



Electrokinetic movement of multiple chlorobenzenes in contaminated soils in the presence of β -cyclodextrin

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Abstract

This study investigated the electrokinetic (EK) behavior of multiple chlorobenzenes, including 1,2,3,4-tetrachlorobenzene (TeCB), 1,2,4,5-tetrachlorobenzene (*i*-TeCB), and 1,2,3-trichlorobenzene (TCB) in contaminated clayed soils. The effect of β -cyclodextrin (β -CD) on the EK removal of the chlorobenzenes was studied. The largest removal was obtained when $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer was used as anodic purging solution without β -CD. The removal efficiencies were related to the aqueous solubilities of chlorobenzenes. With the same cumulative electroosmotic flow, greater solubility led to higher removal efficiency. The addition of β -CD inhibited the EK removal efficiency of all chlorobenzenes. The inhibition increased with the increase of β -CD concentration. With the same β -CD concentration, the inhibition increased with the rise of electric potential. It was found that the inclusion compounds between β -CD and chlorobenzenes were less soluble than chlorobenzenes. The formation of the less soluble inclusion compounds reduced the aqueous solubility of chlorobenzenes and led to the partial immobilization of the chlorobenzenes that desorbed from soil. It was feasible to use the EK technology to remove chlorobenzenes in contaminated soils using water as the anodic flushing solution. The addition of β -CD was not recommended for the EK removal of chlorobenzenes.

Key words: chlorobenzenes; electrokinetic; soil remediation; β -cyclodextrin (β -CD)

Introduction

Chlorobenzenes are intermediates in the industrial production of drugs, scents, dyestuff, herbicides, and insecticides. They are also used as additives to oils, lubricants, and dye-carriers, and are employed in heat exchange systems and for dielectric insulation (Adrian and Görsch, 2002). Large quantities of chlorobenzenes have been released to the environment as a consequence of the wide use during the last decades (Lee and Fang, 1997). Chlorobenzenes are hydrophobic, persistent, and some of them are chronic to animals and humans (Lee and Fang, 1997). They are typically associated with soils through hydrophobic bonding. Sorbed chlorobenzenes may act as a long-term source of groundwater contamination. Therefore, considerable attention has been paid to the environmental behavior of chlorobenzenes (Cornelissen *et al.*, 1997; Kraaij and Connell, 1997; Pavlostathis and Prytula, 2000; Hulscher *et al.*, 2002). Traditional pump-and-treat technologies are often difficult to remove chlorobenzenes from the subsurface. Although alternative methods, such as bioremediation, vapor extraction, surfactant or solvent enhanced flushing, have been developed for the remediation of permeable

contaminated soils, it is still a challenge to restore the contaminated fine-grain soils.

Electrokinetics (EK) remediation is an emerging technology that can effectively remove pollutants from fine-grain soils (Acar and Alshawabkeh, 1993; Shapiro and Probstein, 1993; Virkutyte *et al.*, 2002). Briefly, with the application of electric field to the polluted site, pollutants will migrate towards the anode or cathode by electromigration, electroosmosis, and electrophoresis (Acar and Alshawabkeh, 1993; Shapiro and Probstein, 1993; Virkutyte *et al.*, 2002). Electromigration describes the transport of ions in the pore fluid; cations move to the cathode and anions move to the anode. Soils contaminated with heavy metals have been successfully treated by electromigration (Hicks and Tondorf, 1994; Yeung and Hsu, 2005; Zhou *et al.*, 2006). Electroosmosis is the movement of the pore fluid in soils. Pollutants dissolved in the fluid can be driven out of the site by electroosmosis (Ho *et al.*, 1995; Ko *et al.*, 2000; Saichek and Reddy, 2003; Luo *et al.*, 2005). Electrophoresis is the migration of charged colloids, which has negligible effect in a compact soil system.

As chlorobenzenes are hydrophobic and have preferential sorption on soils, it is very difficult to drive them out by electroosmosis. As a result, facilitating agents such as surfactants must be added to enhance the desorption of chlorobenzenes from soils and the dissolving of chloroben-

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zenes in the soil pore fluid, and thus to enhance the EK movement of chlorobenzenes. However, surfactants such as sodium dodecylsulfonic (SDS) and Tween 80 were reported to be largely adsorbed on soils (Ko *et al.*, 1998a, b). The adsorbed surfactants will further retard the desorption of pollutants, which is unbeneficial for the movement of pollutants in the EK system. Researchers have demonstrated that cyclodextrins were negligibly adsorbed by soils (Ko *et al.*, 1999; Sheremata and Hawari, 2000). Ko *et al.* (2000) revealed that the EK removal of phenanthrene in kaolin was highly enhanced by the addition of hydroxypropyl- β -cyclodextrin (HPCD). In our previous work (Yuan *et al.*, 2006a), β -cyclodextrin (β -CD) has shown potential to enhance the EK movement of hexachlorobenzene (HCB) in contaminated soils. Our group found high concentration of HCB in the soil and sediment along Fuhe river in the vicinity of Wuhan in central China (Yuan *et al.*, 2006a, b). However, HCB in soils could be dechlorinated by micro-organism to less chlorinated benzenes (Fathepure *et al.*, 1988; Pavlostathis and Prytula, 2000), termed as chlorobenzenes in this study. As a consequence, multiple chlorobenzenes are often present in soils simultaneously. Thus, it is necessary to assess the efficiency of the EK process on the remediation of multiple chlorobenzenes in soils.

In the present study, kaolin was simultaneously spiked with multiple chlorobenzenes, including 1,2,3,4-tetrachlorobenzene (TeCB), 1,2,4,5-tetrachlorobenzene (*i*-TeCB), and 1,2,3-trichlorobenzene (TCB). The objectives are: (1) to evaluate the effect of β -CD on the EK removal efficiency of the multiple chlorobenzenes; (2) to investigate the mechanism of the movement of the multiple chlorobenzenes in the presence of β -CD, and (3) to compare and analyze the different removal efficiencies for different chlorinated benzenes.

1 Materials and methods

1.1 Chemicals and materials

TeCB, *i*-TeCB, and TCB were obtained from Sigma. β -CD (analytical grade) was purchased from the Special Chemical Reagent Development Center of North China. Deionized water (18.2 m Ω -cm) obtained from a Millipore Milli-Q system was used for the preparation of solutions. All other reagents used were above the analytical grade. kaolin (Shanghai Fengxian Fengcheng Chemical Reagent Factory, chemical purity) was used as the simulated clayed soil and its properties are shown in Table 1. kaolin was often used as the model clay in the EK laboratory experiments (Acar and Alshawabkeh, 1993; Shapiro and Probstein, 1993; Ko *et al.*, 2000; Saichek and Reddy, 2003; Yuan *et al.*, 2006a) because of its low organic content, low cation exchange capacity, and inertia (Saichek and Reddy, 2003).

1.2 Procedures and equipments

1.2.1 EK remediation of chlorobenzene contaminated soils

The EK schematic diagram is shown in Fig.1. A glass cylinder ($\Phi 5.0$ cm \times 9.0 cm) was used as the EK cell.

Table 1 Main characteristics of kaolin

Main characteristics		Value
Particle size ⁽¹⁾ (%)	0.05–1 mm	1.1
	0.05–0.25 mm	39.6
	< 0.05 mm	59.3
	0.01–0.05 mm	31.8
	0.005–0.01 mm	9.5
	0.001–0.005 mm	1.1
	< 0.001 mm	16.9
Organic content (OC) ⁽²⁾ (%)		0.28
pH ⁽³⁾		5.75
Zero point of charge (ZPC) ⁽⁴⁾		3.36

(¹) Particle size was measured by gravimeter (TM-85 soil densimeter, Shanghai Tianle Electromagnetic Institute, China); (²) organic content was measured by potassium dichromate digestion; (³) pH was measured by the mixture of soil and water (1:1, w/w) with a pH meter (pHS-25, Shanghai Leici Instrument Factory, China); (⁴) zero point of charge was determined according to the literature (Li, 1997).

Perforated graphite ($\Phi 5.0$ cm \times 0.7 cm) was used as anode and cathode, respectively. The anodic compartment (100 ml capacity) and the cathodic compartment (50 ml capacity) were assembled at each end. The anodic purging solution was siphoned from a stocking bottle through a soft rubber tube, which was attached to a piston controlling the inlet flow. Gas vents were set in both electrode cells. The electroosmotic flow in the cathode was collected and measured with a 250 ml cylinder, whose top was sealed with gummed tape to reduce the evaporation of water. A potential of 9.0 V or 18.0 V was supplied by a DC power (GPC-H, 30V/5A, Taiwan Guwei Electronic Ltd., Inc., Taiwan). The electric current was measured by a multimeter connected in the electric circuit.

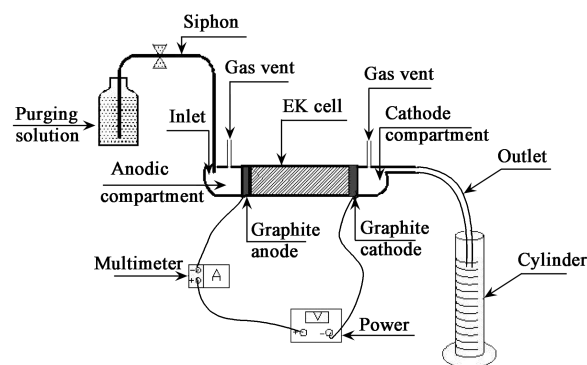


Fig. 1 Schematic diagram of the EK setup.

Simulated chlorobenzenes contaminated soil was prepared by adding certain amount of chlorobenzenes acetone stock solution to 250 g dry and clean kaolin, which was then stirred thoroughly to obtain a uniform distribution of chlorobenzenes in the soil. The concentration of each chlorobenzene was set at 0.18 mmol/kg dry soil. The simulated soil was then dried in air for about 24 h to evaporate acetone. The uniform distribution of chlorobenzenes in the simulated contaminated soil was confirmed by the consistency of gas chromatograph (GC) analysis for three random samples. The simulated chlorobenzenes contaminated soil was mixed with certain volume of deionized water in a beaker to simulate the water content of

45%. The anodic compartment, perforated graphite anode, and the EK cell were first assembled. A filter paper was placed between the electrode and the EK cell to prevent the escape of soil. A fraction of the moist soil was added followed by compacting with a glass rod to remove air bubbles. Another fraction was then added, and the procedure was repeated until the appropriate soil column length was obtained. After the column was filled, a subsample of the remaining soil was extracted as described below to determine the initial concentrations of chlorobenzenes present in the column. When the soil was fully packed into the cell, the perforated graphite cathode and the cathode compartment were assembled likewise. After the system was settled for 8 h, the wires and tubes were connected and the electrode compartments were filled with appropriate solutions. A low constant voltage was supplied by the DC power. The room temperature was maintained at $18 \pm 2^\circ\text{C}$.

The parameters associated with the EK experiments are presented in Table 2. Selected experiments were conducted in duplicate and a good reproducibility was obtained. T1 and T2 presented a comparison of the ability to control the soil pH with H_2O and $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer. The $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffering solution was used because of its better effect on controlling pH higher than NaOH (Yuan *et al.*, 2006a). T3 and T4 were conducted to evaluate the efficiency of the movement of chlorobenzenes in the presence of different concentrations of β -CD. T5 was compared with T4 with a relatively high potential gradient. T6 was performed with a shorter duration time to analyze the rate of movement of chlorobenzenes.

1.2.2 Solubility of β -CD and adsorption of β -CD on kaolin

Firstly, the effect of pH and ionic strength on the solubility of β -CD were investigated. H_2SO_4 (2 mol/L) or NaOH (2 mol/L) was added to 5 ml of 5 mmol/L β -CD to adjust the solution pH, while NaCl was added to the solution to provide ionic strength. If the solubility was reduced by the adjustment of pH and ionic strength, turbidity probably appeared and this was used to evaluate the effect.

Twenty milliliters of different concentrations of β -CD aqueous solution was added to a 100 ml bottle, which contained 1 g dry and clean kaolin. The bottle was sealed and placed in a shaker (25°C , 150 r/min) for 48 h to achieve the desorption equilibrium (Ko *et al.*, 1999). Each experiment was performed in triplicate. When the experiments were completed, 10 ml of aqueous solution was sampled and centrifuged for 10 min (5000 r/min). The supernatant was further filtered with 0.22 μm filtration

membrane (GenerayBiotech (Shanghai) CO., Ltd). The concentration of β -CD in the filtrate was analyzed. The sorbed β -CD on kaolin was calculated by the difference.

1.2.3 Effect of β -CD on the solubility of TeCB

A certain volume of TeCB stock solution was added to a 10-ml glass vial. The quantity of TeCB added was calculated to be highly excessive of its solubility. The vial was allowed to evaporate to dryness over a period of 24 h. 5 ml of β -CD solutions with different concentrations were added to the vial. The vial was sealed immediately with a polytetrafluoroethylene (PTFE) lid and then equilibrated on a shaker for 24 h at $25 \pm 1^\circ\text{C}$ (150 r/min). Each test was conducted in triplicate. After equilibration, the sample was filtered with 0.22 μm filtration membrane. The concentration of chlorobenzenes in the filtrate was extracted with hexane and determined by GC.

1.3 Analysis of the samples

At the end of the EK experiments, soils in the EK cell were pushed out and sliced to six pieces from cathode to anode. Each slice was analyzed for the water content, the pH, the chlorobenzenes concentration, and the β -CD concentration. The water content was measured by drying the sample at 105°C for 6 h. In the analysis of chlorobenzenes, about 0.8 g soil was mixed thoroughly with 3 ml water-aceton mixture (2:1, v/v) in a 10 ml vial sealed with a PTFE lid. Then, 3 ml hexane was added and the extraction process was assisted with 30 min ultrasonication (20 kHz). The sample was further centrifuged for 5 min (3000 r/min) and the supernatant was filtered with 0.22 μm filtration membrane. The concentration of chlorobenzenes in the filtrate was determined by GC. Each sample was prepared in triplicate. The recoveries of chlorobenzenes in the processes were measured to be above 80%.

For the analysis of pH and β -CD, the samples were dried in air for about 48 h, and then ground and sieved by 0.25 mm screen. The pH was measured using a pH meter (PHS-25, Shanghai Leici Instrument Factory, China) by mixing 5 g soil sample with 10 ml deionized water. In the analysis of β -CD, 1 g soil was mixed with 5 ml deionized water thoroughly in a 10-ml vial sealed with a PTFE lid. The extraction process was assisted with 30 min ultrasonication. The sample was centrifuged for 5 min (3000 r/min) and the supernatant was further filtered with 0.22 μm filtration membrane. The concentration of β -CD in the filtrate was determined by photometry (Tong, 2001), which was based on the difference of the absorbency at 553 nm because of the inclusion of phenolphthalein by β -CD. Each sample was prepared in triplicate. The recovery of

Table 2 Parameters associated with the EK experiments

Experimental number	Anodic flushing solution	Duration time (d)	Potential (V)
T1	Deionized water	11	9
T2	0.025 mol/L $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer	11	9
T3	1 mmol/L β -CD in 0.025 mol/L $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer	11	9
T4	5 mmol/L β -CD in 0.025 mol/L $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer	11	9
T5	5 mmol/L β -CD in 0.025 mol/L $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer	11	18
T6	5 mmol/L β -CD in 0.025 mol/L $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer	5.5	18

β -CD in the processes was verified to be above 90%.

An HP 6890 GC equipped with an electron capture detector and an HP-35 column (30 m length, 0.32 mm id, 0.25 μ m film thickness) was used to analyze chlorobenzenes in the extracts. The temperature program of the GC started at 80°C and was held for 1 min. The column was then sequentially heated at a rate of 20°C/min up to 200°C, and held for 10 min. The flow rate of carrier gas (nitrogen 99.999%) was 1.5 ml/min. The inlet temperature and the detector temperature were 250°C and 300°C, respectively. The split ratio was 10. The injection volume of the extract was 1 μ L.

2 Results and discussion

2.1 Distribution of pH and water content

It is known that the EK properties of soils such as potential are directly related to the soil pH (Acar and Alshawabkeh, 1993). In EK processes, H^+ and OH^- , produced on anode and cathode, respectively, will electromigrate to the soil matrix and change the pH temporally and spatially (Acar and Alshawabkeh, 1993; Shapiro and Probst, 1993; Virkutyte *et al.*, 2002). The distribution of pH at the end of the EK process is shown in Fig.2. The relative transport of protons toward the cathode and hydroxide ions toward the anode, the buffering capacity of kaolin, and the water dissociation reaction determine the final pH distribution. Since the electromigration rate of H^+ is 1.76 times that of OH^- (Acar and Alshawabkeh, 1993), low pH values appeared in most regions. At a normalized distance of about 0.3 from the cathode, a sharp decrease of pH occurred in all the tests, demonstrating that H^+ and OH^- met in this region. This result was in agreement with the literature (Ko *et al.*, 2000; Yuan *et al.*, 2006a).

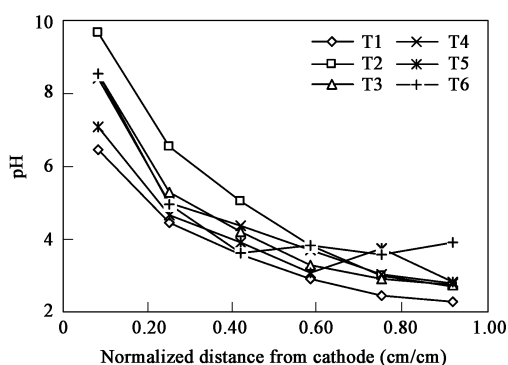


Fig. 2 Distribution of pH in the soils.

Obviously, the soil pH along kaolin in T2 was higher than that in T1, indicating that $Na_2CO_3/NaHCO_3$ buffer had a larger potential to neutralize H^+ produced on the anode. T3 and T4 showed a similar pH distribution, but both led to a lower pH than T2. The lower pH in T5 than that in T4 was because of the higher potential applied (18 V versus 9 V). Higher potential led to more electrolysis of water at the electrodes, resulting in the generation of

more H^+ on the anode and more OH^- on the cathode. Additionally, the slightly higher pH observed in T6 than that in T5 likely stem from the shorter duration of the run (5.5 d versus 11 d). In the tests, the anodic purging solution was supplemented only when the soil pore fluid was driven out. However, the electroosmosis flow (EOF) was slow, and therefore, the retention time of the anodic purging solution in the anodic compartment was very long. It could be inferred that the pH of the solution in the anodic compartment became lower and lower with the increase of duration. In the initial stage of the EK process, H^+ produced at the anode was continuously neutralized by $Na_2CO_3/NaHCO_3$ buffer, but the redundant H^+ may electromigrate to the soil matrix because 0.025 mol/L $Na_2CO_3/NaHCO_3$ buffer was insufficient to neutralize H^+ in the later stage. This was confirmed by the decrease of pH measured in the anodic compartment to about 7.0 after 3 d.

The distribution of water content is given in Fig.3. The relatively low water content occurred at a normalized distance of about 0.6 from the cathode. This result was associated with the distribution of pH in the soil matrix. In the previous section, it has been stated that the electromigration of H^+ and OH^- led to the acidification of soils in most region. Fig.2 presents that the soil pH dropped to the value below ZPC (3.36, Table 1) of kaolin from the normalized distance of 0.6 to the anode. As a result, the direction of EOF was maintained constant in the region from the cathode to the normalized distance of 0.6, but the direction was reversed at some time from the normalized distance of 0.6 to the anode. The water contained in the soils was moved to the anode and cathode simultaneously, resulting in the decrease of the water content in the section of 0.6.

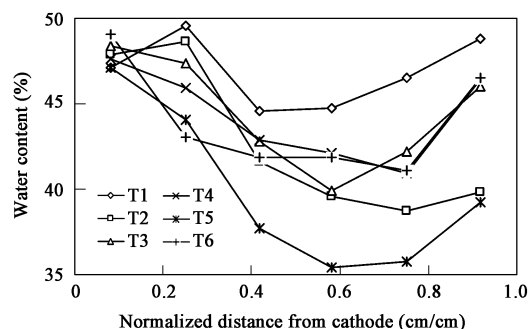


Fig. 3 Distribution of water content in the soils.

2.2 Electric current

In the EK system, electric current is influenced by the conductivity of the soil pore solution, the composition of the solutions in anodic and cathode compartments, and the soil moisture (Yuan *et al.*, 2006a). However, with increasing EK operating time, all factors will change temporally and spatially. Fig.4 shows the changes of electric current. The current generally reached a peak at the start of the test when the quantity of ions in the pore solution was the greatest owing to the dissolution of salts that are associated

with the dry soil particles (Saichek and Reddy, 2003). As the ions electromigrated towards electrodes or precipitated with OH^- , the current gradually declined. When Na^+ and $\text{CO}_3^{2-}/\text{HCO}_3^-$ were introduced, $\text{CO}_3^{2-}/\text{HCO}_3^-$ neutralized some of the H^+ generated on the anode, while Na^+ electromigrated towards the cathode and increased the current. Consequently, after approximately 5 d, a stable low current value was achieved. The initial current of all the tests were different because of the different initial conditions, such as different anodic purging solution and voltage. The electric current in T5 and T6 were about two times that in T4 in the first stage, which was due to the high potential, in agreement with Ohm's law. The consistency of the electric current changes was observed in T5 and T6.

2.3 Electroosmotic flow

The cumulative EOF is depicted in Fig.5. By comparing Fig.5 with Figs.3 and 4, it was found that the cumulative EOF was related to the distribution of the soil pH and the changes of electric current. From T1 to T4, the change of electric current was not significant, and therefore, the cumulative EOF was highly dependent on the soil pH. When compared with deionized water (T1), $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer (T2) significantly increased the cumulative EOF. It has been observed that the $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer leads to higher pH than deionized water. Higher pH leads to more negative ζ potential (Acar and Alshawabkeh, 1993), resulting in the increase of the cumulative EOF. The pH in T3 and T4 was slightly lower than the pH in T2. The dependence of EOF on the soil pH was also reported by

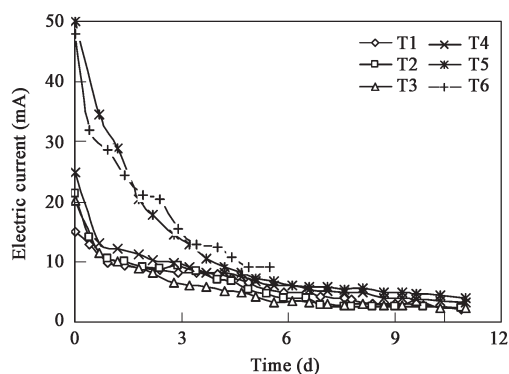


Fig. 4 Electric current changes.

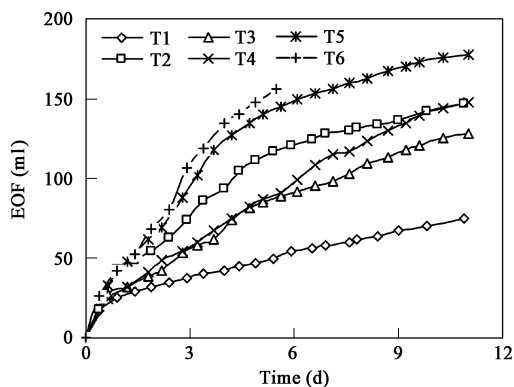


Fig. 5 Cumulative electroosmosis flow (EOF).

Ko *et al.* (2000). In T5 and T6, a higher potential gradient was responsible for the more cumulative EOF. In the first 5 d, the cumulative EOF in T5 and T6 was approximately two times that in T4, where the same conditions except 9 V was used. This result was greatly correlated with the changes of electric current. Electric current represents the transport of ions when the conductive medium has the same resistance. A higher electric current leads to a faster ion transport, which results in a faster transport of water by electroosmosis (Saichek and Reddy, 2003).

2.4 EK movement of chlorobenzenes in the soil

2.4.1 Distribution of chlorobenzenes

(1) **TeCB:** at the end of the EK tests, the distribution of TeCB is shown in Fig.6a. When deionized water was used as the anodic flushing solution (T1), the content of TeCB was low at both ends and was high in the middle. The content in all regions became lower when $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer was used. The cumulative EOF in T2 was considerably larger than that in T1. Since TeCB was weakly solubilized in water (0.0565 mmol/L

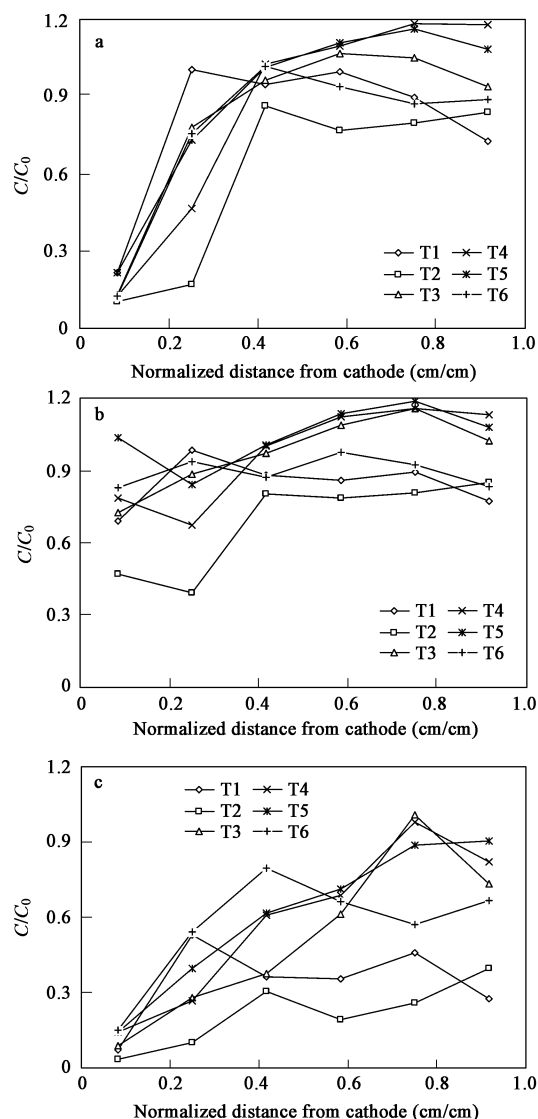


Fig. 6 Distribution of HCB in the soils. (a) TeCB; (b) *i*-TeCB; (c) TeCB.

(Miller *et al.*, 1985)), it is possible that TeCB was removed by electroosmosis. However, with the addition of β -CD (T3 and T4), the movement of TeCB was increasingly inhibited with the increased concentration of β -CD. This result is contradictory to the literature (Ko *et al.*, 2000) and our previous report (Yuan *et al.*, 2006a), where the movement of HCB was enhanced with the addition of β -CD. The detailed mechanism will be discussed in the later section. When 18 V was applied (T5), the cumulative EOF increased greatly, but the distribution of TeCB was similar to that in T5. It can be inferred that the effect of inhibition was so great that the increase of EOF could not remove any more TeCB. When the half duration time lasted (T6), the content of TeCB in the region close to the anode was lower than that in T5. This suggested that TeCB was moved from cathode to anode in the second half duration. The pH distribution of T5 in Fig.2 shows that the pH in most regions dropped to the values below ZPC, which has been interpreted in Section 2.1. As a consequence, the direction of EOF in most regions was reversed in the second half duration, which was responsible for the movement of TeCB from cathode to anode in the second half duration.

(2) ***i*-TeCB**: the distribution of *i*-TeCB is given in Fig.6b. The movement of *i*-TeCB is slight in T1, while a great removal was obtained in T2. However, the removal in both T1 and T2 were less than that of TeCB. The water solubility of *i*-TeCB (0.0109 mmol/L (Miller *et al.*, 1985)) is considerably less than that of TeCB, which is responsible for the less obvious movement. Similarly, the movement of *i*-TeCB was inhibited by the addition of β -CD (T3–T6). The removal of *i*-TeCB in all the regions in T3–T6 was slight. The distribution of *i*-TeCB revealed an increase from cathode to anode and the ratio of C/C_0 was higher than 1.0 in the regions close to the anode, indicating the accumulation of *i*-TeCB in those regions. By comparing the distribution of *i*-TeCB in T5 and T6, it was found that the content of *i*-TeCB in the regions close to the anode increased with a longer duration. The reverse of the movement of *i*-TeCB was further proved.

(3) **TCB**: the distribution of TCB in Fig.6c revealed that the content of TCB decreased from anode to cathode and all values of C/C_0 were below 1.0. When compared with the removal of TeCB and *i*-TeCB, the removal of TCB in all the tests was greater. It could be seen that the removal of TCB was about 70% in T1 and about 80% in T2. The water solubility of TCB (0.0676 mmol/L (Miller *et al.*, 1985)) was larger than that of TeCB and *i*-TeCB, which was accountable for the greater removal efficiency. A similar inhibition was observed in the movement of TCB.

2.4.2 Mechanism of the movement of chlorobenzenes

In this study, the EK movement of the three chlorobenzenes without β -CD was significant, while the movement was highly inhibited by the addition of β -CD. However, in our previous study (Yuan *et al.*, 2006a), negligible movement of HCB appeared without β -CD but significant movement was obtained with 1% β -CD (8.8 mmol/L). For HCB and less chlorinated benzenes, contrary results were

obtained. Therefore, it is necessary to further investigate the mechanism of the movement. Generally, the EK movement of pollutants includes two steps (Ko *et al.*, 2000), the desorption of pollutants from the soil, and the movement of pollutants in pore solution by electromigration and/or electroosmosis.

In the case without β -CD, the mechanism was relatively simple. Chlorobenzenes were first desorbed from the soil and dissolved in the pore solution. Then, the solution containing chlorobenzenes was driven out by electroosmosis. Since chlorobenzenes are uncharged, the effect of electromigration can be neglected. The cumulative EOF in T1 and T2 were 75 and 147 ml, respectively. The removal of all chlorobenzenes in T2 was significantly larger than that in T1, which suggested that the aqueous solubility heavily contributed to the removal. It was noteworthy that the removal efficiencies of chlorobenzenes conformed to the sequence: TCB > TeCB > *i*-TeCB. This sequence was consistent with their aqueous solubility, as stated in Section 2.4.1. However, the removal of chlorobenzenes in T1 and T2 were highly above the largest quantity that could be solubilized by the cumulative EOF. This indicated that solubilization was not absolutely responsible for the movement. Similar result was also obtained in the EK removal of phenanthrene when deionized water or basic solution was used as the anodic flushing solution (Ko *et al.*, 2000; Saichek and Reddy, 2003). The authors proposed that the flushing of the poorly adsorbed phenanthrene particles towards the cathode because of the high EOF and the flushing action through the small pore spaces was accountable for the result (Saichek and Reddy, 2003). It was noteworthy that the content of chlorobenzenes decreased from anode to cathode. The pH was high in the regions near cathode and was low in the regions near anode (Section 2.1). However, pH had great influence on the ζ potential of the soil, which determined the effect of electroosmosis (Acar and Alshawabkeh, 1993). Higher pH leads to more negative ζ potential (Acar and Alshawabkeh, 1993), resulting in the increase of EOF. When pH was less than the ZPC of the soil, the direction of EOF would be reversed. Therefore, the EOF in different regions in the EK cell was different. A high EOF occurred in the region near the cathode, whereas a low EOF appeared in the region near the anode. The different EOF along the EK cell resulted in the different movement rates, which was the reason for the different distribution of chlorobenzenes along the EK cell.

While β -CD was present in the tests, the mechanism became complicated. On one hand, the cumulative EOF was slightly reduced by the addition of β -CD, as discussed in Section 2.3. Hence, the effect of electroosmosis was reduced when β -CD was added. On the other hand, the adsorption/desorption of chlorobenzenes was influenced with the entering of β -CD into the soil matrix. β -CD has a hydrophilic shell and a toroidal-shaped, hydrophobic cavity. It may form inclusion complexes by incorporating suitable sized low-polarity moleculars in its cavity (Ko *et al.*, 1999). It was known that β -CD will be adsorbed onto soil (Martínez *et al.*, 1999; Morello *et al.*, 2001; Badr *et al.*

al., 2004). The state of β -CD in the soil matrix included the aqueous β -CD in pore solution and adsorbed β -CD on the soil. Both states could form inclusion compounds with chlorobenzenes. As a result, the state of chlorobenzenes in the soil matrix included adsorbed chlorobenzenes on kaolin, enclosed chlorobenzenes with adsorbed β -CD on kaolin, enclosed chlorobenzenes with aqueous β -CD in the pore solution, and aqueous chlorobenzenes dissolved in the pore solution. The adsorbed chlorobenzenes on kaolin and the enclosed chlorobenzenes with adsorbed β -CD on kaolin retarded the desorption of chlorobenzenes, whereas the enclosed chlorobenzenes with aqueous β -CD in the pore solution and the aqueous chlorobenzenes dissolved in the pore solution benefited the desorption. The net effect of the desorption was determined by the balance of the two factors. The following section will discuss the effect of β -CD on the desorption of chlorobenzenes in detail.

The solubility of β -CD is low and is sensitive to the pH and ionic strength (Tong, 2001). Nevertheless, the pH and ionic strength of the pore solution changed greatly in the EK process (Acar and Alshawabkeh, 1993; Shapiro and Probst, 1993; Virkutyte *et al.*, 2002). Hence, the preliminary experiments were conducted to study the effect of pH and ionic strength on the solubility. The concentration β -CD was fixed at 5 mmol/L, which was the highest concentration used in this study. When pH was ranged from 1 to 13 or ionic strength from 0 to 2 mol/L, no turbidity was observed in the solution. It has been demonstrated in Section 2.1 that the soil pH was ranging from 2 to 10. It could be concluded that no β -CD was deposited in the EK process and no chlorobenzenes were removed because of the precipitation of β -CD.

It is known that β -CD can be adsorbed onto soils (Martínez *et al.*, 1999; Morello *et al.*, 2001; Badr *et al.*, 2004). Therefore, the adsorption behavior of β -CD on kaolin was critical to understand the inhibition mechanism. The adsorption curve of β -CD on kaolin is depicted in Fig. 7. It could be seen that β -CD was slightly adsorbed on kaolin, particularly at high concentration of β -CD. This result was in agreement with literature (Badr *et al.*, 2004). Adsorbed β -CD and aqueous β -CD will enclose chlorobenzenes. Since β -CD was predominant in the aqueous solution, most chlorobenzenes will be enclosed by aqueous β -CD, instead of adsorbed β -CD.

The adsorption of β -CD on kaolin demonstrated that

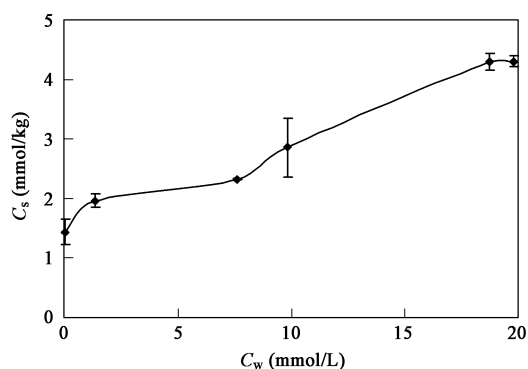


Fig. 7 Adsorption of β -CD on kaolin.

most chlorobenzenes were enclosed by aqueous β -CD, which must be beneficial to the desorption of chlorobenzenes. Contrarily, the addition of β -CD inhibited the movement of chlorobenzenes. Hence, an exceptional interaction between β -CD and chlorobenzenes must take place, which will lead to the inhibition of the movement. In the preliminary experiments, we further examined the effect of β -CD on the aqueous solubility of chlorobenzenes. Using TeCB as a representative chlorobenzene, the effect of β -CD on its aqueous solubility is given in Fig. 8, where C/C_0 refers to the ratio of the TeCB concentration in β -CD solution to that in deionized water. It was unexpected that the aqueous solubility of TeCB decreased sharply with the increase of β -CD concentration from 0 to 0.5 mmol/L and remained almost constant with further increase of β -CD concentration. The prerequisite for solutes to fit completely in the cavity of β -CD is that their molecular volume must be smaller than the cavity volume (Wang and Brusseau, 1993). The cavity of β -CD was reported to be 0.346 nm^3 (Wang and Brusseau, 1993). The molecular volume of TeCB was calculated to be 0.298 nm^3 (Miller *et al.*, 1985). Thus, it was reasonable that TeCB molecular completely entered the cavity. Generally, β -CD forms 1:1 inclusion compounds with low molecular organic compounds (Tong, 2001). Here, the aqueous solubility of TeCB in deionized water (C_0) was determined to be 0.0231 mmol/L , which was less than the β -CD concentration examined. The decrease of the aqueous solubility of TeCB with the increase of β -CD concentration from 0 to 0.5 mmol/L indicated that the inclusion compound, β -CD-TeCB, was less soluble than TeCB (Cao *et al.*, 2000; Tong, 2001; Hanna *et al.*, 2003). Thus, partial TeCB in the inclusion compound was removed owing to the formation of precipitation. With further increase of β -CD concentration, the amount of β -CD-TeCB attained the largest value. Thus, an almost constant aqueous concentration of TeCB was observed when the β -CD concentration was higher than 0.5 mmol/L . The molecular volumes of *i*-TeCB and TeCB were calculated to be 0.298 and 0.264 nm^3 (Miller *et al.*, 1985), respectively. Since both volumes were smaller than the cavity volume of β -CD, similar inclusion compounds will be formed. Consequently, it can be concluded that the enclosed chlorobenzenes with aqueous β -CD reduced their aqueous solubility.

The aqueous solubility of chlorobenzenes was reduced

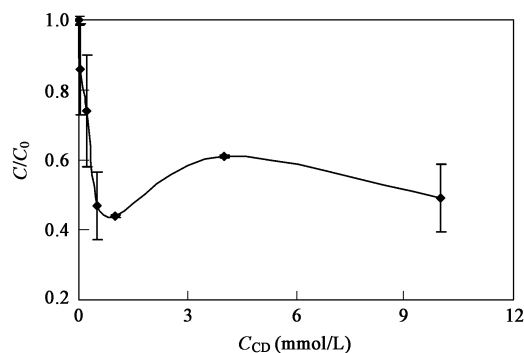


Fig. 8 Effect of β -CD on the aqueous solubility of TeCB.

by the addition of β -CD, and therefore, the distribution of β -CD in the soils played an important role in the explanation of the inhibition mechanism. At the end of tests, the distribution of β -CD along the EK cell is shown in Fig. 9. It can be seen that β -CD entered into the soil matrix and the content of β -CD gradually decreased from anode to cathode. Higher potential and longer duration benefited the entering of β -CD. When β -CD was added to the anodic compartment, it will enter into soil from anode to cathode by electroosmosis and diffusion. The soil near anode first interacted with β -CD. Since most β -CD was present in aqueous solution, chlorobenzenes in the pore solution were enclosed by β -CD. Hence, the aqueous solubility of chlorobenzenes was reduced and a large amount of chlorobenzenes were precipitated in the region. Then, β -CD moved to the next region. However, prior to the arrival of β -CD, the movement of chlorobenzenes in the region near cathode was similar to that in the absence of β -CD. As a consequence, chlorobenzenes in the region near the cathode were significantly removed even with the addition of β -CD and the removal efficiency was related to the aqueous solubility. In addition, an accumulation of TeCB and *i*-TeCB was observed in the region near the anode with the addition of β -CD. It has been stated that the direction of EOF in most regions near the anode was reversed in the second half of the duration. In the region, chlorobenzenes will be moved from cathode to anode, which leads to the accumulation.

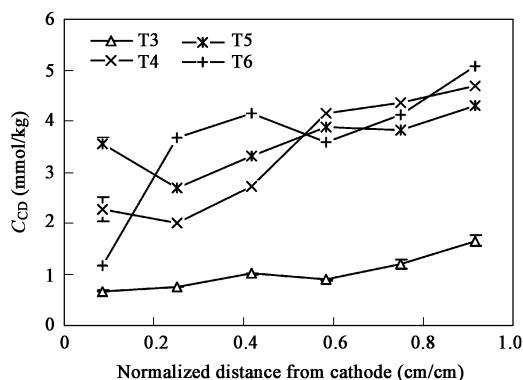


Fig. 9 Distribution of β -CD in the soils.

2.4.3 Comparison of the movement of chlorobenzenes

By comparing the EK movement of the three chlorobenzenes without β -CD, it was found that the removal was related to their aqueous solubility. The aqueous solubility of TCB, TeCB, and *i*-TeCB were 0.0676, 0.0565, and 0.0109 mmol/L, respectively (Miller *et al.*, 1985). A high solubility led to a large removal since high solubility benefited the desorption efficiency. With the same EOF, the higher desorption efficiency resulted in the larger removal.

In the presence of β -CD, the effect of inhibition was similar for the three chlorobenzenes. The total concentration of chlorobenzenes in soils was 0.54 mmol/kg (3×0.18 mmol/kg). Generally, β -CD forms 1:1 inclusion compounds with low molecular organic compounds (Tong,

2001). The formation of inclusion compounds between β -CD and chlorobenzenes was affected by factors such as the molecular size and hydrophobicity (Wang and Brusseau, 1993; Tong, 2001). It has been verified that any of the three chlorobenzenes could be enclosed by β -CD. Since the concentration of β -CD in soil was considerably higher than 0.54 mmol/kg, all chlorobenzenes will be enclosed by β -CD unselectively. As a result, a similar inhibition effect was obtained.

It has been reported in our previous study (Yuan *et al.*, 2006a) that β -CD can enhance the EK removal efficiency of HCB. When compared with the less chlorinated benzenes such as TeCB, *i*-TeCB, and TCB, HCB has a larger molecular size (0.368 nm^3 (Miller *et al.*, 1985)), a far lower aqueous solubility ($6.47 \times 10^{-4} \text{ mmol/L}$ (Miller *et al.*, 1985)), and higher hydrophobicity ($\lg K_{ow} = 5.47$ (Miller *et al.*, 1985)). The molecular size of HCB is slightly larger than the cavity volume of β -CD (0.346 nm^3 (Wang and Brusseau, 1993)), and thus, HCB can be partly enclosed by β -CD (Tong, 2001). Owing to the high hydrophobicity, HCB is attracted by the hydrophobic cavity (Wang and Brusseau, 1993). Furthermore, it has been demonstrated that β -CD can enhance the desorption of HCB from kaolin (Yuan *et al.*, 2006a). It can be inferred that the solubility of the inclusion compound between β -CD and HCB, β -CD-HCB, was higher than that of HCB. However, the solubility of the inclusion compounds between β -CD and less chlorinated benzenes were lower than those of chlorobenzenes. This was the reason why β -CD enhanced the EK removal efficiency of HCB but inhibited the efficiencies of TeCB, *i*-TeCB, and TCB.

In summary, EK technology was feasible to remove less chlorinated benzenes in contaminated soils using water as the anodic flushing solution. The removal efficiencies were related to the solubilities of the benzenes. The addition of β -CD to the anodic flushing solution will inhibit the removal of the less chlorinated chlorobenzenes but enhance the removal of HCB.

3 Conclusions

The EK movement of multiple chlorobenzenes, including TeCB, *i*-TeCB, and TCB, in contaminated soil was investigated in this study. The effect of β -CD on the removal efficiency was discussed. The greatest removal of chlorobenzenes appeared when 0.025 mol/L $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ buffer was used as the anodic purging solution in the absence of β -CD. The EK removal efficiencies were related to the aqueous solubilities of chlorobenzenes. With the same cumulative EOF, greater solubility led to higher removal. The addition of β -CD inhibited the EK removal efficiencies of all chlorobenzenes. The inhibition increased with the rise of the β -CD concentration. With the same β -CD concentration, the inhibition increased with the rise of the potential gradient. The inclusion compounds between β -CD and chlorobenzenes were less soluble than the chlorobenzenes, which were responsible for the inhibition.

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