



Solubility-enhanced electrokinetic movement of hexachlorobenzene in sediments: A comparison of cosolvent and cyclodextrin

Jinzhong Wan, Songhu Yuan, Jing Chen, Taiping Li, Li Lin, Xiaohua Lu*

Environmental Science Research Institute, Huazhong University of Science and Technology, Wuhan 430074, PR China

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ABSTRACT

Though solubility-enhanced electrokinetics (EK) has been investigated in remediation of soils contaminated with hydrophobic organic chemicals (HOCs), few comparative studies were performed regarding the effect of varied solubilizing agents on both EK parameters and contaminant removal. In this study, performances of two solubilizing agents, ethanol and methyl- β -cyclodextrin (MCD), were compared in terms of either EK parameters or enhancement of hexachlorobenzene (HCB) movement in real contaminated sediments. Six bench-scale EK tests were conducted under a voltage gradient of 2 V cm^{-1} for 14 or 21 d. Results reveal that ethanol had a more negative effect on cumulative electroosmotic flow (EOF) than MCD. Furthermore, the distribution of ethanol in the sediment upon the completion of EK tests was lower than that of MCD. The movement of HCB in sediments was observed to increase with increasing concentrations of ethanol or MCD. Test with 50% ethanol exhibited the highest performance, followed by test with 50 g L^{-1} MCD. The different performance of HCB removal for tests with varied solubilizing agents was found to be a combined effect of the distribution of solubilizing agents in sediments, the dissolution of HCB by pore liquid and the quantity of cumulative EOF. Finally, an integrated consideration of both EK parameters and contaminant removal suggests that MCD can perform better than ethanol for a long-term field application.

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1. Introduction

The continuous release of polychlorinated aromatic hydrocarbons (PAHs), such as hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and dioxin, has posed great threat to public health and the environment [1,2]. Due to their high hydrophobicity, PAHs are eventually accumulated in soils or sediments, making the sediments long-term sources of contaminants that are directly associated with water pollution [3,4]. As a consequence, remediation of these PAHs contaminated sediments is of great significance.

Electrokinetic (EK) remediation is considered as a feasible and cost-effective technique especially for low permeable soils [5–7]. It has shown great potential to remove heavy metals and soluble organic pollutants from soils [8–11]. Unfortunately, the EK removal of hydrophobic organic chemicals (HOCs) from soils is rather difficult due to the poor dissolution and minimal desorption efficiency. The removal can be greatly enhanced with the aid of solubilizing agents such as surfactants [12,13], cosolvents [14] and cyclodextrins [15]. However, increasing reports

have suggested that the dramatic adsorption of surfactants on soils/sediments especially with high organic contents and the bio-toxicity of the adsorbed surfactants limit their field application [16,17]. Comparatively, cyclodextrins and organic cosolvents offer significant advantages in the field of EK soil remediation [17].

Although EK removal of HOCs from soils enhanced by organic cosolvents and cyclodextrins has been reported increasingly, sparse attention was paid to the comparison of the two solubilizing agents regarding their effect on EK parameters and HOCs removal. In addition, more information is needed in the EK remediation of real contaminated sediments with PAHs, which is more challenging than kaolin, a commonly used model clayed soil.

The purpose of this study is to investigate the comparative performance of cyclodextrins and organic cosolvents on the enhancement of EK removal of PAHs from fine-grain sediments. Real sediments contaminated with HCB for decades were used, and ethanol and methyl- β -cyclodextrin (MCD) were chosen as representative cosolvent and cyclodextrin, respectively. Various EK parameters, as well as the distribution of the solubilizing agents and residual HCB in the sediments were measured. These results were interpreted in terms of the different effects of the two facilitating agents on EK parameters and essentially, the performance of HCB removal.

* Corresponding author. Tel.: +86 27 87792159; fax: +86 27 87792159.
E-mail address: hust-esri@hotmail.com (X. Lu).

2. Materials and methods

2.1. Chemicals and sediments

HCB (99.0%) was purchased from Shanghai General Reagent Factory, China. MCD (>98%), obtained from Wuhan Shenshi reagent Co. Ltd., was used without further purification. Ethanol (>99.7%) was above analytical purity. MCD and ethanol were selected from three cyclodextrins (β -cyclodextrin, hydroxypropyl- β -cyclodextrin and MCD) and four organic cosolvents (methanol, ethanol, acetone and acetonitrile), respectively, considering their higher performance and lower toxicity, according to preliminary experiments of HCB solubilization. The sediments were sampled from the bottom of a trench, where wastewater containing HCB from a chemical plant had been discharged for decades. The sediments were air-dried, ground and passed through a 0.105 mm sieve. The concentration of HCB in the sediments was determined as 14.3 mg kg⁻¹. The main physicochemical characteristics in Table 1 reveal that the sediment is highly clayed, with a relatively high organic content of 4.1%.

2.2. Enhanced desorption of HCB by ethanol and MCD

Prior to the EK test, batch equilibrium experiments were conducted to investigate the performance of MCD and ethanol on HCB desorption from the sediments. The volume fraction of ethanol was 0–50%, and the concentration of MCD was 0–100 g L⁻¹. A total of 0.5 g of sediment was mixed with 5 mL of ethanol or MCD solutions in 10 mL glass tubes, sealed with Teflon screwed lines caps. The tubes were then shaken end-over-end in a reciprocating shaker at 25 ± 1 °C for 72 h. The suspension was centrifuged at 4000 rpm for 10 min and passed through a 0.45 μm filter membrane to separate the solid from solution. A total of 2 mL of the filtrate was extracted by 1 mL of hexane, and the concentration of HCB was determined by gas chromatogram (GC) (details in Section 2.4).

2.3. EK remediation

The experimental setup comprised a cylinder plexiglass cell (Ø 5 cm × 10 cm), two electrode compartments (100 mL), a direct current power supply (GPC-H, 30V/5A, Taiwan Guwei Electronic Ltd., Inc., Taiwan), a multimeter and a solution-circulation system, as shown in Fig. 1. Two perforated graphite plates (Ø 5 cm × 1 cm), used as anode and cathode, were clamped in the compartments and arranged 2 cm away from the cell. The compartments, cell and electrodes were assembled and tightened by steel screws. Working solution was circulated between the electrode compartment and the corresponding reservoir by a peristaltic pump at a flow rate of 10 mL min⁻¹. For the test with working solution circulation system

Table 1
Main physical–chemical properties for the sediments.

Main properties	Value	Method or instrument
Particle size (mm)		
0.25–0.10 (%)	1.2	TM-85 soil densimeter
0.10–0.05 (%)	0.6	
0.05–0.005 (%)	25.9	
0.005–0.001 (%)	32.6	
<0.001 (%)	39.7	
Special gravity	2.65	Pycnometer method
Organic content (%)	4.1	Potassium dichromate digestion
Porosity	0.55	–
pH	5.47	pH meter
Cation exchange capacity (mequiv./100 g)	37.7	BaCl ₂ –H ₂ SO ₄ method (ISO 11260-1997)
Zero point of charge	2.62	According to Li [18]
USCS classification	CL	–

(WSCS), the working solution was circulated between the two electrode compartments and the reservoir, as shown in the dashed line in Fig. 1.

The sediments and deionized water were mixed manually to achieve a water content of about 37%. About 290 g of the slurry was loaded into the cell fractions by fractions with a glass rod to minimize the void space. Filter paper was attached to each end of the cell. The cell was then assembled with the electrodes and compartments. Working solutions were added into the compartments and reservoirs. Prior to the run, the solutions were circulated for 6–8 h to achieve the hydraulic stability. A voltage of 20 V was applied across the cell. Electrical current and cumulative EOF were measured every 12 h during the run.

Six EK experiments were conducted with different parameters listed in Table 2. Ethanol (20 or 50%) and MCD solutions (20 or 50 g L⁻¹) were supplied as anode purging solutions, with deionized water as the blank. NaOH was contained to neutralize H⁺ produced at anode. To better reveal the effect of pH control of the electrical current and EOF, Test Eth20 was subjected to a periodic pH control for additional 7 d after proceeding without pH control in the initial 14 d. In Test Eth50 & WSCS, a special processing mode, EK combined WSCS, was adopted as a modification for Test Eth50, with the expectation to achieve an efficient pH control [19,20], a potential higher electrical current and EOF, and consequently, a higher HCB removal.

2.4. Sample analysis

Upon the completion of the EK process, the sediments were extruded and separated equally into six sections. Analysis of ethanol or MCD, HCB and pH value was performed for each section. The ethanol in the sediment was determined by the potassium dichromate digestion method. In details, 2 g of moist sediment was mixed with 20 mL of deionized water, and the aqueous ethanol was digested by potassium dichromate under a strong acidity and high temperature. The concentration of ethanol can be determined from the consumption of potassium dichromate. Control test for the moist ethanol-free sediment showed that the dissolved organic matter (DOM) contributed negligibly to potassium consumption, thereby having a neglectable influence on the ethanol determination.

After air-dried, the sediments were ground and passed through a 0.105 mm sieve. The samples were analyzed for pH value and HCB concentration, as well as MCD for tests with MCD. For pH measurement, sediment was mixed with deionized water at a solid–liquid ratio of 1:1, and pH of the slurry was measured by a pH-211 meter (Hanna, Italy). MCD in the sediment was analyzed by ultraviolet–visible (UV–vis) spectrophotometry [21]. A mass of 1 g of sediment was mixed with 5 mL of deionized water, and the aqueous MCD was determined by an UV–vis spectrophotometry (Varian Cary 50, USA) in the presence of phenolphthalein and Na₂CO₃. For HCB determination, 0.5 g of dry sediment was extracted with 5 mL of 1:1 acetone and hexane. The extraction process was assisted with ultrasonication (20 kHz) for 60 min. After centrifugation, to minimize the interference of sediment organic matter, 2 mL of the supernatant was filtrated through a packed column which was sequentially filled with glass wool, anhydrous sodium sulfate and florisil soil (2MgO·3SiO₂·nH₂O). Then 3 mL of 1:1 acetone and hexane was used as the eluting agent. HCB in the extractant was analyzed by a Hewlett-Packard 6890 GC equipped with an electron capture detector and a ZB-5 capillary column (Phenomenex, USA). The oven was heated at a rate of 10 °C min⁻¹ from 160 to 240 °C, held for 2 min. The flow rate of carrier gas (nitrogen 99.999%) was 1.5 mL min⁻¹. The inlet and detector temperature was 250 and 300 °C, respectively. The split ratio was two and injection volume was 1 μL.

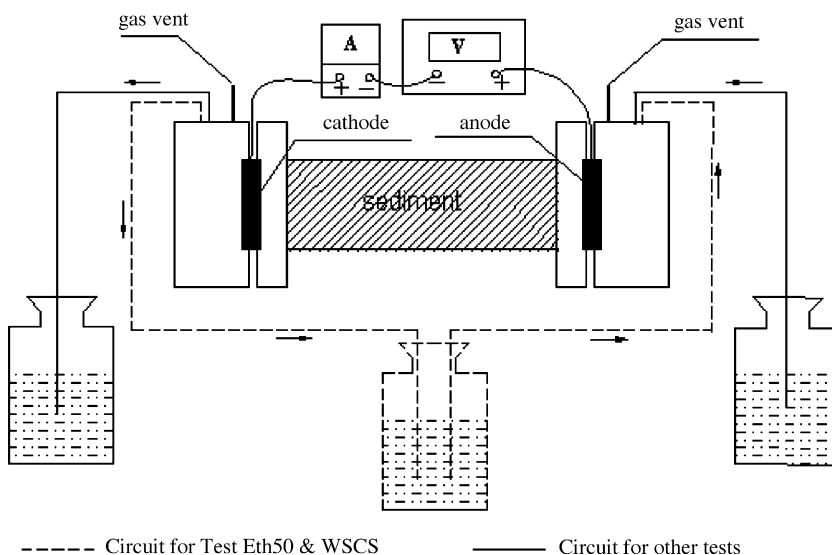


Fig. 1. Schematic diagram of EK setup.

Table 2
Parameters associated with EK tests.

Test	Anolyte	Catholyte	pH control ^a	Duration
DI ^b	DI, 0.05 M NaOH	DI	Yes	14 d
MCD20	20 g L ⁻¹ MCD, 0.05 M NaOH	DI	Yes	14 d
MCD50	50 g L ⁻¹ MCD, 0.05 M NaOH	DI	Yes	14 d
Eth20	20% ethanol, 0.05 M NaOH	DI	From 15 d	21 d
Eth50	50% ethanol, 0.05 M NaOH	DI	Yes	14 d
Eth50 & WSCS ^c	50% ethanol, 0.05 M NaOH		No	14 d

^a Adjusting the pH at anode with concentrated NaOH to above 8 in the process.

^b Deionized water.

^c Working solution circulation system.

3. Results and discussion

3.1. Variation of electrical current and cumulative EOF

Fig. 2 reveals that all six tests show similar trends in electrical current during the EK process. The current declined promptly in the initial 5 d, then reached a relatively stable level during the following days. Comparison of the electrical currents at the stable level suggests that the addition of MCD promotes the current. In particular, MCD at the concentration of 20 g L⁻¹ induced an evidently higher current than deionized water. In the study of

Maturi and Reddy [22], hydroxypropyl-β-cyclodextrin (HPCD) at the concentration of 1 and 10% was observed to stimulate and inhibit the electrical current, respectively. As shown in Fig. 2, Test Eth50 exhibited a dramatically lower current compared to deionized water, and the combination of EK and WSCS failed to promote the current efficiently. This decrease caused by high fractions of ethanol was also reported by Reddy and Saichek for both kaolin and glacial till [23]. At high fractions, the dielectric constant of ethanol solution is much lower than that of water, which means less ion dissociation in the pore liquid and a relatively lower conductivity [23].

EOF is considered as one of the most essential parameters in the EK removal of molecular organics from soils [5–7]. Fig. 3 reveals

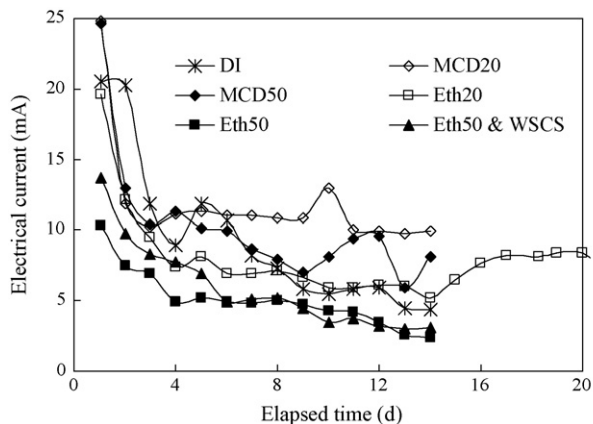


Fig. 2. Variation of electrical current. The initial values were excluded to give a legible difference of electrical current at stable level for each test.

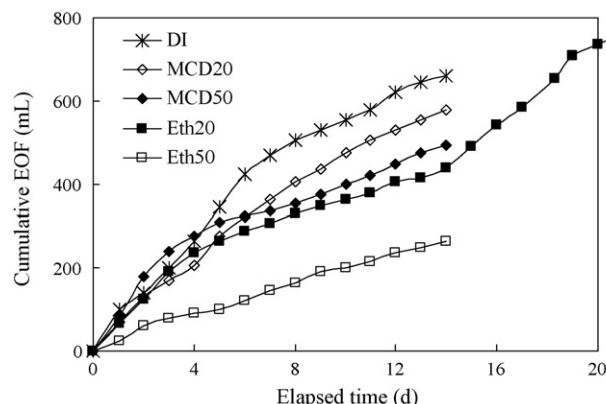


Fig. 3. Variation of cumulative EOF.

that both of the solubilizing agents had a negative effect on cumulative EOF, the higher the concentration of the agents, the lower the EOF. Furthermore, ethanol exhibited a more significant effect of inhabitation on EOF than MCD. For instance, the cumulative EOF in Test Eth50 is nearly half of that in Test MCD50. The negative effect of ethanol or cyclodextrins on EOF is in agreement with previous studies by Reddy et al. [22–24]. The authors found that EK test with 40% ethanol obtained greatly less cumulative EOF compared with deionized water and 3% Tween 80 for either kaolin [23] or glacial till [24]. In another study, EK test with 10% HPCD obtained only 0.95 pore volumes of cumulative EOF, relative to 10.7 and 17.8 pore volumes for test with deionized water and 1% HPCD, respectively [22]. The difference in cumulative EOF between each test can be mainly attributed to different dielectric constants of the purging solutions. According to Helmholtz–Smoluchowski (H–S) theory, EOF is directly proportional to the dielectric constant [5]. As reported, ethanol has the lowest dielectric constant, much lower than that of water and cyclodextrin [22,25,26]. However, since various parameters are associated with EOF, the cumulative EOF is not the result of single parameter. For example, as mentioned above, 1% HPCD exhibited a stimulative effect on cumulative EOF according to Maturi and Reddy [22]. They attributed this stimulation to the higher observed electrical current. While in our study, although higher electrical current was observed in the test with 20 g L⁻¹ (2%) MCD, less cumulative EOF was collected compared with deionized water, suggesting that the negative effect of lower dielectric constant at the MCD concentration dominated the EOF. But overall, the negative effect of MCD on EOF is insignificant relative to both ethanol and Tween 80, given the results herein and Reddy et al. [27]. Furthermore, relatively high electrical current and constant cumulative EOF were observed for tests with MCD, indicating a more considerate quantity of cumulative EOF in a long-term running.

3.2. Profile of pH distribution

It is known that the electrolysis of water produces H⁺ at the anode and OH⁻ at the cathode. Migration of the two ion species toward the opposite electrode leads the regions near anode acidic and cathode alkaline [5]. Fig. 4 shows the pH distribution across the sediments upon the completion of the tests. For all six tests, the sediment pH increased dramatically from anode to cathode. The pH fell below the initial value of 5.5 for the sediment in most sections across the cell (four out of six sections), particularly with sections near anode. In general, relatively higher pH profile was achieved in tests with 50% ethanol, and the lowest profile was found in test

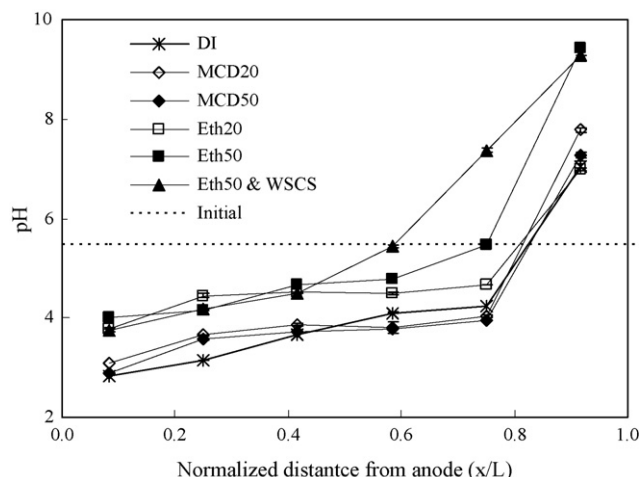


Fig. 4. Profile of pH distribution.

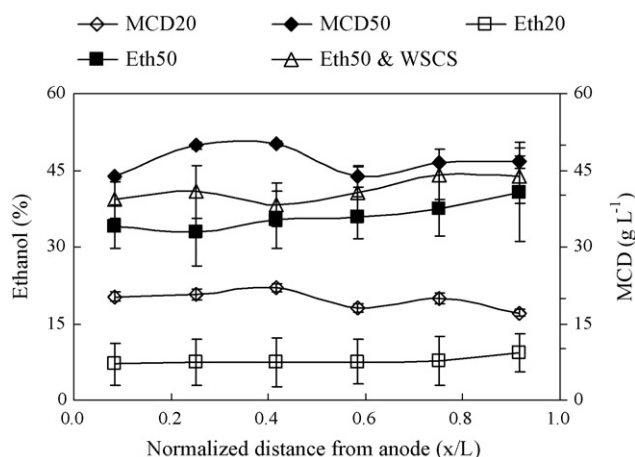


Fig. 5. Ethanol/MCD distribution.

with deionized water. The pH profile in tests with MCD fell between that of 20% ethanol and deionized water. Maturi and Reddy [22] found that EK test with HPCD had a relatively higher pH distribution profiles than test with deionized water, and increased profile was observed with increasing concentration of HPCD. By comparing the cumulative EOF of each test, it seems that pH profile was negatively correlated with the quantity of cumulative EOF. The observation of Maturi and Reddy [22] also indicates a negative relation between pH distribution and the cumulative EOF. Reddy et al. [27] suggested that higher EOF may aid the transport of H⁺ toward the cathode, resulting in a lower pH distribution. Additionally, as has been ignored before, the different rates of water electrolysis at the anode are expected when various solubilizing agents are present, which may also influence the pH distribution in the soil/sediment matrix. Herein, the presence of MCD and particularly ethanol in the anodic purging solution could probably prohibit the generation of H⁺, thus with less H⁺ entering the sediment and lowering the pH. Note that Test Eth50 & WSCS exhibited the highest pH distribution profile, which may be further resulted from counteraction of H⁺ of OH⁻ by circulating the anolyte and catholyte, therefore maintaining a relatively higher anolyte pH, as observed by Chang and Liao [19].

3.3. Distribution of solubilizing agents

To give an insight view in the delivery of two solubilizing agents by electroosmosis and to better understand their difference in performance of HCB movement, the concentration of ethanol or MCD in the sediment pore liquid was measured. Fig. 5 displays the distribution of volume fractions of ethanol and mass concentration of MCD across the sediment upon the completion of EK tests. The ethanol fractions were in the range of 30–45% in Test Eth50 (& WSCS), and were below 10% in Test Eth20. For Test MCD50 and MCD20, the concentrations of MCD in sediment pore solution were in the range of 45–50 and 15–20 g L⁻¹, respectively, almost identical with the initial values. The results suggest that the delivery of ethanol into the sediment by electroosmosis was less efficient than that of MCD. Other than less cumulative EOF, loss of ethanol via volatilization or anodic oxidation may be also responsible to the lower profile of solubilizing agents in sediments for tests with ethanol [14], as the ethanol fractions in the anolytes after EK process revealed losses of about 10–20%. Cyclodextrins, on the other hand, are not prone to be decomposed under low-voltage electric field or volatile into the atmosphere, as suggested by this present study. Furthermore, recovery of the solubilizing agents in each test also suggests a much more pronounced mass loss of ethanol than that of MCD (a gen-

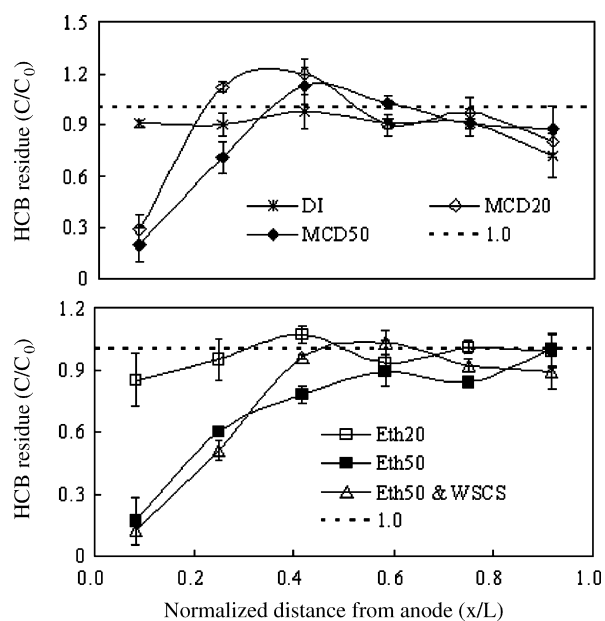


Fig. 6. Distribution of residual HCB.

eral recovery of the agents in sediment, the anolyte and catholyte is about 87% for tests with MCD, while that for tests with ethanol ranges from 50 to 67%).

3.4. HCB movement in the sediments

The distribution of HCB remained in the sediment upon the completion of EK test is presented in Fig. 6, and the overall removal of HCB is listed in Table 3. Generally, when purging with deionized water or 20% ethanol, negligible movement of HCB across the cell was observed. While in tests with 50% ethanol and 20 or 50 g L⁻¹ MCD, remarkable movement of HCB was achieved especially in regions near the anode (with residues ranging from 20 to 60%). As Table 3 shows, Test Eth50 exhibited the highest HCB removal from the sediments, slightly higher than Test Eth50 & WSCS, though the latter had a relatively higher pH (Fig. 4) and ethanol profile in sediment (Fig. 5). In tests with MCD, 50 g L⁻¹ MCD yielded a moderate HCB removal of 19.2%, higher than 20 g L⁻¹ MCD. In Test DI, the overall HCB removal was up to 11.1%, and removal at the cathodic section was higher than 25%. Our previous study also revealed similar results for EK removal of HCB from spiked kaolin without the aid of solubility-enhancing agents [13]. A plausible explanation for the appreciable HCB disappearance in Test DI at the cathodic section is the electrochemical degradation near/on the cathode [13].

The EK movement of HOCs in soils generally involves two steps: desorption of HOCs from sediments to the pore liquid, and the subsequent movement of dissolved HOCs by electroosmosis. It is therefore essential in a solubility-enhanced EK that the facilitating agent has the ability to enhance the desorption of HOCs, and

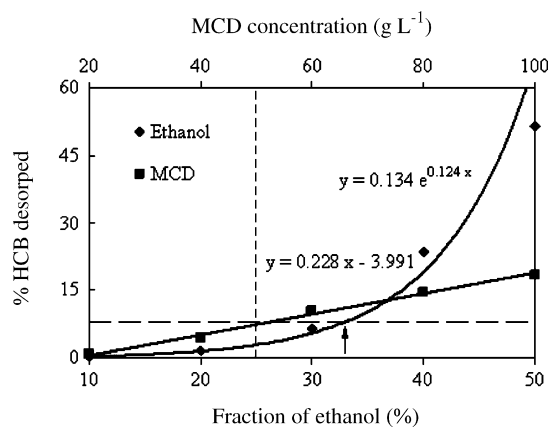


Fig. 7. Efficiency of HCB desorption by ethanol or MCD solutions.

EOF is sufficient to move the dissolved HOCs [28]. Organic cosolvent can solubilize and mobilize the contaminants by reducing the interface tension and the polarity of the fluid significantly [29]. Cyclodextrins have a unique structure of a hydrophilic shell and a relatively apolar cavity. They can solubilize HOCs by forming inclusion complexes between HOCs and the interior cavity of CDs [30]. As shown in Fig. 7, the HCB desorption efficiency yielded by 50 g L⁻¹ MCD is approximately equal to that by ethanol at a fraction of 32%. Above this ethanol fraction, as the performance increases exponentially, much higher percentage of HCB desorption can be achieved by ethanol solutions compared to 50 g L⁻¹ MCD. Data in Fig. 5 suggest that in tests with 50% ethanol, the ethanol fractions across the sediment matrix are all above 32%, thus higher HCB dissolution was expected than that with Test MCD50. Based on the results of HCB desorption and the distribution of solubilizing agents (Fig. 5), the average concentration of the dissolved HCB in the pore liquid was estimated for each EK test. Furthermore, the theoretical percentage removal of HCB from the sediment was calculated from the average HCB concentration in pore liquid and the quantity of cumulative EOF. The results are listed in Table 4. It can be found that appreciable dissolution and desorption of HCB was expected in tests with 50 g L⁻¹ MCD and 50% ethanol, and a moderate performance was expected in Test MCD20. Consequently, though lower cumulative EOF was obtained with these tests compared to deionized water, the significant enhancement of HCB mobility could ensure a dramatic promotion in HCB movement by electroosmosis. In comparison, Test Eth50 exhibits 2.5 times higher HCB dissolution than Test MCD50, while the latter obtained 1.9 times more volume of cumulative EOF. Thus the theoretical removal of HCB in Test Eth50 was 1.3 times higher than that of Test MCD50, very close to the ratio of 1.5 for the observed HCB removal between the two tests (Table 3). However, it is noteworthy that compared with ethanol, MCD could maintain a relatively desirable electrical current and cumulative EOF, and the mass loss of MCD is not significant, both offer critical advantages to contaminants removal from soils/sediments. As for a field application, the EK progress will last for several weeks

Table 3
Mass balance of HCB upon the completion of EK tests.

Test	%Catholyte ^a	%Anolyte	%Sediment	%Removal	Recovery, %
DI	0.1	nd ^b	88.8	11.2	88.9
MCD20	0.1	nd	88.0	12.0	88.1
MCD50	0.4	nd	80.8	19.2	81.2
Eth20	0.1	nd	96.7	3.3	96.8
Eth50	0.1	nd	71.3	28.7	71.4
Eth50 & WSCS	0.4	nd	73.8	26.2	74.2

^a Percentage of HCB in the catholyte to the initial mass. Similar with % anolyte and % sediment.

^b Not detected or the value far below 0.1%.

Table 4
Dissolution and theoretical removal of HCB from sediment.

	DI	MCD20	MCD50	Eth20	Eth50
C_{dis}^a , $\mu\text{g L}^{-1}$	1.7	9.6	69.3	4.8	180.1
R_{theo}^b , %	0.05	0.23	1.40	0.15	1.95

^a Concentration of HCB dissolved in pore liquid, average of six sections across the sediment matrix.

^b Theoretical percentage removal of HCB, the ratio of mass of HCB theoretically dissolved by cumulative EOF to that initially contained in the sediments.

or months to remove the contaminants completely. In this case, constantly stable electrical current and cumulative EOF are of critical significance for a long-term running. As a result, although MCD exhibits lower temporary HCB removal compared with 50% ethanol in our present tests, it may exhibit certain superiority in a practical field remediation.

Inspection of the observed and the theoretical removal of HCB in Tables 3 and 4 reveals a great discrepancy. Furthermore, the mass balance of HCB in the sediments and electrolytes in Table 3 shows that around 20–30% of HCB disappeared in the tests with 50% ethanol and 50 g L^{-1} MCD. The results may imply that the flushing induced by electroosmosis is more efficient than traditional soil washing, or certain physical–chemical reactions are also responsible for the removal. Similar observation was also reported in our previous study [13]. We suggest that both in situ degradation of HCB in regions near the cathode [31] and the direct electrochemical degradation of HCB at the electrodes were expected to contribute to the loss of HCB [32].

4. Conclusions

EK removal of HCB from contaminated sediments enhanced by ethanol or MCD was investigated in this study. The difference of HCB movement using the two solubilizing agents was interpreted in terms of EK parameters, such as electrical current, cumulative EOF and pH distribution, and distribution of solubilizing agents in sediments. Results show that compared with MCD, ethanol had a more negative effect on cumulative EOF, and a lower concentration profile in the sediment upon the completion of EK tests. Test with 50% ethanol showed much more enhancement of HCB dissolution from sediment and slightly more evident HCB movement toward the cathode than test with 50 g L^{-1} MCD. However, MCD is supposed more suitable in practical application given the relatively reliable EOF and chemical stability.

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