



# Hydroxypropyl- $\beta$ -cyclodextrin enhanced electrokinetic remediation of sediment contaminated with HCB and heavy metals

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## ABSTRACT

This work aimed to evaluate hydroxypropyl- $\beta$ -cyclodextrin (HPCD) enhanced electrokinetic (EK) remediation of aged sediment contaminated with hexachlorobenzene (HCB) and heavy metals (Zn and Ni) in bench-scale. Deionized water, 5 and 20% HPCD were used as anodic flushing solutions, respectively, with constant voltage gradient of  $1.0 \text{ V cm}^{-1}$ . The experimental results showed that HCB migration and removal from sediments was significantly affected by HPCD concentrations and cumulative electroosmotic flow (EOF). In test with deionized water, only 7% of HCB was removed with 4.0 pore volumes (PVs) of EOF, while 15–26% of HCB was removed with 2.5–4.5 PVs using 5% HPCD solution. With 20% HPCD solution, nearly 40% of HCB removal efficiency achieved with 2.6 PVs. For Zn and Ni, the mobilization was greatly dependent upon sediment pH. In all tests, heavy metals migrated from anode to cathode, and accumulated near cathode due to the high pH, with little removal efficiency. This study indicated that EK process combined with HPCD flushing and pH buffering was a good alternative for HCB removal from sediments, and other enhancement was needed for heavy metals removal.

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## 1. Introduction

Soils/sediments contaminated with mixed pollutants such as hydrophobic organic compounds (HOCs) and heavy metals are frequently found as a result of improper disposal and accidental spillage of toxic and hazardous chemicals from domestic, agricultural and industrial activities [1], and result in serious threat to the public health and environment. For example, in the vicinity of a point at Wuhan city central China, high concentrations of hexachlorobenzene (HCB) and heavy metals (Zn and Ni) have been detected in soils and sediments along a river due to wastewater discharge from a chemical plant [2]. The heavily polluted soils and sediments become a long-term source of pollution to groundwater and ecosystem. It is therefore of great importance to remediate those contaminants in subsurfaces. For the remediation technologies such as washing/flushing, bioremediation and solidification/stabilization, the low permeability of soils/sediments limits the application because of the hydraulic delivery difficulty of the reactive agents [3].

Electrokinetic (EK) technology has been proposed as a promising method for soils/sediments remediation, particularly for fine-grained media [4]. It has been proved of great potential to remove heavy metals and organic pollutants from low permeable subsurface [5–7]. Under a direct current (DC) electric field, the ionic

contaminants can be transported to the oppositely charged electrode by electromigration, and the soluble nonionic contaminants in pore fluid can be moved by electroosmosis. Increasing studies have been reported on EK treatment of contaminants from soils/sediments. In the case of heavy metals, many studies were performed to evaluate EK removal of lead, copper, zinc, cadmium, manganese and nickel from various soils [1,8–12], and significant mobilization of heavy metals was observed. Enhancement techniques such as cathode depolarization [8,11], addition of complexing agents [9], use of ionic exchange membranes [8,10] and polarity exchange [12] have also been proposed and implemented to improve the remediation efficiency. Meanwhile, EK cleanup of organic contaminants from soils/sediments was also extensively investigated. The relative soluble organic contaminants like *p*-xylene and trichloroethylene, were reported to be easily removed from soils by electroosmosis [13,14]. For the organic pollutants with low water solubility and high distribution coefficient on soils like HOCs, solubilizing agents such as cosolvents, surfactants and cyclodextrins were introduced to enhance the remediation [15–17], and satisfactory results were also addressed. However, the reported studies were focused on simultaneous EK removal of HOCs and heavy metals from contaminated soils was rarely evaluated [3], particularly for the contaminated field soils/sediments.

In this study, bench-scale EK experiments were conducted to evaluate simultaneous removal of HCB and heavy metals from aged contaminated sediment. Emphasis was put on the movement of HCB due to its high hydrophobicity and low mobility. Hydroxypropyl- $\beta$ -cyclodextrin (HPCD) was used as facilitating

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agent because it was effective to increase the desorption of HOCs with negligible adsorption on soils [18]. Our previous work also proved that  $\beta$ -cyclodextrin was effective to enhance the EK movement of HCB [16].

## 2. Materials and methods

### 2.1. Chemicals and materials

HPCD ( $\geq 98\%$ ) was purchased from Zibo Qianhui Fine Chemical Co. Ltd, Qingdao, China, without further purification. HCB (99%) was provided by Shanghai General Reagent Factory, Shanghai, China. All the other reagents were above analytical grade. Deionized water (18.2 M $\Omega$  cm) from a Millipore Milli-Q system was used for the preparation of solutions.

The test sediment was sampled from the bottom of a trench, where wastewater containing HCB and heavy metals discharged from a chemical plant has flowed for over 20 years [2]. The initial contents of HCB, Zn and Ni were measured as  $46.4 \pm 4.1$ ,  $2415 \pm 9$  and  $42.1 \pm 1.2$  mg kg $^{-1}$  dry sediment, respectively. The sediment was air-dried, ground and sieved by a 140-mesh screen (0.105 mm). The sample was stirred thoroughly to achieve uniform distribution. The analytic methods for the main characteristics of the sediments were introduced in our previous study [2]. The pH, zero point of charge (ZPC), electrical conductivity (EC), organic content (OC), cation exchange capacity (CEC) and porosity were determined to be 5.87, 2.78, 2.55 mS cm $^{-1}$ , 3.23%, 38.8 mmol 100 g $^{-1}$  and 0.55, respectively. And the fractions of particle size with 0.25–0.1, 0.1–0.05, 0.05–0.005, 0.005–0.001 and <0.001 mm were 1.2, 0.6, 25.9, 32.6 and 39.7%, respectively. The data shows that the sediment can be classified as silt clay according to the USDA triangle

### 2.2. Procedures and equipments

#### 2.2.1. Desorption experiment

Preliminary desorption experiments were performed to obtain adsorption/desorption information of contaminants in EK transport. Eight milliliter of solution of different concentrations of HPCD was added into 11 mL vial containing 0.5 g of sediment. The vials were sealed immediately and equilibrated on a reciprocating shaker at 150 rpm for 72 h ( $25 \pm 1$  °C). After equilibration, the samples were centrifuged at 4000 rpm for 30 min. The supernatant was further filtered through a 0.45  $\mu$ m acetic cellulose membrane. Two milliliter of filtrate was extracted with 3 mL of hexane for HCB analysis. Zn and Ni contents in solution were measured by atomic absorption spectrophotometry (AAS, WFX-110, Beijing Ruili

Analytical Instrument Co. Ltd.) after acidification by HNO $_3$ . Each measurement was conducted in triplicate.

#### 2.2.2. EK remediation

The EK remediation setup used in this study is shown in Fig. 1. The setup consisted of a cell, a power supply, two electrode compartments and reservoirs, and solution circulation system. The EK cell ( $\Phi 5$  cm  $\times$  L 10 cm) was made of plexiglass. Perforated graphite ( $\Phi 5$  cm  $\times$  L 0.7 cm) was used for both anode and cathode. The two electrode compartments were placed at each end of cell isolated from sediment by 100-mesh nylon mesh (0.149 mm) and filter paper. Peristaltic pumps were used to circulate electrolytes from reservoirs to compartments for adjusting the compartment solutions. The tube on the top of the electrode compartments acted as gas vent. The electroosmotic flow (EOF) in cathodic reservoir was measured with a scaled bottle, whose top was sealed with gummed tape to avoid the evaporation of water. The constant voltage was supplied by a DC power (GPC-3060D, Taiwan Goodwill Electronic Ltd., Inc., Taiwan), and the electric current was monitored with a multimeter.

Approximately 250 g of real contaminated sediment was mixed with 150 mL of deionized water. A fraction of the moist sediment was added into column and compacted with a glass rod to remove air bubbles and the procedure was repeated until the appropriate sediment column length was obtained. The anodic compartment, perforated graphite anode and the cell were assembled in turn. After the column was filled, a subsample of the remaining sediment was used to determine the initial water content. The wires and tubes were connected, and the electrode compartments were filled with solutions, circulated by peristaltic pumps. A constant voltage gradient of 1.0 V cm $^{-1}$  was applied in all tests, and the experiment was carried out at room temperature.

Parameters associated with each experiment are listed in Table 1. T1 was conducted to use 0.05 M of NaOH as anodic flushing solution, which served as the control test. T2, T3 and T4 were carried out to compare the EK behavior with or without controlling of anodic flushing solutions and different duration of 5% HPCD. T5 was conducted to evaluate the enhanced EK remediation of contaminated sediment enhanced by 20% HPCD.

### 2.3. Analysis

At the completion of EK experiments, the sediment was extruded from the EK cell and evenly divided into five sections along the length of the column, and then analyzed the spatial distribution of the pH, redox potential, EC, water content, HPCD as

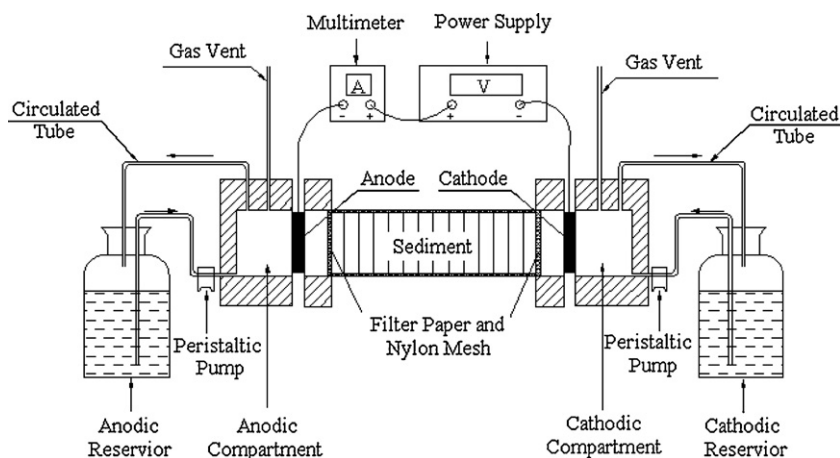


Fig. 1. Schematic of EK remediation setup.

**Table 1**  
Parameters associated with EK experiments.

Test number	Anodic flushing solution	Cathodic solution	Total duration (days)	Number of pore volumes
T1	0.05 M NaOH	Deionized water	10.5	4.0
T2	5% HPCD, 0.05 M NaOH	0.025 M H <sub>2</sub> SO <sub>4</sub>	10.5	2.5
T3 <sup>a</sup>	5% HPCD, 0.05 M NaOH	0.025 M H <sub>2</sub> SO <sub>4</sub>	10.5	3.9
T4 <sup>a</sup>	5% HPCD, 0.05 M NaOH	0.025 M H <sub>2</sub> SO <sub>4</sub>	21.0	4.5
T5 <sup>a</sup>	20% HPCD, 0.05 M NaOH	0.025 M H <sub>2</sub> SO <sub>4</sub>	21.0	2.6

<sup>a</sup> Denotes that the pH of anodic flushing solution was controlled with NaOH solution periodically during the EK process when pH was declined to neutral.

well as the residual HCB and heavy metals in sediments. Sediment water content was measured by drying the sample at 105 °C for 6 h. The wet samples were air-dried for about 48 h, ground and sieved by 60-mesh screen (0.250 mm). Sediment pH, redox potential and EC were measured with a pH meter (pH211, HANNA) and EC meter (DDS-307<sup>+</sup>, Chengdu Fangzhou Science and Technology Co. Ltd), respectively, with a ratio of sediment to water of 1:2.5 (w:v). HPCD in sediment pore fluid was analyzed by ultraviolet–visible (UV–vis) spectrophotometry [19]. The analytic method for HCB analysis has been provided in our previous work [2]. For Zn and Ni analysis in sediments, 0.5 g of sediment was digested with 7 mL of concentrated HNO<sub>3</sub> at 170 °C for 10 min, and analyzed by AAS. Each sample was prepared in triplicate. The procedure described by Tessier et al. [20] was adopted for analyzing the speciation distribution of Zn in contaminated sediments. The exchangeable, carbonate bound, Fe/Mn oxide bound, organic bound and residual Zn in sediments were measured as 16.5, 5.8, 48.4, 20.4 and 8.9%, respectively.

### 3. Results and discussion

#### 3.1. Electric parameter variation

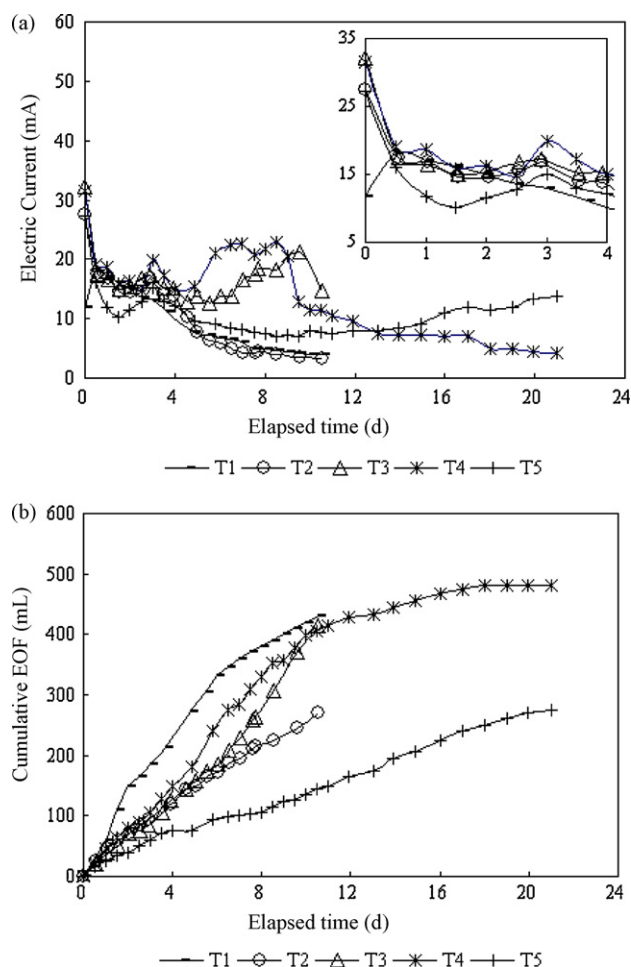
##### 3.1.1. Electric current

Electric current during the EK process is reported to be associated with the EC of soil/sediment pore solution, the composition of anolyte and catholyte, soil/sediment moisture and electrolysis reaction at the electrodes etc [5,16]. The change of electric current versus elapsed time during the experiments is shown in Fig. 2a. An initially maximal current was reached because of large quantity of ions in the pore solution [21]. Higher initial current was inspected in the tests with HPCD solution (T2–T5) than in control test (T1). It can be explained by the different cathodic solutions for the tests, wherein 0.025 M H<sub>2</sub>SO<sub>4</sub> solution in T2–T5 offered more ions than deionized water in T1. Without pH control (T1 and T2), the current gradually declined during EK process, and ultimately attained a relatively stable value. In the tests with 5% HPCD (T3 and T4), a significant increase in current was observed after NaOH was added into anolyte, but not obvious in the test with 20% HPCD (T5). When Na<sup>+</sup> and OH<sup>-</sup> were introduced, OH<sup>-</sup> neutralized H<sup>+</sup> generated at anode, while Na<sup>+</sup> electromigrated toward cathode, which led to an increase of current. The slight increase of current in T5 with addition of NaOH was possibly due to the disturbance of ions mobilization under high concentration of HPCD solution. It is noted that the EC value of 5% HPCD in 0.05 M NaOH solution was 9.61 mS cm<sup>-1</sup>, which was greatly decreased to 5.82 mS cm<sup>-1</sup> for 20% HPCD in 0.05 M NaOH solution. It was inferred that mobility of ions was highly inhibited in high content of HPCD solution, resulted in smooth current changes in T5 when NaOH was added.

##### 3.1.2. Cumulative EOF

Generally, removal of HOCs from sediments could be highly determined by the EOF rate generated during the EK process. As shown in Fig. 2b, the flow behavior was dependent on the purging solutions and elapsed time. Within 10.5 days EK process, maximum EOF was observed within control test (430 mL for T1), and

followed by the tests with 5% HPCD (270, 415, 405 mL for T2, T3, T4, respectively) and 20% HPCD (145 mL for T5). With increasing operating time, cumulative EOF in T4 and T5 increased continuously, and reached 480 and 275 mL, respectively. The maximal EOF in T1 during the first 10.5 days was attributed to the higher dielectric constant of water according to H–S theory [22]. For T2–T4, similar variation of cumulative EOF was observed in the first 3 days under identical conditions, but for T3 and T4 with pH control at the anode exhibited more cumulative EOF compared to T2 after 3 days. Several other researchers have also observed similar results [21,23,24]. When NaOH was introduced into anodic reservoir in EK process, H<sup>+</sup> generated at anode by the electrolysis reaction was neutralized and kept the sediment pH at high level. Higher pH leads to more negative  $\zeta$  potential [5], resulting in the increase of the cumulative EOF. In T5, cumulative EOF was smaller than the other experiments. The low dielectric constant and high viscosity with 20% HPCD solution was responsible for the result [3]. By comparing Fig. 2b with Fig. 2a, it is noteworthy that the variation of cumulative EOF was greatly



**Fig. 2.** Variation of (a) electric current and (b) cumulative EOF with elapsed time.

correlated to the changes of electric current. High current provides substantial momentum for the surrounding fluid molecules, which results in a significant volume of EOF [23].

### 3.2. Variation of sediment characteristics

#### 3.2.1. Sediment pH

During the EK process,  $H^+$  and  $OH^-$  are generated at anode and cathode, respectively by the electrolysis of water. In a DC electric field,  $H^+$  electromigrates toward cathode and  $OH^-$  electromigrates toward anode, which result in the low and high pH conditions in anodic and cathodic regions, respectively [5,22].

As shown in Fig. 3a, for the tests without pH control, control test (T1) and 5% HPCD test (T2) have similar pH distribution along the column. Sediment pH dropped to about 3 near anode and increased to about 10 near cathode. For most sections, the pH value was lower than the initial pH value, which was resulted from the higher mobility of  $H^+$  relative to  $OH^-$ . In addition, EOF could accelerate  $H^+$  transport from anode to cathode and inhibit electromigration of  $OH^-$ . With periodic addition of NaOH into anolyte, sediment pH in most sections of column were maintained at a high level in T3 and T5, which was beneficial for creating appreciable EOF rates across sediment. However, under the same experimental conditions, lower pH was observed in T4 at anodic regions compared to T3 and T5. The inconsistent distribution of pH between T3–T5 was ascribed to the blockage of the graphite anode holes with sediments in T4, which was possibly attributed to the migration of fine sediment particles toward anode under electric field with larger electric current and longer running time. As a result,  $H^+$  generated at anode was hardly neutralized by  $OH^-$  in anodic compartment, which led to more  $H^+$  electromigration into sediments. Even though pH at anode was controlled with NaOH, sediment pH near anode was still declined at the end of the tests. Sediment acidification occurred at anodic regions attributed to heavy metals desorption and removal from sediment, but possibly inhibited HCB transport across sediments as EOF rate may be decreased. Thus, rational adjusting sediment pH was important for EK treatment of both heavy metals and HOCs from sediments.

#### 3.2.2. Sediment redox potential

Fig. 3b presents the final sediment redox potential distribution in the column after EK treatment. The initial redox potential of sediment is 168 mV. At the completion of the EK processing, sediment redox potential decreased from anode to cathode across the column, and the distribution of redox potential showed opposite trend as pH distribution in Fig. 3a. Similar results were also reported by Reddy et al. [25,26] and Shen et al. [27]. As sediment redox potential increased in anodic regions with low pH values, an oxidative environment was generated, which was beneficial to heavy metals desorption from sediments [28]. Contrarily, reductive environments formed close to the cathode were not helpful for heavy metals transport. Both low pH and high redox potential contribute to release heavy metals from sediment particles and speed up the EK remediation effect, especially near anode [28].

#### 3.2.3. Sediment EC

Fig. 3c shows sediment EC distributions after EK treatment. The initial sediment EC was  $2.55 \text{ mS cm}^{-1}$ . After EK process, sediment EC changed significantly in all tests. Without NaOH addition during EK processing, sediment EC dropped sharply to the values from 0.10 to  $0.87 \text{ mS cm}^{-1}$  for control test (T1) and 0.21 to  $0.96 \text{ mS cm}^{-1}$  for the test with 5% HPCD (T2), respectively. The lowest sediment EC was observed in the middle column and increased at both ends. Water formation and heavy metals precipitation in this region were accountable for the decrease of EC. It is also found that sediment

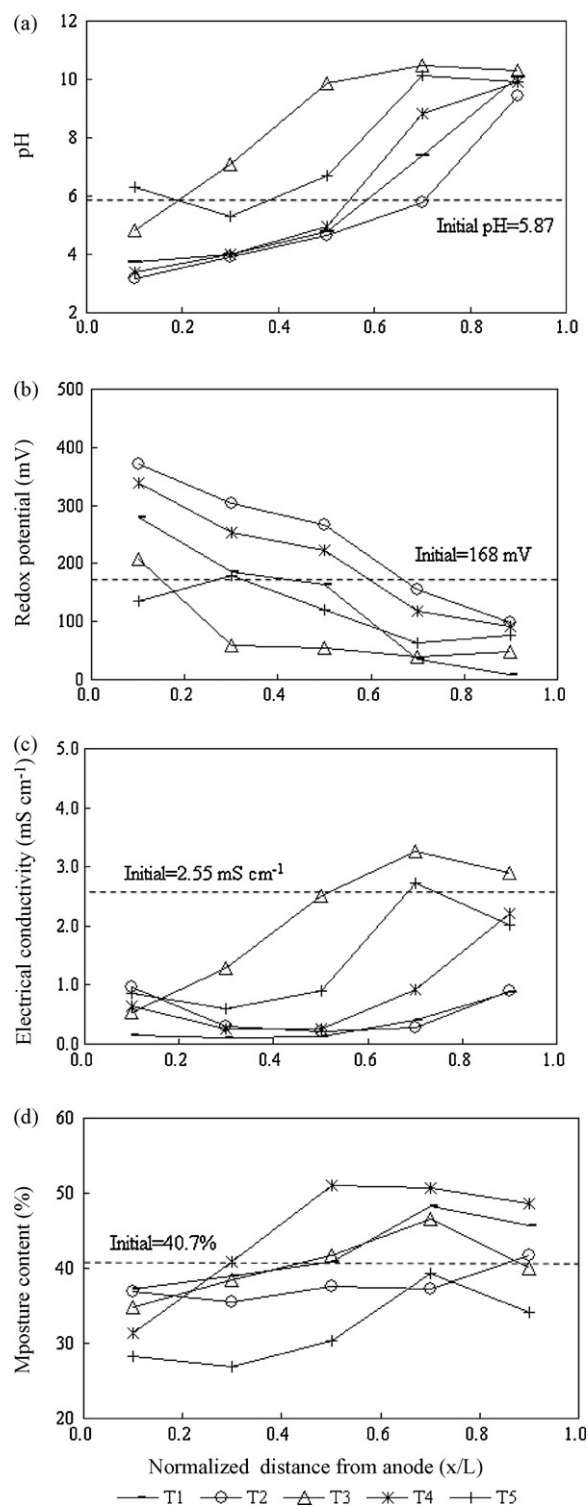


Fig. 3. Variation of sediment (a) pH, (b) redox potential, (c) EC and (d) water content.

EC near anode in T2 was slightly larger than in T1, which is due to the lower pH in T2 and more cations dissolved from sediments.

For the tests with the addition of NaOH, similar distributions of sediment EC were observed in T3–T5. In T3 and T5, sediment EC increased from anode to cathode except for the sections near cathode. The maximal ECs were  $3.27$  and  $2.73 \text{ mS cm}^{-1}$  for T3 and T5, respectively, at the normalized distance of 0.6 from anode, which exceeded the initial value. A slight decrease of EC occurred close to cathode, which was due to a slight decrease of pH in the regions. It

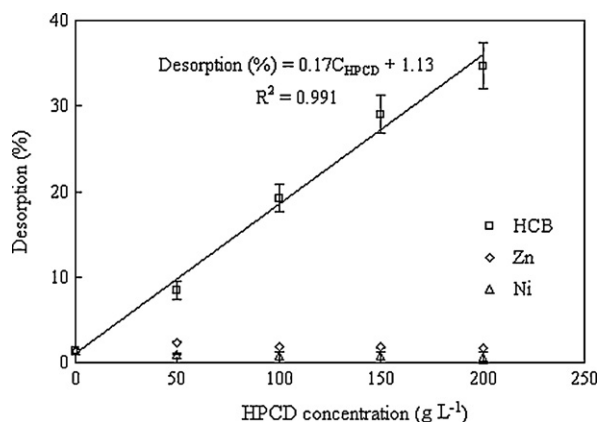


Fig. 4. Desorption of HCB and heavy metals from sediments by different HPCD concentrations.

is noticed that the distribution of sediment EC in T4 was similar to T1 and T2. Compared with T3 and T5, lower sediment EC in most sections of sediments was resulted from the blockage of graphite anode holes, which further inhibited the electrolyte into column. In all tests, the sequence of the lowest EC was: T5 > T3 > T4 > T2 > T1, which interpreted the corresponding electric current in the last stage.

#### 3.2.4. Sediment water content

The initial water content of sediments was 40.7%, and the variation of water content after EK treatment is shown in Fig. 3d. In all tests, low moisture regions occurred near anode and sediment water content clearly increased from anode to cathode, but decreased close to cathode except in T2. Similar results were observed in our previous study [16]. Change in water content was attributed to the variations of the EOF. In the test with 5% HPCD (T4), it was obtained that water content in most of the sections across the column increased after EK treatment. This could be attributable to the enhanced EOF as a result of high pH produced with pH control at anode. However, in the test with 20% HPCD (T5), it was observed that the water content of all the sediment specimens was lower than the initial value. Low dielectric constant with 20% HPCD solution was responsible for the decrease of EOF according to H-S theory [22], thus decreased the water content in sediments.

### 3.3. Transport of contaminants in sediments

#### 3.3.1. Enhanced desorption of contaminants from sediments

Prior to the EK tests, batch equilibrium experiments were conducted to evaluate the effects of HPCD on the desorption of HCB, Zn and Ni from sediments. Previous research has shown that modified CDs were potential to simultaneously remove organics and heavy metals from soils [29,30]. In this study, HCB desorption increased linearly with the increase of HPCD concentration ( $R^2=0.991$ ) (Fig. 4), which indicated the formation of a 1:1 HPCD–HCB inclusion complex. When  $200\text{ g L}^{-1}$  HPCD solution was used, the maximal HCB desorption was obtained as about 35%. The low-polarity cavity of HPCD provided a capacity to increase the apparent solubility of HCB [15]. In contrast, the influence of HPCD concentrations on Zn and Ni desorption was negligible.

#### 3.3.2. Distribution of HPCD and HCB in sediments

The profiles of HPCD and HCB in sediment upon the completion of EK tests are shown in Fig. 5. When 5% HPCD was used as anodic flushing solution (T2–T4), HPCD transported throughout the column with cumulative EOFs of 2.5, 3.9 and 4.5 PVs for T2, T3 and T4, respectively. It was observed that HPCD concentra-

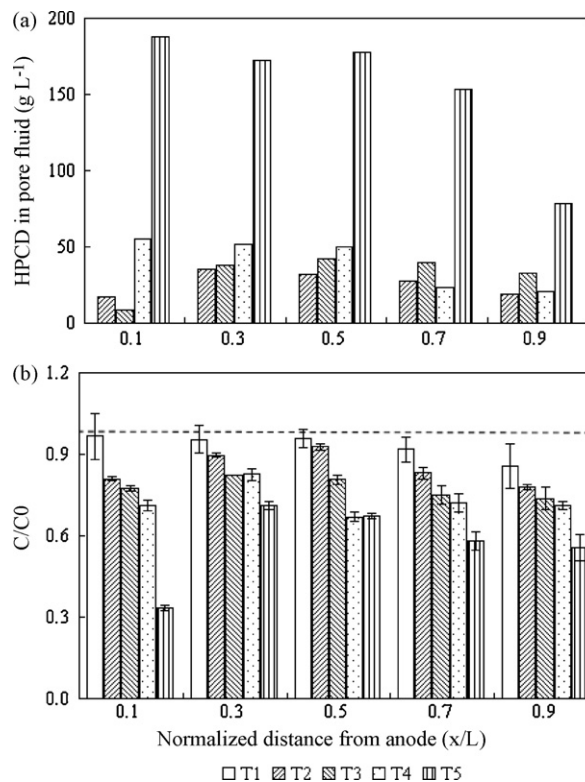


Fig. 5. Distributions of (a) HPCD in sediment pore fluid and (b) HCB in sediments.

tion of pore fluid in T4 was larger than in T2 and T3 near anode. In the test with 20% HPCD (T5), the cumulative EOF corresponds to approximately 2.6 PVs and HPCD concentration in sediment pore fluid near anode was  $188\text{ g L}^{-1}$  and decreased to  $78\text{ g L}^{-1}$  in sediment sections near cathode (HPCD concentration was determined by the amount of HPCD and water content in sediment pore fluid). Little sorption on sediments and negligible blockages in sediments pores [18] enable HPCD solution successful transport across sediments by electroosmosis, which resulted in a better sediment–solution–contaminant interaction and facilitated HCB desorption from sediments.

Fig. 5b displays the normalized HCB concentration in sediments upon the completion of EK tests. The movement of HCB with deionized water (T1) as anodic flushing solution was minimal in all the sections but near cathode. As HCB was strongly adsorbed on sediments, its movement by electroosmosis was rather difficult. 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 [16,31].

When 5% HPCD was added to the anolyte (T2), it is found that HCB concentration increased gradually from anode to middle, and decreased toward the cathode. But all the values of  $C/C_0$  were below 1, which implied that HCB was partly removed from sediments. The sediment close to anode suffered the largest quantity of HPCD and better soil–solution–contaminant interaction, which resulted in remarkable desorption and movement of HCB in the sections [16]. Meanwhile, low pH in the section close to anode could cause clay particles to have an open structure and hence enhance HCB desorption [21]. The decreased HCB concentration occurred near cathode was also possible attributed to the reductive dechlorination of HCB on carbon cathode [16,31]. With pH control in anolyte (T3) and increased operating time (T4), more cumulative EOF was obtained, which improved the movement of HCB in sediments. It was deduced that more sorbed HCB in sediments could interact with more cumulative EOF containing HPCD. Hence, HCB

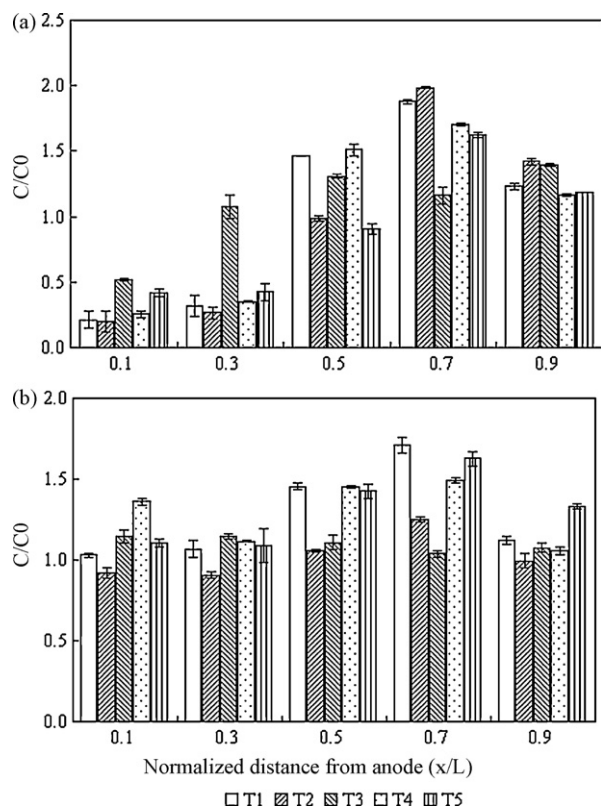


Fig. 6. Distribution of (a) Zn and (b) Ni in sediments.

desorption from sediments was enhanced, and the dissolved HCB in the pore fluid was then driven out by electroosmosis.

In the test with 20% HPCD (T5), similar HCB distribution was observed as with 5% HPCD tests. Compared with T4, even though less EOF was produced in T5, significant mobilization of HCB was observed in sediments, particularly near anode with normalized HCB concentration of about 0.3. Researchers found that HOCs removal was dependent on the HPCD concentrations [3,15]. A high HPCD concentration in the pore fluid provided more apolar cavities of cyclodextrin to accommodate HCB molecules, which resulted in enhanced desorption and dissolving of sorbed HCB into pore fluid from sediments.

At the end of each test, HCB removal efficiency was calculated from the total initial HCB mass present in sediments and the final mass in sediments and electrode compartments. In control test (T1), only about 7% of HCB was removed from the sediment. For comparison, the 5% HPCD purging solution showed approximately 15, 20 and 26% removal for T2, T3 and T4, respectively. In T5 with 20% HPCD, HCB removal was approximately 40%. These results confirmed that HPCD could enhance HCB desorption from sediments. Further removal of HCB from the contaminated sediments could be possibly attained with longer EK operating time as a result of obtaining more EOF with HPCD solution. The results obtained from this preliminary study also show that an EK process combined with HPCD flushing and pH buffering may be a good remediation alternative for removing HCB from low permeable sediments.

### 3.3.3. Distribution of heavy metals in sediments

Fig. 6 shows the normalized Zn and Ni concentrations in sediments at the end of EK tests. It can be seen from Fig. 6a that significant mobilization of Zn was observed in all tests. Large amount of Zn was transported from anodic sections and accumulated near cathode. The normalized Zn concentration was below

0.5 at the normalized distance of 0.1–0.3 for T1, T3, T4 and T5, and increased to above 1.5 except T3. However, little Zn was removed from sediments, about 10, 14, 6, 4 and 2% removal for T1–T5, respectively. It was noted that HPCD added in anodic purging solution did not improve the Zn removal efficiency, which was consistent with the results discussed in Section 3.3.1.

The mobilization of Zn across sediments was mainly dependent upon pore fluid pH [32]. It was reported that the limit pH controlling Zn desorption from sediment was about 6.0–6.5 [33]. As initial sediment pH was 5.87, Zn could be slightly desorbed from sediments and be present in pore fluid as positively charged ions. Under the DC electric field, Zn could be transported toward cathode. With sediment acidification near anodic regions as a result of water electrolysis at anode, more adsorbed Zn released into pore fluid and transported forwards by electromigration and electroosmosis. However, due to the significant amounts of OH<sup>-</sup> generated at cathode, sediment pH in the sections near cathode increased, causing Zn precipitation and limiting its removal from sediments. Meanwhile, Zn might exist as HZnO<sub>2</sub><sup>-</sup> in pore fluid closest to cathodic regions within high pH and electromigrated toward anode. Consequently, less Zn in sediments could be moved out during EK process, resulting in little removal efficiency.

According to the speciation distribution of Zn in sediments, the exchangeable fraction was about 16%, and Fe/Mn oxide bound and organic bound fraction accounted for about 69%. As reported by Zhou et al. [11] that most of exchangeable Zn could be effectively transported toward cathode under the electric field, and the fractions of Fe/Mn oxide bound and organic bound Zn were difficult to move, even with increased applied voltage. This suggested that only a small part of Zn could be transported across sediments during EK process herein. Although an acidic front developed in sediments from anode toward cathode could possibly increase the removable fraction of Zn, more hydroxide Zn was formed from the exchangeable fraction in cathodic high pH regions, ultimately resulting in little Zn removal efficiency.

The mobilization of Ni across sediments was not significant compared to Zn. It was observed that Ni was slightly migrated from anode toward cathode and accumulated at the normalized distance of 0.5–0.7 from anode, except in T3. As reported by Capuyns et al. [33] that the limit pH controlling Ni desorption from sediment was about 5.0–6.0, which was smaller than the limit pH of Zn, suggesting that Ni was more difficult to release from sediments as compared to Zn. And it was also found that the potential mobility of Ni was slower than Zn under the same acidic condition. The lower Ni desorption efficiency from sediments caused insignificant Ni mobilization.

Therefore, enhancement techniques such as cathode depolarization, pre-treatment of sediment with acidic solution [34] are considered to enhance the removal efficiency of heavy metals from sediments.

## 4. Conclusions

In this study, bench-scale EK experiments were conducted to evaluate simultaneous removal of HCB and heavy metals from real aged contaminated sediment enhanced with HPCD and electrolyte conditioning. The main conclusions can be drawn as follows:

- (1) Within 10.5 days EK process, a cumulative EOF of 4.0 PVs was achieved in control test, followed by 2.5 and 3.9 PVs for 5% HPCD tests without/with pH control, respectively. And within 21 days, 4.5 and 2.6 PVs were also obtained for 5 and 20% HPCD test with pH control, respectively. It was concluded that more cumulative EOF could be achieved by pH control and increased operating time.

- (2) Upon the completion of EK test, sediment characteristics were significantly changed. Sediment pH reduced near anode even with addition of NaOH into anolyte, and increased near cathode. The distribution of redox potentials followed the opposite trend to pH distribution. Sediment EC in most sections markedly decreased, and sediment water content clearly increased from anode to cathode. According to HPCD distribution, it was showed that HPCD was successfully transported across sediments by electroosmosis.
- (3) HCB migration and removal from sediments was dependent upon cumulative EOF and HPCD concentrations. In test with deionized water, little HCB movement was observed and only about 7% of HCB was removed from sediments with 4.0PVs of EOF. With HPCD solution and anolyte conditioning, obvious movement of HCB from anode to cathode across sediments was observed during EK process, particularly in test with 20% HPCD, nearly 40% of HCB was removed with 2.6PVs of EOF. It was encouraging that sustained high EOF with HPCD solution was able to achieve great removal of HCB from sediments.
- (4) The removal of heavy metals was greatly dependent upon sediment pore solution pH. In all tests, significant mobilization of Zn from anode toward the cathode was found, and most was accumulated close to the cathodic regions due to high pH condition, while the mobilization of Ni was not significant compared to Zn. As a result, little amount of heavy metals was removed from sediments.
- (5) This study inferred that EK process combined with HPCD flushing and pH buffering is feasible to remove HCB from sediments, and enhancement techniques such as cathode depolarization, pre-treatment method should be considered to improve the removal efficiency of heavy metals.

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