%, 26%, 58% of the PCBs eluted from soil by 1 g/L, 5 g/L, 10 g/L, 20 g/L, and 50 g/L, respectively. Meanwhile, we increase the value of the volume but kept

the concentration of HP- β -CD constant, results were shown in Figure 2b, the molar number of HP- β -CD molecule was constant but the elution amount was observed to increase. This might be due to a different arrangement of HP- β -CD molecules in aqueous solution. When the volume increases, HP- β -CD molecules become dispersed and PCBs have a greater chance to be trapped by arrayed HP- β -CD molecules and form inclusions (Figure 4). The maximum elution capacity of 60 mL of 50 g/L HP- β -CD solution was 5.14 mg/g higher than that of 20 mL of 5 g/L HP- β -CD solution at the lowest point, and the elution rate was increased by 77.5%. It is clearly demonstrated that the simultaneous increase of volume and concentration can greatly improve the eluting efficiency. The mechanism of removing PCBs by HP- β -CD from soil is the complex reaction of HP- β -CD with PCBs. HP- β -CD has the potential to increase the aqueous solubility of PCBs, and the formation of complex depends on two aspects: first, the

molecular size must be matched with HP- β -CD cavity size; second, there must be certain acting force between CDs and PCBs molecules to ensure stability of complex. Actually, the cavity of HP- β -CD is not empty but full-filled with water, so the complex is a spontaneous process of replacement of non-polarity molecular and non-polarity cavity. Aroclor 1242 is a commercial mixture of PCBs homologues, we can predict several binding forms of PCBs and HP- β -CD, as shown in Figure 4. The smaller PCBs homologues can enter the HP- β -CD cavity, HP- β -CD and Aroclor1242 molecular may complex like a cage or pipe. While the bigger molecules containing substitutions like 2,2',3,5',2,2',4,5' can be trapped by two HP- β -CD molecules or by self-aggregated molecules.

Effect of contact time

The 20 mL of the HP- β -CD solutions with 1 g/L, 10 g/L, 20 g/L and 50 g/L were put in the shaker for 15 min, 1 h, 2 h,

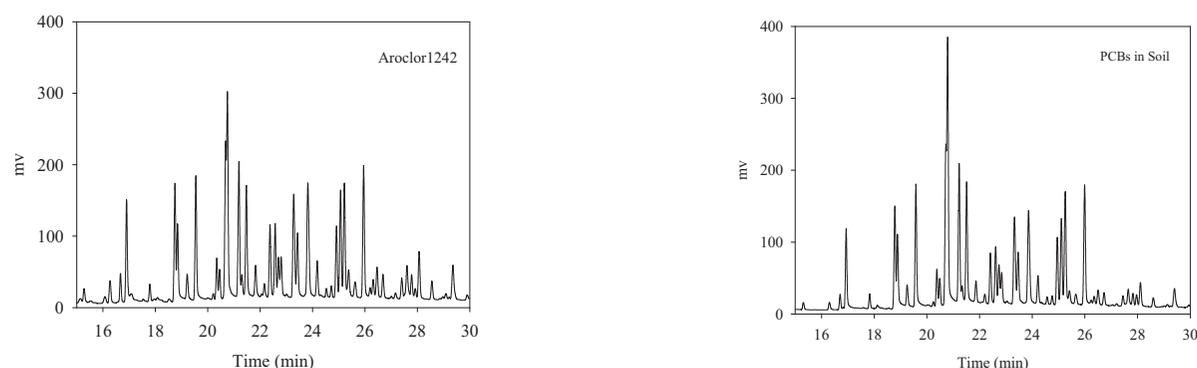


Fig. 1. Gas chromatogram of PCBs from standard and contaminated soil

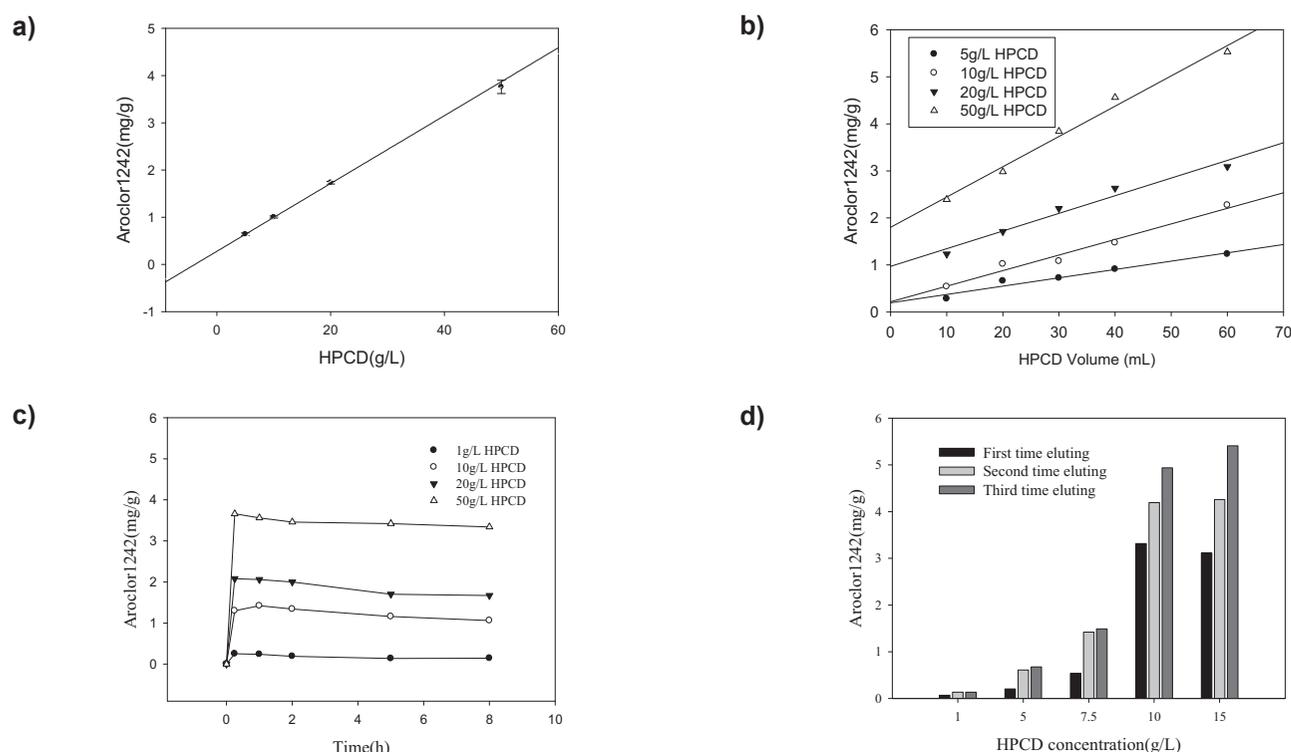


Fig. 2. a) Eluting of PCBs at different HP- β -CD concentrations; b) Eluting of PCBs at different HP- β -CD volumes; c) Effect of contact time on PCBs eluting; d) Effect of eluting cycles at different HP- β -CD concentrations

5 h and 8 h, respectively. As can be seen from Figure 2c, the eluted Aroclor 1242 increased rapidly to its maximum value within the first 15 min, and then remained almost constant, i.e., the inclusion reaction of HP- β -CD reached equilibrium within 15 min. Generally, the reaction time and the stirring time are prolonged to facilitate the formation of solid inclusions. For example, the fragrance and β -CD inclusion should be

stirred at room temperature for 2h (McCray et al. 2015), while the 4,4'-bipyridyl- β -CD inclusion reaction requires 8 h (Brusseau et al. 1994). But the results obtained in the study showed that as the reaction time increased, the eluting value decreased slightly, this might be attributed to the adsorption of cyclodextrin on soil particles or soil colloids or the degradation of microorganisms in soil.

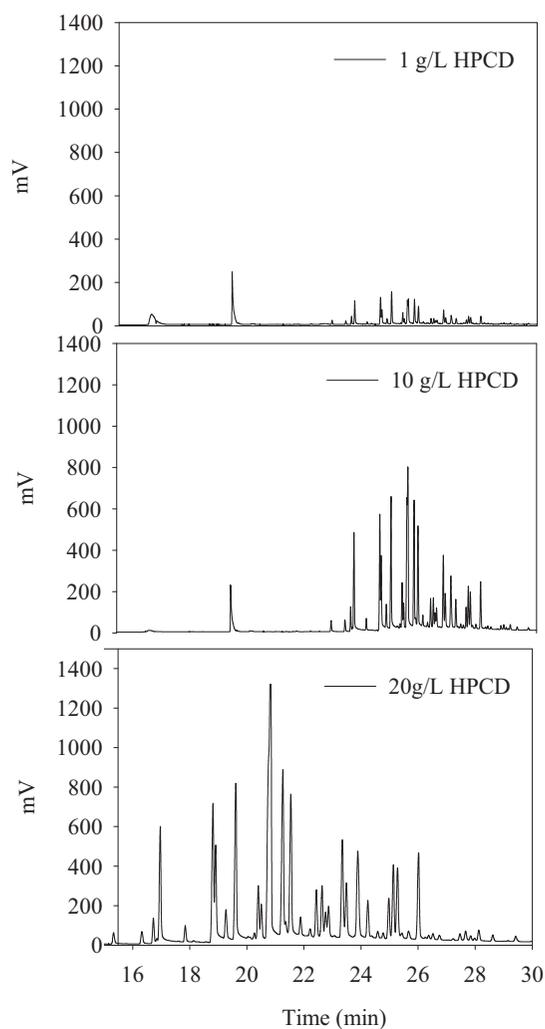


Fig. 3. Gas chromatogram at different HP- β -CD concentrations

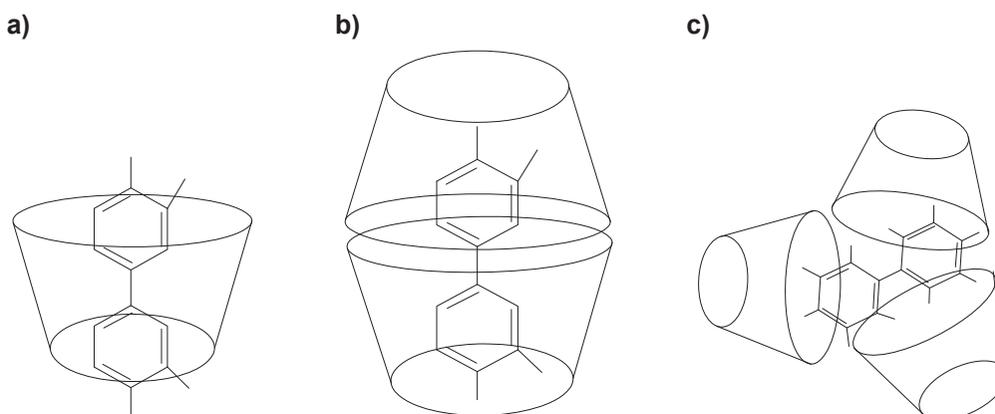


Fig. 4. Proposed inclusion forms of HP- β -CD – PCBs: a) cage model of single CD – PCBs; b) pipe model of two CD moleculars – PCBs; c) self aggregated CD moleculars – PCBs inclusions

Effect of eluting cycles

The effect of repeated eluting on the PCBs removal efficiency was evaluated here. Before each eluting cycle, the previous HP- β -CD eluents were centrifuged out, and new HP- β -CD solutions with the same volume and concentration were added. It can be seen from Figure 2d that after three cycles by 1 g/L, 5 g/L, 7.5 g/L, 10 g/L and 15 g/L of HP- β -CD solution, the eluting amount was almost doubled. Most PCBs were removed after triplicate washing, while additional increasing of washing times did not bring a significant increase of eluting efficiency. On contrary, increasing eluting cycles will increase the operation cost.

Previous studies also demonstrated that several cycles are needed to improve the extraction efficiency, for example, a field experiment of surfactant soil remediation in Alaska, USA showed that the concentration of PCBs in soil decreased from 300 mg/kg to 6 mg/kg, but 57 cycles of extraction were needed. The experimental data of pesticide extraction carried out by a company (Ecological Environmental Consulting, China) showed that the concentration of pesticide decreased by 98% after three cycles of extraction. The great contrast between

cycles is caused by soil properties, types and concentrations of pollutants.

Effect of salt content

It has been previously reported in the literature that self-polymers could form between cyclodextrins or cyclodextrin-guest inclusion complexes, and the aggregation could be promoted by organic salts (Loftsson et al. 2003). The aggregating molecules have better chance to entrap bigger PCBs molecules. Therefore, the effect of salt content was evaluated in the present study.

A series of 0 mol/L, 0.025 mol/L, 0.1 mol/L, and 0.5 mol/L of sodium acetate and calcium chloride solution was prepared in the 20 mL of HP- β -CD solution, respectively. The mixture system was well mixed in a shaker. As can be seen from Figure 5a and 5b, the results showed that both calcium chloride and sodium acetate had little effect on the inclusion reaction, which was not consistent with the previous report studying the effects of organic salts on the cyclodextrin solubilization of drugs (Loftsson et al. 2003).

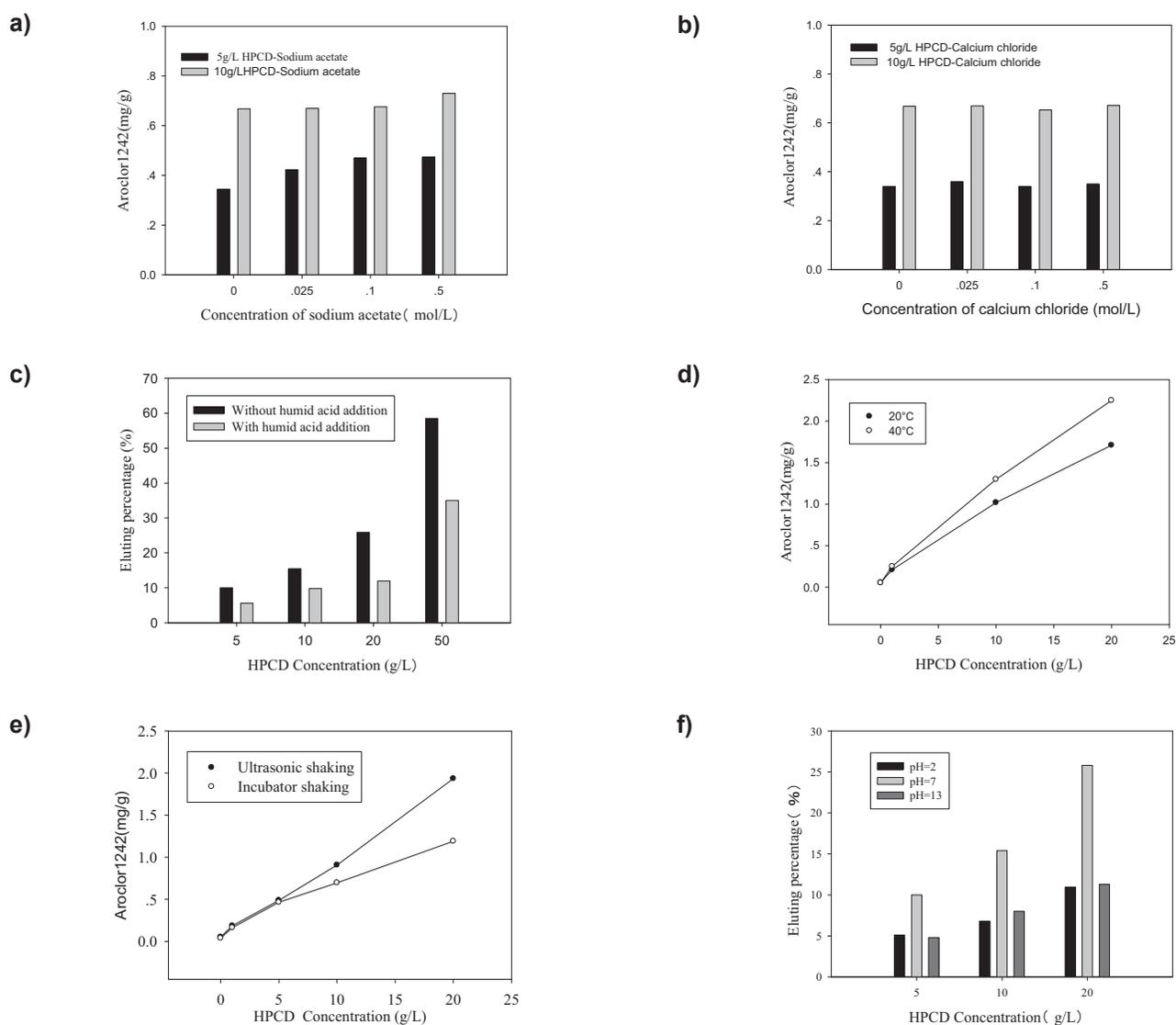


Fig. 5. a) The effect of organic salts on the complex reaction (sodium acetate); b) The effect of organic salts on the complex reaction (calcium chloride); c) The impact of humid acid addition on HPCD eluting; d) Effect of temperature on PCBs eluting; e) The impact of ultrasonic on PCBs eluting; f) Effect of pH on PCBs eluting

Effect of humid acid addition

The organic matter in the soil could have great impact on eluting efficiency because the PCBs could combine with hydrophobic group of humid acid, bring competition between adsorption of PCBs on humid acid substances and desorption of PCBs by HP- β -CD. In order to study the impact of organic matter on eluting efficiency, 50 mg/L of humid acid solution was prepared and mixed with soil to increase the organic matter content in the soil. After mixing and air-drying, the organic matter content of the soil was increased from 1.09% to 2.12%. As shown in Figure 5c, the removal of PCBs by HP- β -CD from humid acid amended soil decreased almost half as compared with the soil without humid acid. The results obtained here indicated that organic matter content in soil is an important factor that needs to be considered.

Effect of temperature, ultrasounds, and pH

The formation of the inclusions is expected to be affected by reaction temperature and stirring. The inclusion reaction can generally be carried out at room temperature, and some reactions are carried out at a certain temperature. The present experiment studied the effect of temperature on the eluting of PCBs from soil by HP- β -CD. Two temperatures of 20°C and 40°C were tested to evaluate the temperature effect. The results are shown in Figure 5d. It can be seen that together with the increase of the HP- β -CD concentration, the impact of temperature was more obvious. For example, at the HP- β -CD concentration less than 5 g/L, the eluting of PCBs did not change much with the increase of temperature. While at the HP- β -CD concentration greater than 10 g/L, the eluting efficiency was increased by the increase of the temperature from 20°C to 40°C. The results evidence that temperature could facilitate the inclusion formation and further promote desorption of PCBs from the soil.

In order to further investigate the effect of elution mode, the effect of ultrasonic oscillation elution was also studied in the present study. The ultrasonic impact on PCBs eluting from the soil at the frequency of 80 MHz at 20°C was studied. The results of the experiment shown in Figure 5e indicated that the trend was similar to the impact of temperature. The impact of ultrasonic was more obvious at higher HP- β -CD concentration. The ultrasonic oscillation promotes a better soil particles dispersion in the solution, and can accelerate desorption of PCBs from soil particles.

pH is another important factor affecting the removal efficiency of PCBs from soil. It is noted that there was no

obvious change in PCBs removal from soil without humid acid, however, there was clear impact of pH on washing efficiency from soil containing humid acid, at pH2 and pH13, the eluting percentage was apparently decreased, as shown in Figure 5f. This is because at lower pH, the polarity of humid acid was weakened and its hydrophobicity increased, in this way, the absorbance of PCBs on humid acid substances was enhanced, which led to the competition between adsorption of PCBs on humid acid substances and desorption of PCBs by HP- β -CD. Whereas, at higher pH, it was speculated that HP- β -CD hydroxylation occurred resulting in decreased eluting efficiency.

Column washing

In the column eluting experiment, distilled water, 5 g/L of HP- β -CD, and 10 g/L of HP- β -CD solution was flowed through the three columns, and samples were taken every 10 min with 60 mL at the same time. As can be seen in Figure 6a, with the increase of the HP- β -CD concentration, PCBs eluting was improved, which was constant with the batch-scale experiment. After the accumulated 3100 ml of HP- β -CD solution flowed through the column, a total 0.62%, 8.42%, and 18.3% of PCBs were eluted from the soil column by distilled water, 5 g/L HP- β -CD, and 10 g/L HP- β -CD, respectively.

Right after the column eluting experiment, the soil in the column was sectioned by every 2 cm from bottom to the surface. After air drying, the sectioned soil columns were extracted with acetone-n-hexane. Based on GC analysis, the profile of the residual amount of PCBs along the column is shown in Figure 6b. It can be seen that as the accumulated eluting solution flew into the column, the PCBs migrated from the surface layer to the bottom layer. The surface soil was in contact with fresh HP- β -CD solution and pushed the PCBs downward towards the bottom, and there was still a considerable amount of PCBs remaining in the soil column, which may be due to the fact that during the eluting process, the soil was agglomerated, resulting in the poor migration of PCBs in the soil.

Conclusion

A comprehensive investigation of Aroclor1242 polluted soil eluting by HP- β -CD has been conducted. The batch scale experiment demonstrated that HP- β -CD was capable of removing Aroclor1242 effectively from soil. The eluting efficiency could be improved by increasing the HP- β -CD concentration, increasing the number of the HP- β -CD

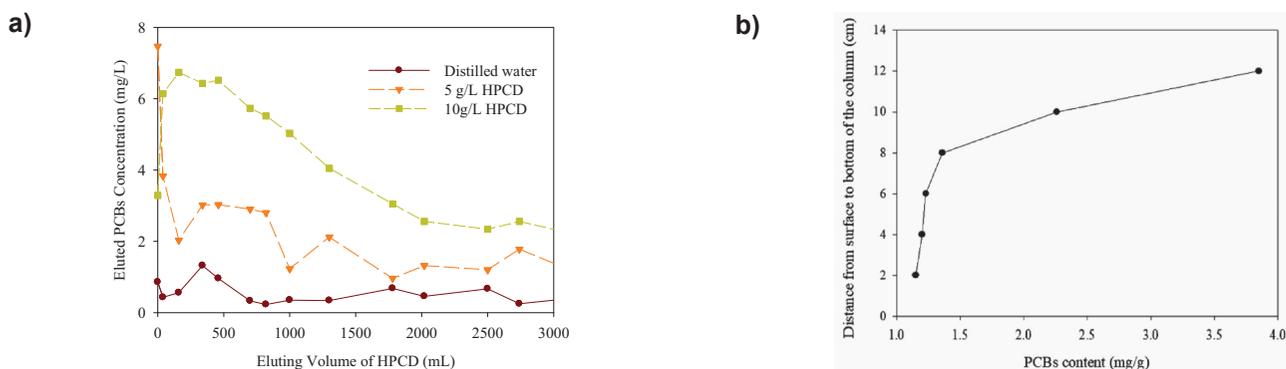


Fig. 6. a) Column eluting curve of PCBs from soil by HPCD; b) Mass distribution profiles of PCBs along the soil column depth

molecules in aqueous solution, increasing the eluting cycle, and by using ultrasonic oscillation. Other factors like pH, organic content and temperature would also affect eluting efficiency, which also needs to be considered in practical remediation.

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