

# Electrokinetic movement of hexachlorobenzene in clayed soils enhanced by Tween 80 and $\beta$ -cyclodextrin

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## Abstract

This study describes the comparative behavior of hexachlorobenzene (HCB) contaminated clayed soils in an electrokinetic (EK) system enhanced by Tween 80 and  $\beta$ -cyclodextrin ( $\beta$ -CD). The pH of the soils was controlled by  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer. Negligible HCB movement was observed when NaOH or  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer was used as anodic flushing solution. While Tween 80 or  $\beta$ -CD was introduced to  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer, obvious HCB movement was achieved. Although  $\beta$ -CD led to a less desorption of HCB from kaolin than Tween 80, the removal of HCB with  $\beta$ -CD was much higher than that with Tween 80 in the EK system. Tween 80 could be sorped by kaolin more than  $\beta$ -CD, which was responsible for the result. The mechanism of the movement of HCB was proposed as the enhanced desorption of HCB from soil, the dissolving of HCB in the soil pore fluid and the movement of HCB with the electroosmotic flow. Obvious movement of HCB was also observed in the EK treatment of real HCB-contaminated clayed soil enhanced by  $\beta$ -CD. It is an alternative approach to use facilitating agents such as  $\beta$ -CD to enhance the EK movement of HCB in the contaminated clayed soils.

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**Keywords:** Hexachlorobenzene (HCB); Electrokinetic movement; Soil remediation

## 1. Introduction

Hexachlorobenzene (HCB) is one of the typical persistent organic pollutants (POPs). It semi-volatile, mobile in the environment and tends to accumulate and biomagnify in organisms owing to its lipophilicity and persistence [1]. Because of the low cost and versatility in controlling various insects, HCB has been widely used as a fungicidal dressing of seed grains and is a waste by-product in many industrial processes [2]. Large quantity of HCB has been released to the environment as a consequence of agricultural and industrial development. For example, high concentration of HCB has been tested in the soils and sediments along Fuhe river in the vicinity of Wuhan city [3], central China.

Researchers have investigated the remediation of HCB-contaminated soils by microbial dechlorination [4–8], enhanced desorption [9–13] and physicochemical processes such as dechlorination by metal alloy [14], sonochemistry [15], radiation [16], photochemistry [17] and zero-valent iron [18]. However,

microbial dechlorination requires highly selectivity bacteria or plants and is time-consuming. While desorption and physicochemical processes are only applicable to permeable soils, but not clayed soils. Therefore, it is necessary to explore new approaches to remediate HCB-contaminated clayed soils.

Electrokinetics (EK) remediation is an emerging technology that can effectively remove pollutants from fine-grain soils [19–21]. Briefly, with the application of electric field to the polluted site, pollutants will migrate towards anode or cathode by electromigration, electroosmosis and electrophoresis [19–21]. Electromigration describes the transport of ions in the pore fluid, cations move to cathode and anions toward anode. Electroosmosis is the movement of the pore fluid in the soils. Pollutants dissolved in the fluid can be driven out of the site by electroosmosis. Electrophoresis is the migration of charged colloids, which has negligible effect in a compact system.

As HCB is weakly water-soluble and preferential sorption on soils, it is very difficult to drive it out by electroosmosis. As a result, facilitating agents such as surfactants should be added to enhance the desorption of HCB from soils and the dissolving of HCB in the soil pore solution, thus to increase the removal of HCB by electroosmosis. Ko et al. [22] found the EK removal of

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phenanthrene in kaolin could be greatly enhanced by the addition of hydroxypropyl- $\beta$ -cyclodextrin (HPCD). The result was explained as the enhanced desorption/solubilization of phenanthrene by HPCD. Reddy and co-workers [23,24] observed Tween 80 highly benefited the EK movement of phenanthrene in kaolin. The enhanced solubilization of phenanthrene by Tween 80 was considered as the reason. The detailed mechanism of the EK movement was not discussed in the literatures. Up to now, there is no report on the EK remediation of HCB-contaminated soils.

This study presents a preliminary evaluation and a detailed mechanism of EK process for removing HCB from contaminated clayed soils.  $\beta$ -Cyclodextrin ( $\beta$ -CD) or Tween 80 dissolved in  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer was used as anodic flushing solution to enhance the process. The results were interpreted in terms of the EK properties and HCB movement. The emphasis was put on the mechanism of the movement of HCB in the system.

## 2. Materials and methods

### 2.1. Chemicals and materials

HCB (99.0%) was provided by Shanghai General Reagent Factory, Shanghai, China. Tween 80 (analytical grade) was from Tianjin Kermel Chemical Reagent Development Center, China.  $\beta$ -CD (analytical grade) was from the Special Chemical Reagent development Center of North China. Acetone (analytical grade) was used for the dissolution of HCB and hexane (analytical grade) for the extraction of HCB. Deionized water (18.2 m $\Omega$  cm) from a Millipore Milli-Q system was used for the preparation of solutions. All the other reagents were above analytical grade.

Kaolin (Chemical Reagent Company of Guoyao Group, China, 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 [22–24] due

to its low organic content (OC), low cation exchange capacity (CEC) and inertia. Besides, it is weakly acidic (pH 4.70) and has a high content of clay, negligible content of organic matter and low cation exchange capacity.

Preparation of simulated HCB-contaminated soil at concentration of 50.00 mg/kg, i.e., the typical HCB concentration found in the vicinity of Wuhan city, was made by adding 25 mL HCB acetone solution (1000 mg/L) to 500 g dry and clean kaolin, then stirred thoroughly to obtain a simulated HCB-contaminated soil. The simulated soil was then dried in air for 24 h and stored in dark bottle in refrigerator (4 °C) for treatment. The uniform distribution of HCB in the simulated HCB-contaminated kaolin was verified by the consistency of gas chromatography (GC) analysis for three random samples.

Real HCB-contaminated soil was sampled from the vicinage of Fuhe river, which is located in the vicinity of Wuhan city, central China. The soil was first dried at 105 °C for 6 h. Then, it was ground and sieved by 50 mesh screen. The sample was stirred thoroughly to achieve uniform distribution and stored in dark bottle in refrigerator (4 °C) for treatment. The content of HCB was measured as 55.00 mg/kg. The main characteristics of the real contaminated soil are presented in Table 1.

### 2.2. Procedures and equipments

#### 2.2.1. EK remediation of HCB-contaminated soils

A schematic diagram of the EK setup for this study is shown in Fig. 1. A glass cylinder ( $\Phi$  4.5 cm  $\times$  8.0 cm) was used as the EK cell. Perforated graphite ( $\Phi$  5.0 cm  $\times$  0.7 cm) was used as anode and cathode. Anodic compartment (60 mL capacity) and cathode compartment (40 mL capacity) were assembled at each end. The anodic flushing solution was siphoned from a stocking bottle by a soft rubber tube, which attached a piston to control the inlet flow. The inlet in the left top of the anodic cell acted as gas vent meanwhile. The electroosmotic flow in the cathode was collected and measured with a 250 mL cylinder, whose top was sealed with gummed tape to avoid the evaporation of water. The constant potential was supplied by a dc power (GPC-H, 30V/5A, Taiwan Guwei Electronic Ltd., Inc., Taiwan). The electric current was monitored with a multimeter.

In the EK experiments, approximately 100 g simulated HCB-contaminated kaolin or real HCB-contaminated soil were mixed with a certain amount of deionized water. The anodic compartment, perforated graphite anode and the EK cell were assembled firstly. A filter paper was placed between the electrode and 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 HCB concentration present in the column. When the soil was fully packed into the cell, the perforated graphite cathode and 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

Table 1  
The main characteristics of kaolin and real soil

Main characteristics	Kaolin	Real soil
Particle size <sup>a</sup> (%)		
0.05–1 mm	0	7.2
<0.05 mm	100	92.8
0.01–0.05 mm	0	32.4
0.005–0.01 mm	35.8	16.0
0.001–0.005 mm	25.4	20.4
<0.001 mm	38.8	24.0
OC <sup>b</sup> (g/kg)	0	3.58
CEC <sup>c</sup> (mmol/100 g)	1.85	5.71
pH <sup>d</sup>	4.70	7.97

<sup>a</sup> Particle size was measured by gravimeter (TM-85 soil densimeter, Shanghai Tianle Electromagnetic Institute, China) [25].

<sup>b</sup> Organic content, which was measured by potassium dichromate digestion [25].

<sup>c</sup> Cation exchange capacity, which was measured by ammonium acetate method.

<sup>d</sup> pH was measured by the mixing of soil and water (1:1, w/w) with a pH meter (pHS-25, Shanghai Leici Instrument Factory, China).

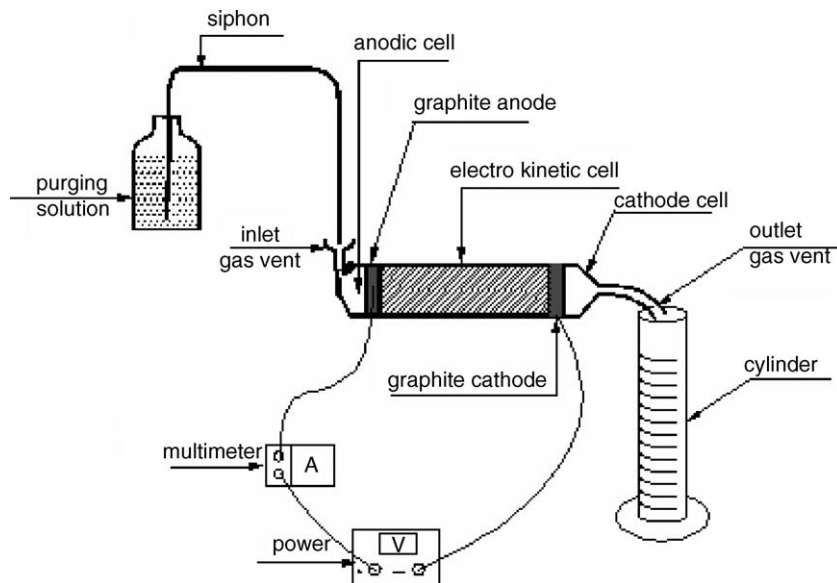


Fig. 1. Schematic diagram of EK reactor.

solutions. A low constant voltage gradient was supplied by the dc power. All the EK experiments were carried out at room temperature.

Parameters associated with each experiment are listed in Table 2. The tests were run until the current decreased and became stable or the effluent volume reduced or stabilized. T1 and T2 were performed to investigate the ability of controlling the soil pH with NaOH and Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> buffer; T3 and T4 were carried out to compare the EK behavior of HCB enhanced by β-CD and Tween 80; T5 is conducted to estimate the feasibility of EK remediation of real HCB-contaminated soil enhanced by β-CD.

#### 2.2.2. Desorption of HCB from kaolin enhanced by β-CD and Tween 80

About 20.00 mL of β-CD (1%) or Tween 80 (1%) aqueous solution was added to 1.0000 g HCB simulated contaminated kaolin in a 100 mL bottle. The bottle was sealed and placed in a shaker (25 °C, 150 rpm) for 72 h to achieve the desorption equilibrium [9]. Each experiment was conducted in triplicate. When the experiments were ended, 10.00 mL aqueous solution was sampled and centrifuged for 10 min at 5000 rpm. About 1.00 mL supernatant was extracted with 5.00 mL hexane assisted by 30 min ultrasonication (20 kHz). The supernatant of hexane was analyzed by GC.

#### 2.3. Analysis of the samples

At the end of the EK experiments, soil was extruded from the electrokinetic cell and divided into five 1.60 cm sections along the length of the cell to analyze the spatial distribution of the moisture, pH as well as the residual HCB remaining in the soil. Moisture was measured by drying the sample at 105 °C for 6 h. pH was measured with a pH meter (pHS-25, Shanghai Leici Instrument Factory, China) by mixing 10.00 g soil sample with 10.00 mL deionized water. For the analysis of HCB in the electroosmotic flow, 5.00 mL electroosmotic flow was extracted with 2.00 mL hexane assisted by 30 min ultrasonication. The supernatant was analyzed by GC.

For the analysis of HCB in moist soils, samples were dried in air for about 48 h. Each sample was prepared twice. Then, the samples were ground and sieved by 50 mesh screen. 1.0000 g dry soil was extracted by 5 mL hexane assisted by 30 min ultrasonication. After the sample was centrifuged for 10 min (5000 rpm), the supernatant was poured out to another vial for GC analysis. The recovery of HCB in the processes was verified to be above 80%.

A Hewlett-Packard Model 6890 GC equipped with an electron capture detector (ECD) and an HP-1 column (30 m length, 0.32 mm i.d., 0.25 μm film thickness) was used to analyze HCB in the extracts. The temperature program of the GC started at

Table 2  
Parameters associated with the EK experiments

Experiment number	Anodic flushing solution	Soil moisture (%)	Potential (V)
T1	0.1 mol/L NaOH	31	10
T2	0.05 mol/L Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub> buffer	45	8
T3	1% Tween 80 in 0.05 mol/L Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub> buffer	45	8
T4	1% β-CD in 0.05 mol/L Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub> buffer	45	8
T5	1% β-CD in 0.05 mol/L Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub> buffer	45	8

Note: 0.05 mol/L Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> buffer consisted of 0.05 mol/L Na<sub>2</sub>CO<sub>3</sub> + 0.05 mol/L NaHCO<sub>3</sub>; simulated HCB-contaminated kaolin was used in T1–T4 and real HCB-contaminated soil was treated in T5.

150 °C and was held for 1 min. Then, the column was sequentially heated at a rate of 20 °C/min to 200 °C, held for 10 min. The flow rate of carrier gas (nitrogen 99.999%) was 1.5 mL/min. The inlet temperature and detector temperature were 250 and 300 °C, respectively. The split ratio was 10. The injection volume of extract was 1.00  $\mu$ L.

### 3. Results and discussion

#### 3.1. Electric current

In an EK system, electric current is influenced by the conductivity of soil pore solution, the composition of the solutions in anodic and cathode compartments, and soil moisture. However, as the EK process proceeds, all the factors change temporally and spatially. It is difficult to roundly interpret the change of electric current. The change of electric current in this study is shown in Fig. 2. In general, the maximal current reached at the start of test when the quantity of ions in the pore solution is greatest [23]. As the ions electromigrated towards electrodes or precipitated with  $\text{OH}^-$ , the current gradually declined. When  $\text{Na}^+$  and  $\text{OH}^-$  or  $\text{CO}_3^{2-}/\text{HCO}_3^-$  were introduced,  $\text{OH}^-$  or  $\text{CO}_3^{2-}/\text{HCO}_3^-$  partly neutralized  $\text{H}^+$  generated on anode, while  $\text{Na}^+$  electromigrated towards the cathode, which led to an increase of current. Consequently, after about 3 days, the residual current was stabilized. The initial current of all the tests was different due to the different initial conditions, such as different anodic flushing solution, voltage gradient or soil type. Because of the additional effects of the composition of the solutions in anodic and cathode compartments and the soil moisture, the residue current fluctuated.

Comparing the changes of the current, a peak current appeared at 2.0 days in the test controlled by Tween 80 and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer (T3). Researchers found that nonionic surfactant molecular might acquire charges and/or became protonated [25,26]. The sorption of Tween 80 on kaolin will reduce the sorption of mobile ions, release the ions that have been adsorbed and reduce the formation of precipitation [23]. So an increase of electric current appeared from 0.5 day to 2.0 days. When kaolin is gradually covered with Tween 80, the changes

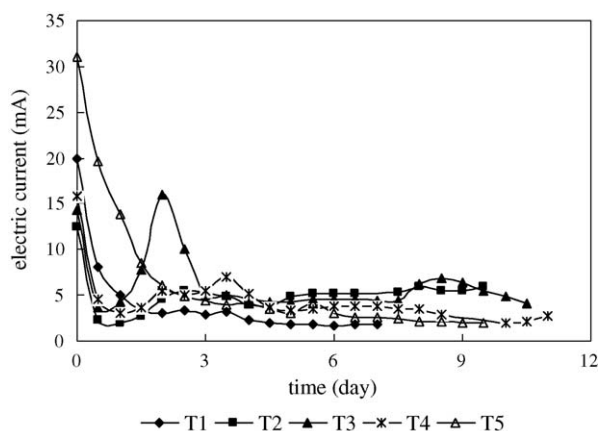


Fig. 2. Electric current changes.

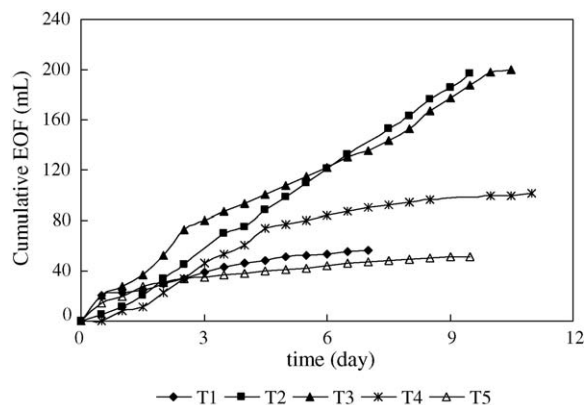


Fig. 3. Cumulative EOF.

of electric current are similar to that of the test without Tween 80 (T2).

#### 3.2. Electroosmotic flow

The cumulative electroosmotic flow (EOF) is shown in Fig. 3. Compared with NaOH (T1),  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer (T2) significantly increased the cumulative EOF.  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer is more effective to control the soil pH at high level than NaOH [22]. Higher pH leads to more negative  $\zeta$  potential [19], resulting in the increase of the cumulative EOF. With the addition of Tween 80 (T3), the cumulative EOF of T3 was more than that of T2 in the first 6 days. As discussed in Section 3.1, the sorption of Tween 80 on kaolin will reduce the sorption of mobile ions, release the ions and reduce the formation of precipitate [23]. Besides, as a kind of dispersing agent, Tween 80 could improve the permeability of kaolin. Thus, the pore fluid could be mobilized more smoothly in T3 than in T2. The gradual sorption of Tween 80 on kaolin increased the content of the organic matter, which is unbeneficial to electroosmosis. The  $\zeta$  potential of kaolin was reported to increase from  $-60$  to  $-32$  mV when the sorbed Tween 80 concentration increased from 0.3 to 30  $\mu\text{mol/g}$  [25]. The increase of  $\zeta$  potential led to the decrease of EOF. As a result, the cumulative EOF of T3 was less than that of T2 after 6 days. By comparing Figs. 4 and 3, it is noteworthy that the changes of the cumulative EOF were greatly correlated to the changes of electric current. The same correlation was also reported by several researchers [23,24]. Electric current represents the transport of ions when the conductive medium has the same electric resistance. The higher electric current leads to the faster ion transport, which results in the faster transport of water by electroosmosis [22]. In the test with  $\beta$ -CD (T4), the increase of cumulative EOF was minute after 4.5 days. And in the test of real soil (T5), the increase of cumulative EOF became insignificant after 2.5 days. The results were also correlated to the corresponding changes of electric current.

#### 3.3. Distribution of pH

In an EK system,  $\text{H}^+$  and  $\text{OH}^-$ , produced on anode and cathode, respectively, will electromigrate to the soil matrix

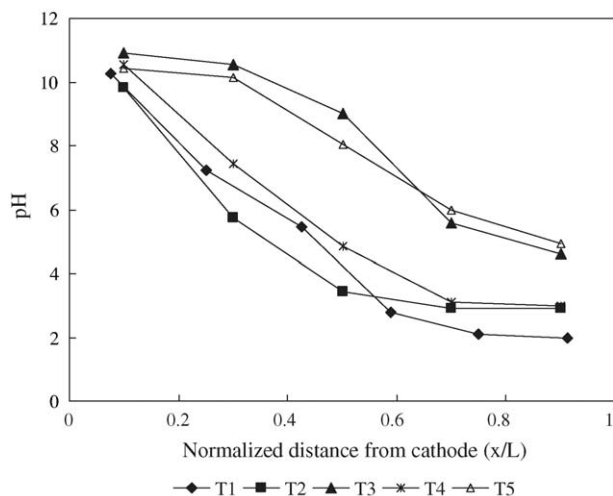


Fig. 4. Distribution of pH in the soils.

and change pH temporally and spatially [19,20]. The distribution of pH at the end of EK process is shown in Fig. 4.  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer has a higher capacity to control pH at high level than NaOH. The duration of T2 was a little longer than that of T1. So, the soil pH in the sections close to cathode was higher in T2 than in T1. The addition of Tween 80 (T3) to the buffer (T2) resulted in the higher pH. Besides the minute difference of duration, the sorption of Tween 80 by kaolin was another reason. Hydrogen bonding will be formed when Tween 80 is adsorbed by kaolin, which contributes to the capture of  $\text{H}^+$  [25].  $\beta$ -CD (T4) controlled the soil pH higher than the buffer (T2), but lower than Tween 80 (T3). This result was possible related to the special molecular structure of  $\beta$ -CD and the minute sorption of  $\beta$ -CD on kaolin [22]. Tween 80 (T3) and  $\beta$ -CD (T4) controlled the soil pH higher than buffer (T2), but more cumulative EOF is achieved in the later one. Similar results were also reported by Saichek and Reddy [23]. The author demonstrated that the efficiency of electrode reactions could not achieve 100% and distribution of local voltage gradient was uneven [23]. The higher pH distribution of the real soil is mostly due to its intrinsic characteristics. A high initial pH of 7.97 appeared in T5. Moreover, the cation exchange capacity and organic content of the real soil were much higher than those of kaolin. This may lead to a greater capacity to neutralize  $\text{H}^+$ .

### 3.4. Distribution of moisture

The distribution of moisture is given in Fig. 5. In all the EK processes, low moisture regions occurred in the section of 0.6 (normalized distance of 0.6 from cathode). It could be inferred that fluid in the region was dragged to both anode and cathode. This could be attributable to the distribution of pH in the soil matrix. In the section of 0.6, pH dropped sharply to the value below ZPC of kaolin reported [23,24]. Therefore, the direction of EOF maintained constant in the region from the section of 0.6 to cathode, but the direction was reversed in the region from the section of 0.6 to anode at some time in the treatment. The phenomenon was particularly obvious for NaOH (T1),  $\beta$ -CD

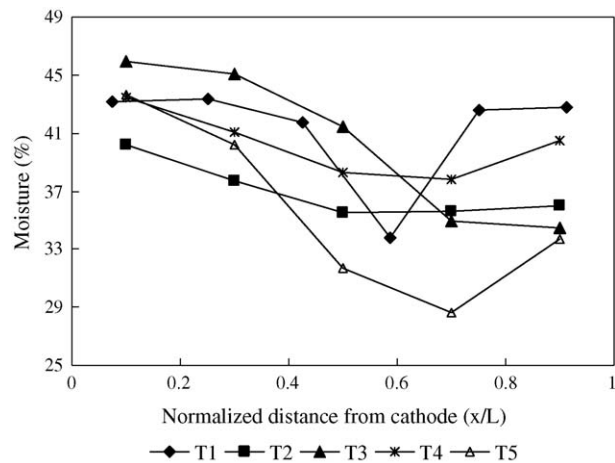


Fig. 5. Distribution of moisture in the soils.

(T4) and real soil (T5). This result was responsible for the slight increase of cumulative EOF in the later stage. In addition, electric current was also affected by moisture. The sequence of the lowest moisture in all the tests was:  $\text{T5} \gg \text{T1} > \text{T3} > \text{T2} > \text{T4}$ . The lowest moisture appeared in T5 (section 0.7), which further interpreted the low electric current in T5 in the later stage.

### 3.5. Distribution of HCB in the soils

HCB is highly insoluble in water and is preferential sorped on soils. It is therefore difficult to drive it out by electroosmosis. In order to realize the EK remediation of HCB contaminated soils, the first step is to desorb HCB from soils and dissolve it in the pore solution. Surfactants have both hydrophilic and lipophilic groups, so it can improve the solubilities of many HOCs [22–24]. In this study, a preliminary experiment was conducted to investigate the enhanced desorption of HCB from kaolin by the addition of Tween 80 (1%) and  $\beta$ -CD (1%). The desorption of HCB (the mass of HCB in aqueous divided the initial mass of HCB in kaolin) was obtained as 37.7% and 8.5% for Tween 80 and  $\beta$ -CD, respectively. The critical micelle concentration (CMC) of Tween 80 is as low as 0.0092 mmol/L [32]. About 1% Tween 80 is 829.3 times of CMC. The formation of large quantity of micelle increased the affinity of Tween 80 and HCB, which resulted in the transfer of HCB from kaolin to aqueous solution.  $\beta$ -CD has a hydrophilic shell and a toroidal-shaped, apolar (hydrophobic) cavity. It may form water-soluble inclusion complexes by incorporating suitable sized low-polarity molecules in their cavities [33]. Therefore, the relative size of the cavity versus HCB molecular is a critical parameter affecting the desorption of HCB. The cavity of  $\beta$ -CD and the volume of HCB molecular are  $0.341 \text{ nm}^3$  [33] and  $0.368 \text{ nm}^3$  [34], respectively, which indicates that only partial HCB molecular can enter into the cavity. This was the reason of the lower desorption ability of  $\beta$ -CD than that of Tween 80. In an EK system, when a low electric field was applied, the desorption behavior of HCB might be influenced. Since the electric field exerts polarizing forces on water molecules, the effect was negative [28]. Such a force worked against the solubilization of hydrophobic organic

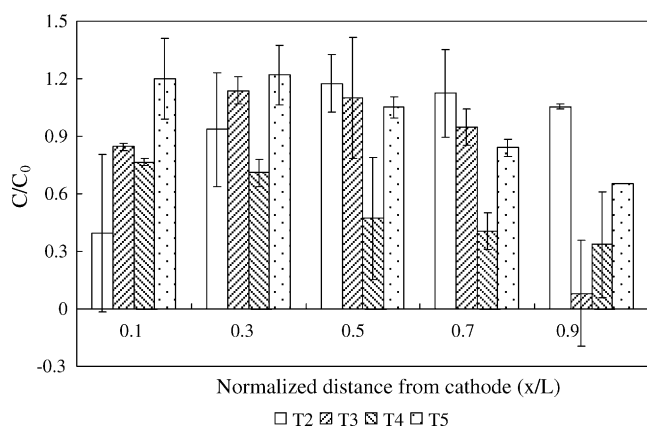


Fig. 6. Distribution of HCB in the soils.

contaminants. The effect was confirmed to be minute by many researchers [28,29].

At the end of EK processes, the profiles of the distribution of HCB from cathode to anode are shown in Fig. 6. The result of NaOH (T1) was deleted due to its ineffectiveness. Fig. 6 shows that the movement of HCB with  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  (T2) was minimal in all the regions but near cathode. The soil was compact in T2, so the effect of electrophoresis was negligible [19]. Electromigration has little effect since HCB is apolar and cannot be ionized in this system. Electroosmosis is the only possible force for the movement of HCB. However, HCB was hydrophobic and nearly insoluble in water, it was highly difficult to desorb it from kaolin, dissolve it in the soil pore fluid and flush it out by electroosmosis. The lower concentration close to cathode was probably because of the reductive dechlorination of HCB on carbon cathode [30,31].

When Tween 80 was added to the buffer (T3), HCB was moved to the middle section and accumulated there. Tween 80 can significantly enhance the desorption of HCB from kaolin, as a result, the movement of HCB was more obvious in T3 than in T2. Nevertheless, the sorption of Tween 80 on kaolin was found to be great [25]. Moreover, the sorbed Tween 80 on kaolin was rather beneficial to retard the desorption of HCB [32]. In the EK cell, the system consisted of kaolin, sorbed Tween 80, aqueous Tween 80 micelle in soil pore fluid, aqueous Tween 80 monomer in soil pore fluid and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  in soil pore fluid. Aqueous Tween 80 monomer and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  in soil pore fluid have negligible contribution to the desorption and dissolving of HCB. HCB was present at three possible forms: sorbed HCB on kaolin, sorbed HCB on sorbed Tween 80 on kaolin and sorbed HCB on aqueous Tween 80 micelle in soil pore fluid. Therefore, the distribution of Tween 80 on kaolin and soil pore fluid highly influenced the desorption and dissolving of HCB. The increase of the aqueous Tween 80 micelle in soil pore fluid and the decrease of sorbed Tween 80 on kaolin led to the enhancement of the desorption and dissolving of HCB. With the entering of Tween 80 into the soil matrix, Tween 80 was first sorbed on the soil close to anode until the soil was saturated. Then, the soil in the next region began to interact with Tween 80. The maximal sorption capacity of Tween 80 by kaolin was reported to be about 38 mg/g [32]. The cumulative EOF in

T3 was 196 mL. Suppose that the flushing solution that entered into the soil contained 1% Tween 80 and the change of fluid volume due to the change of the soil moisture was neglected, the quantity of Tween 80 that entered into the soil was 1.96 g. The kaolin used was about 100 g, which could sorb 3.8 g Tween 80. This indicated that all Tween 80 that entered into the soil was sorbed and entrapped. However, the soil close to anode suffered sufficient Tween 80 that exceeded its maximal sorption capacity. After the saturation of Tween 80 in this region, the aqueous Tween 80 micelle in soil pore fluid increased with the further entering of anodic flushing solution. Consequently, HCB in this region could be desorbed and dissolved to the aqueous Tween 80 micelle, and further moved with the pore fluid. With the movement of the fluid, Tween 80 would be sorbed by the soil in the next region. So the aqueous Tween 80 micelle reduced and the sorbed Tween 80 increased. The sorbed HCB on the aqueous Tween 80 micelle would be transformed to the sorbed HCB on the sorbed Tween 80 on kaolin. So an accumulation of HCB in the middle section was observed. The lower concentration of HCB in the section close to cathode than the initial concentration was possible due to the reductive dechlorination of HCB on carbon cathode [31,32]. As discussed in Section 3.2, the sorption of Tween 80 on kaolin reduced the absolute value of  $\zeta$  potential. This would result in the decrease of electrophoresis, suggesting a minimal effect of electrophoresis on the movement of HCB.

When  $\beta$ -CD (T4) was used, the gradual increase of HCB concentration from anode to cathode was observed. But all the values of  $C/C_0$  were below 1, which implied that HCB was partly removed from the soil. Compared with T3, T4 achieved less cumulative EOF (105 mL versus 196 mL) and more significant enhancement on the EK movement of HCB. Similarly, the possible form of HCB in T4 included sorbed HCB on kaolin, enclosed HCB with sorbed  $\beta$ -CD on kaolin, enclosed HCB with aqueous  $\beta$ -CD in soil pore fluid and dissolved HCB in  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  aqueous solution. The sorption of cyclodextrins on soils is minute [22–33,35] and the dissolving of HCB in  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  aqueous solution is minimal. As a result, the sorbed HCB on kaolin and enclosed HCB with aqueous  $\beta$ -CD were the competitive form of HCB. With the continuous entering of anodic flushing solution,  $\beta$ -CD moved from anode to cathode, the soil in all the sections interacted with the pore fluid containing  $\beta$ -CD. It has been confirmed that  $\beta$ -CD could enhance the desorption and dissolving of HCB. Therefore, the sorbed HCB on kaolin was increasingly desorbed from kaolin and dissolved in the pore fluid, which was then driven out by electroosmosis. The soil close to anode suffered the largest quantity of  $\beta$ -CD, then the next section, so the HCB in the section close to anode was remarkably desorbed, dissolved and moved, and the concentration of HCB increased from anode to cathode. With the increasing of cumulative EOF, HCB was removed little by little.

For the real HCB-contaminated soil (T5), the gradual increase of HCB concentration from anode to cathode was also observed. However, the values of  $C/C_0$  were above 1.0 in the region close to cathode, which implicated that HCB was accumulated there. Compared with kaolin, the real soil had higher values of OC (3.58 g/kg versus 0 g/kg) and CEC (5.71 mmol/100 g versus 1.85 mmol/100 g). Organic matter is effective to sorb HCB

Table 3  
Mass balance of HCB

Process	HCB mass ( $\mu\text{g}$ )			Discrepancy (%)
	Initial	Final in soil	Final in EOF	
T2	4262	3773	2	12.7
T3	3737	3291	7	11.9
T4	3655	2477	31	32.2
T5	4104	4056	10	1.2

and  $\beta$ -CD. The sorption of  $\beta$ -CD in this case was similar to the sorption of Tween 80 on kaolin (T3). The sorbed  $\beta$ -CD on the organic matter in kaolin could sorb HCB and retard the desorption of HCB. In this system, the main form of HCB included sorbed HCB on kaolin, sorbed HCB on the organic matter on kaolin, sorbed HCB on the sorbed  $\beta$ -CD on the organic matter, sorbed HCB on the aqueous  $\beta$ -CD in soil pore fluid. Due to the sorption of  $\beta$ -CD on the organic matter, the content of  $\beta$ -CD in the soil pore fluid decreased from anode to cathode. The reason and mechanism of the EK movement of HCB in T5 was proposed to be the same as that in T3.

### 3.6. Mass balance calculation

At the end of the EK processes, the mass balance of HCB was calculated. The mass of HCB in each slice was calculated by the concentration of HCB multiplied by its weight. The sum was the total mass of HCB in the soils. The mass of HCB in the cumulative EOF was obtained by the concentration of HCB multiplied by its volume. The results of mass balance are listed in Table 3. All the discrepancies were acceptable except the test with  $\beta$ -CD and kaolin (T4). The discrepancy of T4 probably resulted from the cathode reduction of HCB on carbon electrode [30,31]. The reductive dechlorination of HCB on the cathodes, such as Hg, Pb and glass carbon, was found in micellar aqueous solution of Triton-SP by Merica et al. [30]. In the EK remediation of hexachlorobutadiene, hexachlorobutene isomers and octachlorobutane contaminated soil conducted by Rohrs et al. [31], the removal of the contaminants was also observed, particularly for octachlorobutane (89.2% removal). The authors [31] assumed that the removals of the substances were owing to the presence of 'microconductors' inside the soil matrix. These microconductors could lead electrode reactions to the chlorinated hydrocarbons. Furthermore, the decrease of the substances was found to be the highest in the region close to cathode [31], where high pH and reducing environment existed. Therefore, it was reasonable to suppose that the large discrepancy in T4 was due to the reduction of HCB in the vicinity of cathode.

## 4. Conclusions

This study investigated the EK behavior of hexachlorobenzene (HCB) contaminated clayed soils enhanced by Tween 80 and  $\beta$ -cyclodextrin ( $\beta$ -CD). Negligible HCB movement was observed when NaOH or  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer was used as anodic flushing solution without addition of facilitating agent.

With the addition of Tween 80 or  $\beta$ -CD to  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer, obvious HCB movement was achieved. Although  $\beta$ -CD led to a less desorption of HCB from kaolin than Tween 80, the removal of HCB with  $\beta$ -CD was much higher than that with Tween 80 in the EK system. Tween 80 could be sorbed by kaolin more than  $\beta$ -CD, which was responsible for the result. The mechanism of the movement of HCB was proposed as the enhanced desorption of HCB from soil, the dissolving of HCB in the soil pore fluid and the movement of HCB with the electroosmotic flow from anode to cathode. Obvious movement of HCB was also observed in the EK treatment of real HCB-contaminated clayed soil enhanced by  $\beta$ -CD. It is an alternative approach to use facilitating agents such as  $\beta$ -CD to enhance the EK movement of HCB in the contaminated clayed soils.

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