

Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin

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Received 26 April 2004; received in revised form 19 August 2005; accepted 23 August 2005
Available online 10 November 2005

Abstract

Thousands of sites are contaminated with both heavy metals and organic compounds and these sites pose a major threat to public health and the environment. Previous studies have shown that electrokinetic remediation has potential to remove heavy metals and organic compounds when they exist individually in low permeability soils. This paper presents the feasibility of using cyclodextrins in electrokinetic remediation for the simultaneous removal of heavy metals and polycyclic aromatic hydrocarbons (PAHs) from low permeability soils. Kaolin was selected as a model low permeability soil and it was spiked with phenanthrene as well as nickel at concentrations of 500 mg kg⁻¹ each to simulate typical mixed field contamination. Bench-scale electrokinetic experiments were conducted using hydroxypropyl β-cyclodextrin (HPCD) at low (1%) and high (10%) concentrations and using deionized water in control test. A periodic voltage gradient of 2 VDC cm⁻¹ (with 5 d on and 2 d off) was applied to all the tests, and 0.01 M NaOH was added during the experiments to maintain neutral pH conditions at anode. In all tests, nickel migrated as Ni²⁺ ions towards the cathode and most of it was precipitated as Ni(OH)₂ within the soil close to the cathode due to high pH condition generated by electrolysis reaction. The solubility of phenanthrene in the flushing solution and the amount of electroosmotic flow controlled the migration and removal of phenanthrene in all the tests. Even though high flow was generated in tests using deionized water and 1% HPCD, migration and removal of phenanthrene was low due to low solubility of phenanthrene in these solutions. The test with 10% HPCD solution showed higher solubility of phenanthrene which caused it migrate towards the cathode, but further migration and removal was retarded due to reduced electric current and electroosmotic flow. Approximately one pore volume of flushing resulted in approximately 50% removal of phenanthrene from the soil near the anode. Sustained higher electroosmotic flow with higher concentration cyclodextrin and maintaining low soil pH near cathode should be investigated to increase removal efficiency of both phenanthrene and nickel. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Soil; Clays; Electrokinetics; Heavy metals; PAHs; Cyclodextrin; Remediation; Complexation; Contaminant mixture

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1. Introduction

Numerous sites require remediation for co-existing heavy metal and organic contamination to protect public health and the environment. Soil washing/flushing, bioremediation, and solidification/stabilization technologies have been the most common technologies to treat soils at these sites. Treatment trains combining several treatment technologies in a series (e.g., flushing followed by bioremediation) have also been used to address multiple contaminants in the soils. These technologies, however, fail when low permeability soils are encountered because of the difficulty with the hydraulic delivery of the reactive agents required for the treatment.

Previous research has shown that electrokinetic remediation has the potential to remove either heavy metals (e.g., Reddy and Chinthamreddy, 2003; Reddy et al., 2003) or PAHs (e.g., Reddy and Saichek, 2004) from low permeability soils. However, the efficiency of electrokinetic remediation was not tested when these contaminant groups co-exist. Because of the different nature of the two contaminant groups, suitable extracting solutions should be selected which could solubilize or form complexes with both the contaminant groups. Modified cyclodextrins are shown to have potential to complex with low-polarity organic compounds as well as heavy metals (Wang and Brusseau, 1995). Cyclodextrins are cyclic oligosaccharides that are formed from the degradation of starch by bacteria (Wang and Brusseau, 1993; Ko et al., 2000). Cyclodextrins have been used for enzyme mimics, catalysis, and encapsulation of drugs because of their ability to form *inclusion complexes* with wide range of substrates in aqueous solution. Because of their nontoxicity, biodegradability, and low affinity of sorption to the solid phase at a wide range of pH values, cyclodextrins are considered advantageous over regular surfactants. β - and γ -cyclodextrins form complexes with PAHs and enhance their solubilization to a great extent (Wang and Brusseau, 1995). A modified cyclodextrin, namely hydroxypropyl β -cyclodextrin (HPCD), exhibits the ability to significantly enhance the solubilization of number of PAHs and also has the potential to remove heavy metals simultaneously (Wang and Brusseau, 1993, 1995).

The present study was performed to evaluate HPCD for the simultaneous removal of heavy metals and PAHs from low permeability soils using electrokinetics. Bench-scale electrokinetic experiments were conducted using low permeability kaolin soil spiked with nickel and phenanthrene. In these experiments, HPCD was used at low (1%) and high (10%) concentrations, and deionized water was used in control test. These experiments were conducted with the application of a periodic voltage gradient. The results of these experiments helped to assess the migration and removal of contaminants from the soil.

2. Experimental methodology

2.1. Electrokinetic test setup

The electrokinetic test setup used in this study is described in detail in Reddy and Saichek (2004). Fig. 1 shows the schematic of the electrokinetic test setup. The setup consisted of a cell, two electrode compartments, an anode electrode reservoir, a peristaltic pump to circulate the solution in the anode reservoir, a cathode sample collection flask, a power supply, wiring, stands, and tubing such as C-Flex and M-Flex. C-Flex tubing was used to make the connections to the cell and also for the gas-vents, while M-Flex tubing was used for the circulation pump. The electrokinetic cell was made of Plexiglas with 6.2 cm inside diameter and 19.1 cm length, and it was supported on a raised aluminum stand. Each electrode compartment was also made of Plexiglas and contained a Whatman filter paper, a porous stone, and a perforated graphite electrode. The filter paper was placed between the soil and the porous stone and both were placed in front of the electrode. Gas-vents were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape.

2.2. Materials

2.2.1. Soil

Kaolin was selected as the model soil for the present study as it represents a low permeability soil. The composition and properties of this soil are summarized in Table 1. The laboratory grade kaolin was obtained from VWR Scientific Products Corporation (West Chester, PA) and the manufacturer was EM Science (Gibbstown, NJ). Kaolin mainly consists of the kaolinite mineral.

2.2.2. Contaminants

Phenanthrene ($C_{14}H_{10}$), a neutral organic compound that contains three aromatic rings, was selected as a representative PAH. It has environmental properties such as aqueous solubility, octanol–water partition coefficient, and vapor pressure that are similar to other PAHs. All PAHs are hydrophobic, and phenanthrene has an aqueous solubility of 1.1 mg l^{-1} at 25°C (Schwarzenbach et al., 1993).

Nickel was selected as a representative heavy metal as it is one of the most prevalent heavy metals at many contaminated sites. In low pH regions, nickel exists in the form of the nickelous ion (Ni^{2+}). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide ($Ni(OH)_2$), which is a stable compound. This precipitate readily dissolves in acid solutions forming Ni^{2+} and in very alkaline conditions, nickel exists in the form of stable nickelo-nickelic oxide (Ni_3O_4) that is soluble in acid solutions. Other nickel oxides such as nickelic oxide

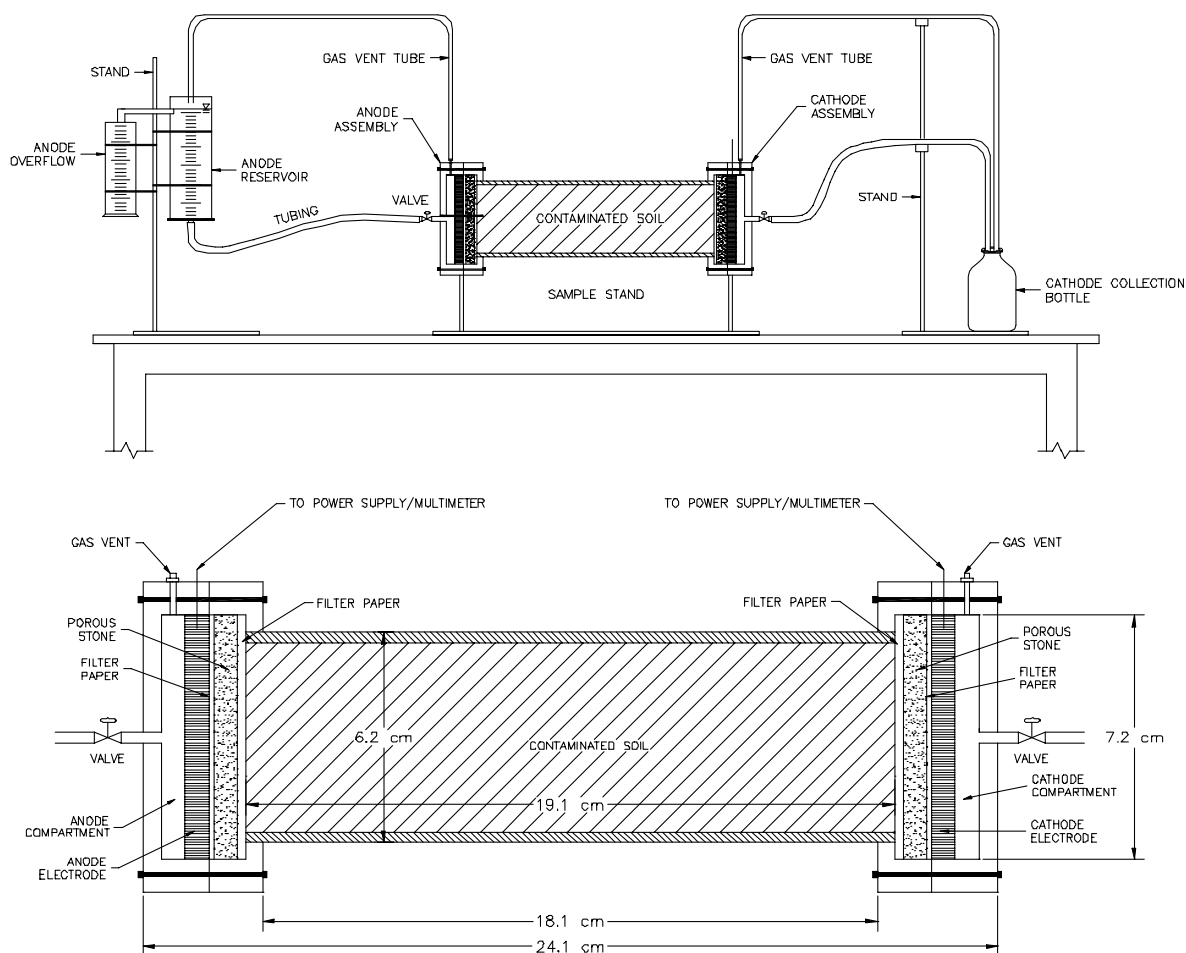


Fig. 1. Schematic of the electrokinetic test setup and cell details.

Table 1
Properties of kaolin soil

Mineralogy	Kaolinite: 100% Muscovite: trace Illite: trace
Particle size distribution (ASTM D422) ^a	
Gravel (%)	0
Sand (%)	4
Silt (%)	18
Clay (%)	78
Specific gravity (ASTM D854)	2.54
Hydraulic conductivity (cm s ⁻¹) (ASTM D5084)	1.0 × 10 ⁻⁸
Organic content (%) (ASTM D2974)	Near 0
pH (ASTM D4972)	4.9
Cation exchange capacity (meq (100 g) ⁻¹) (ASTM D9081)	1.0–1.6
USCS classification (ASTM D2487)	CL

^a American Society of Testing and Materials (2004).

(Ni₂O₃) and nickel peroxide (NiO₂) are unstable in alkaline solutions and decompose by giving off oxygen. However, in acidic regions, these solids dissolve producing Ni²⁺ (Pourbaix, 1978).

2.2.3. Flushing solutions

HPCD was selected based on the literature for its ability to significantly enhance the solubilization of number of hydrophobic organic compound including PAHs (Wang and Brusseau, 1993). Previous research has shown that modified cyclodextrin has the potential to remove both organic compounds and heavy metals simultaneously (Wang and Brusseau, 1995). Moreover, Saichek and Reddy (2005) suggested the use of cyclodextrins as they are more compatible with the environment and the remediation process. Among the three cyclodextrin homologues (α , β , γ -cyclodextrins), β -cyclodextrin is the least expensive. Unfortunately, β -cyclodextrin has limited water-solubility, and its complexes are therefore only slightly water-soluble. Thus, β -cyclodextrin is often

Table 2
Bench-scale electrokinetic testing program

Test	Soil	Contaminants (mg kg ⁻¹)	Anode solution	Anode buffering solution	Voltage gradient (VDC cm ⁻¹)	Voltage application	Total duration (d)
1	Kaolin	Nickel—500; phenanthrene—500	Deionized water	0.01 M NaOH	2	Periodic: 5 d on/2 d off	193
2	Kaolin	Nickel—500; phenanthrene—500	1% HPCD	0.01 M NaOH	2	Periodic: 5 d on/2 d off	151
3	Kaolin	Nickel—500; phenanthrene—500	10% HPCD	0.01 M NaOH	2	Periodic: 5 d on/2 d off	44

chemically modified to enhance its water solubility. HPCD is one of these derivatives that is found to be very water-soluble (Wang and Brusseau, 1993).

2.3. Testing program

The testing program for the present study is shown in Table 2. A series consisting of three electrokinetic tests was conducted. One test was conducted using deionized water as flushing solution, which served as the control or baseline test. The other two tests were conducted using HPCD at 1% and 10% concentration each. A periodic or pulsed voltage application of 2 VDC cm⁻¹ was applied in all tests, and 0.01 M NaOH was added in anode during the experiments to maintain neutral pH conditions. Periodic or pulsed voltage application consisted of a cycle with 5 d of continuous voltage application followed by 2 d of “down-time” where the voltage was not applied to allow for kinetic chemical reactions to occur (Reddy and Saichek, 2004).

2.4. Testing procedure

Approximately 1200 g of kaolin was used for each test. Kaolin was spiked with phenanthrene at an initial target concentration of 500 mg kg⁻¹ as described in Reddy and Saichek (2004). Initially, the phenanthrene was completely dissolved in hexane, and the hexane–phenanthrene mixture was subsequently mixed with the measured amount of kaolin soil. The soil–hexane–phenanthrene mixture was then placed in a fume hood for nearly a week until hexane completely evaporated and the contaminated soil was dry. Then the soil was spiked with nickel at a target concentration of 500 mg kg⁻¹ as described in Reddy and Chinthamreddy (2003). Required amount of nickel chloride was dissolved in deionized water and then added to the soil. The soil and solution were mixed homogeneously and air-dried in a fume hood. The final moisture level of soil was adjusted to 35% by adding deionized water. The actual initial concentration of phenanthrene in the soil was measured by Soxhlet extraction and gas chromatography (GC), while the initial concentration of nickel in the soil

was determined by acid digestion and atomic absorption spectrophotometer (AAS) (USEPA, 1986; Reddy and Chinthamreddy, 2003; Reddy and Saichek, 2004).

The moist soil was then placed into the electrokinetic cell in layers, and each layer was compacted thoroughly using a stainless steel rammer so that the amount of void space was minimized. Once the cell was filled with soil, the anode and cathode compartments and the anode reservoir were connected to the cell, and the anode reservoir was filled with the selected flushing solution. For all experiments, 0.01 M NaOH was added periodically to the anode reservoir and the anode solution was circulated using a peristaltic circulation pump to maintain neutral to alkaline (pH > 7) conditions. The cathode compartment was initially filled with deionized water. A periodic DC voltage gradient of 2 VDC cm⁻¹ (with 5 d on and 2 d off) was applied (Table 2).

The electric current and the effluent volume at the cathode were measured at regular intervals of time throughout the testing period. The effluent samples were collected in bottles so that the nickel and phenanthrene concentrations could be measured. The tests were conducted until the current greatly decreased, the effluent volume significantly reduced, or it appeared that the phenanthrene and nickel in the effluent concentrations had reached a steady-state condition.

At the completion of each test, the anode reservoir and the electrode assemblies were disconnected, and the soil specimen was extruded from the cell using a mechanical extruder. The soil specimen was sectioned into five equal parts. Each part was weighed and preserved in a glass bottle and was used to analyze nickel and phenanthrene concentrations. From each soil section, 10 g of soil was weighed and mixed with 10 ml of 0.01 M CaCl₂ solution in a glass vial. The soil–solution mixture was shaken thoroughly by hand for several minutes and the solids were allowed to settle for an hour. This soil–solution was then used for measuring the soil pH and electrical conductivity. The pH and electrical conductivity of the aqueous solutions collected near the cathode were also measured. The moisture content of each soil section was also determined in accordance with ASTM D2216.

The phenanthrene and nickel concentrations of each soil section were measured following the same procedures used to measure the initial concentrations in the soil. The liquid samples collected near the cathode were analyzed for phenanthrene by liquid–liquid extraction and GC and for nickel directly using AAS (USEPA, 1986; Reddy and Chinthamreddy, 2003; Reddy and Saichek, 2004).

3. Results and analysis

The initial soil conditions for each test are shown in Table 3. The test results included the variation of electric current, electroosmotic flow, and cumulative mass removal of phenanthrene and nickel with the total elapsed time (including the downtime when the voltage gradient was not applied). The pH, electrical conductivity, and the concentration profiles of phenanthrene and nickel in soil after the tests were terminated were also

determined. These results helped to assess the efficiency of HPCD to remove both nickel and phenanthrene from the soil.

3.1. Electric current and electroosmotic flow

Fig. 2 shows the changes in the current during the experiments at different total elapsed times for the baseline, 1% HPCD, and 10% HPCD tests. All of the experiments began with relatively high current values, but then the current reduced rather quickly within the first 500 h of operation. After this time period, the current values were different in each test. The current in the 1% HPCD test was significantly greater than the baseline and the 10% HPCD tests. At later stages, when the fresh deionized water was added into the baseline test, the current increased to the same levels as the 1% HPCD test. The current in the 10% HPCD test continued to decrease and remained at low value with the test duration. During electrokinetics, the fluctuations

Table 3
Initial soil conditions and number of pore volumes flushed

Test	Extracting solution	Water content (%)	Dry density (g cm^{-3})	Void ratio	Porosity (%)	Degree of saturation (%)	Pore volume (ml)	Number of pore volumes flushed
1	Deionized water	32.5	1.367	0.90	47.4	93	273.2	10.6
2	1% HPCD	36.4	1.353	0.88	46.7	100	269.4	17.8
3	10% HPCD	34.8	1.381	0.84	45.6	100	262.9	0.95

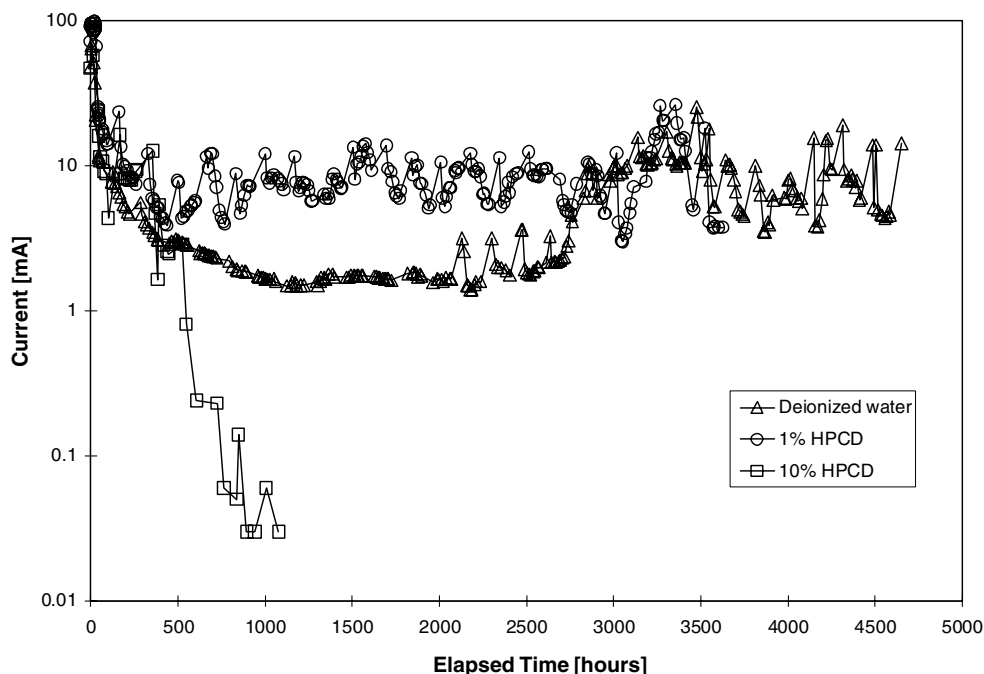


Fig. 2. Measured electric current during testing.

in current can occur due to different reasons. Initially, high currents result due to the presence of salt precipitates that go into solution (Mitchell, 1993), but over time these ions are depleted as they electromigrate and move into the electrode chambers. At the same time, ions that are constantly being generated at the anode have a high mobility and they move into the soil due to the electrokinetic transport mechanisms of electromigration and electroosmosis (Acar et al., 1995). The initial higher current in the tests may be attributed to the inflow of acidic solution that lowers the pH of the soil, and this may lead to additional mineral dissolution and a higher current.

Fig. 3 shows the cumulative electroosmotic flow versus total elapsed time during the baseline, 1% HPCD and 10% HPCD tests. The maximum electroosmotic flow was 4795 ml in the test with 1% HPCD, 250 ml in the test with 10% HPCD, and 2896 ml in the baseline test. Table 3 shows the calculated pore volume and the number of pore volumes flushed in each of the tests. The number of pore volumes flushed was the maximum in the test with 1% HPCD and minimum in the test with 10% HPCD. The number of pore volumes flushed in the deionized water, 1% HPCD and 10% HPCD tests were 10.6, 17.8, and 0.95, respectively.

Cyclodextrins possess low dielectric constants and this electrical property decreases with increasing concentration (Yim et al., 2003). Hence, HPCD possesses a low dielectric constant, so the concentration of HPCD during electrokinetics should be minimized to maintain a

sufficient amount of electroosmotic flow because electroosmotic flow is directly proportional to the dielectric constant according to the Helmholtz–Smoluchowski theory (H–S theory). The electroosmotic flow in the baseline test was more than the test in which 10% HPCD was employed. The lower dielectric constant of HPCD may be one of the reasons for low flow. However, dielectric constant is not the only parameter governing the current and electroosmotic flow in these experiments. Initially, in all the three tests, the electroosmotic flow was more as the current was high. Gradually, there was a reduction in the flow as the current decreased. In the test with 10% HPCD, due to the rapid depletion of the mobile ions, the current almost reduced to zero and it resulted in low electroosmotic flow.

The higher current and higher flow in 1% HPCD test when compared to the test with 10% HPCD may be due to relatively higher dielectric constant and lower viscosity of 1% HPCD solution when compared to 10% HPCD solution. Since the larger currents are the indication of larger movement of the ions, it appears that 1% HPCD contained a higher amount of initial mobile ion concentration than in 10% HPCD. The fluctuations of the current in the 1% HPCD test even after 500 h indicates that many changes occurred in the solution chemistry. Due to the higher HPCD concentration, a more rapid depletion of ions may have occurred. Although deionized water has high dielectric constant, the current values were lower than in the test with 1% HPCD. This

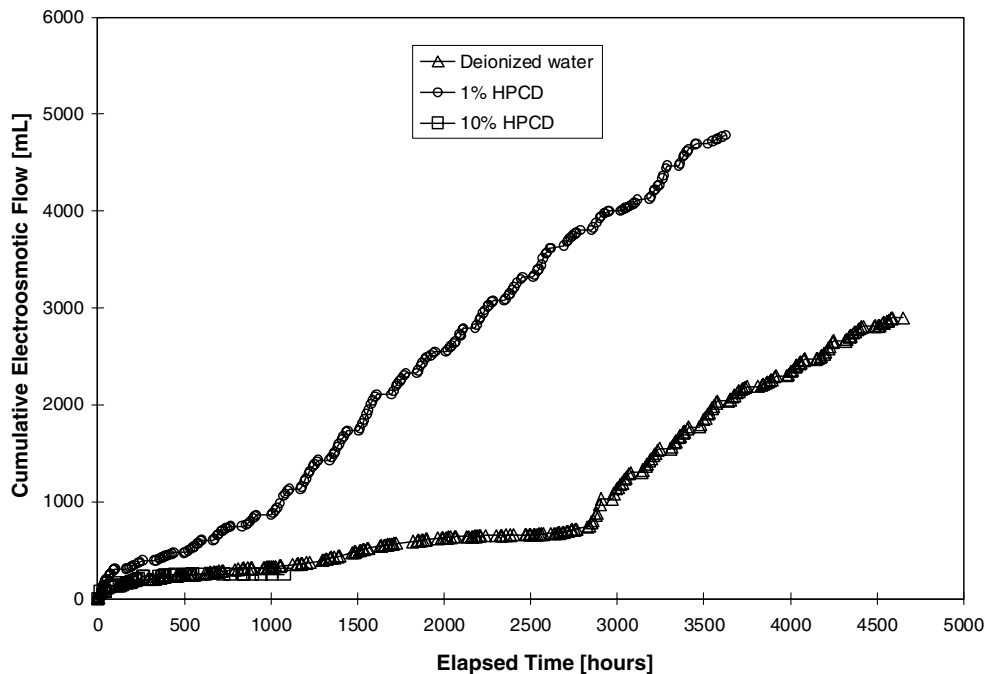


Fig. 3. Measured cumulative electroosmotic flow during testing.

behavior may be due to the relative movement of the ions. In the deionized water test, when the entire anode solution was replaced with a fresh deionized water solution after about 3000 h, an increase in current and electroosmotic flow was observed.

3.2. Soil pH and electrical conductivity

Fig. 4a shows the soil pH distribution profiles of the three tests. When voltage potential is applied to the electrokinetic cell, electrolysis reaction takes place and H^+ and OH^- ions are generated at anode and cathode, respectively. This results in a low pH near the anode and a high pH near the cathode. During the course of testing, the acidic solution generated at the anode gradually moves through the soil towards the cathode by electromigration and electroosmotic flow, and this lowers the pH of the soil (Acar et al., 1995).

The initial pH of the spiked soil was 5.9. As shown in Fig. 4a, the soil pH varied from anode to cathode after the application of electric potential. For the test with deionized water, the soil pH value was 1.6 near the anode and then gradually increased to 6.4 towards the cathode. The soil pH was in the range of 2.75 and 4.01 increasing from anode towards cathode for the test in which 1% HPCD was employed. The soil pH was 3.59 near the anode and 6.86 near the cathode for the test in which 10% HPCD was used as flushing solution.

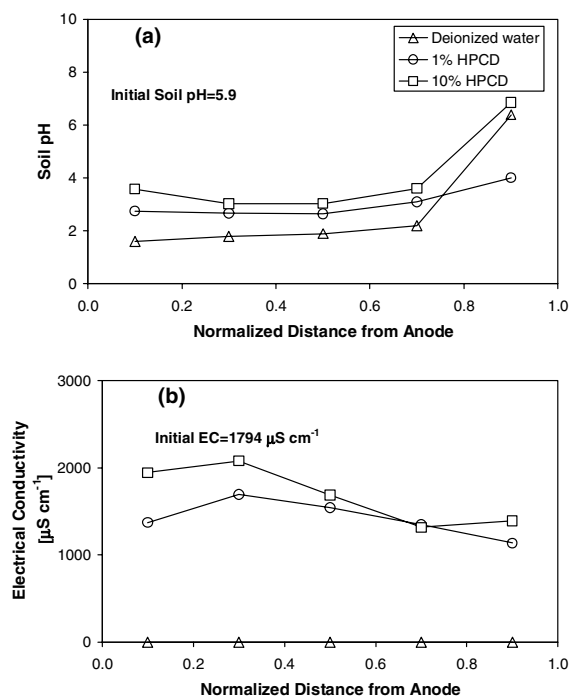


Fig. 4. (a) Soil pH and (b) soil electrical conductivity profiles.

The pH of the anode solution was above 7 (due to addition of 0.01 M NaOH; otherwise it would have been 2–3 due to electrolysis reactions as demonstrated in previous studies), and the pH of the cathode solution was 10–12.

Even though the anode pH was increased with the periodic addition of 0.01 M NaOH, the pH of the soil near the anode was reduced at the end of the experiments. This reduction in soil pH is attributed to faster electromigration of H^+ generated in the anode compartment into the soil and also potential exhaustion of small amount of 0.01 M NaOH added at different time intervals during the testing. For the most part, the pH values for the baseline test were lower than the tests in which HPCD was used as flushing solution. Unlike the baseline test and the test in which 10% HPCD was used, the entire soil specimen was acidic in the test with 1% HPCD because of more number of pore volumes flushed. Electroosmotic flow was a dominant transport mechanism in this case and it may have inhibited electromigration of OH^- ions into the soil sample. The OH^- ions generated at cathode by the electrolysis reaction may have been neutralized by the migrated H^+ ions from anode. As the electromigration of H^+ ions is twice faster than that of OH^- ions, the resulting soil pH was observed to be low (less than the neutral pH). Hence, the pH was lower than the neutral pH near the cathode region in the test in which 1% HPCD was used as flushing solution. However, in the small region adjacent to the cathode, the soil pH may be significantly increased due to the highly alkaline conditions existing in the cathode (with pH 10–12).

The low soil pH in the region near the anode indicates a greater H^+ concentration and a more positively charged mineral surface. When the mineral surface becomes positively charged, the zeta potential becomes positively charged, and by H-S theory, the electroosmotic flow towards the cathode is reduced. Additionally, OH^- ions generated by the electrolysis reaction at the cathode may electromigrate into the soil sample against the electroosmotic flow and increase the pH in the region near the cathode or neutralize the migrating H^+ ions. This may cause a low conductivity region with a somewhat neutral pH to exist near the cathode (Dzenitis, 1996).

Fig. 4b shows the electrical conductivity distribution profiles of all the tests. The initial electrical conductivity of the soil was $1794 \mu S cm^{-1}$. The electrical conductivity of the soil sections from the deionized water test was very low and it ranged from 0.05 to $0.62 \mu S cm^{-1}$. The tests in which cyclodextrin was used had high electrical conductivity values when compared to the values in the deionized water test. Moreover, the electrical conductivity values for the soil sections near the anode were high in the 10% HPCD test than in the 1% HPCD test.

3.3. Phenanthrene removal

The initial concentration of phenanthrene in the soil was found to be 448, 499 and 492 mg kg⁻¹ for the deionized water test, 1% HPCD test, and 10% HPCD test, respectively. Fig. 5a shows the cumulative mass of phenanthrene in solution removed in deionized water, 1% HPCD, and 10% HPCD tests by the application of electric potential. As seen in the figure, all the three tests resulted in very low removal of phenanthrene. The test in which 1% HPCD was employed had greater removal of phenanthrene than the baseline and 10% HPCD test. Almost 18 pore volumes were flushed in the test with 1% HPCD, resulting a better soil–solution–contaminant interaction. This may be the reason for the higher phenanthrene removal in the test with 1% HPCD when compared to the removal in other tests. There was no significant removal of phenanthrene in both baseline and 10% HPCD tests. Although 11 pore volumes were flushed in the baseline test, the poor removal of phenanthrene may be attributed to its low solubility in water. Overall, the phenanthrene removal was not significant in all the three tests. For significant mass removal, desorption, solubilization as well as soil–solution–contaminant interaction are essential. In the case of the test with 1% HPCD, the poor removal may be due to insuf-

ficient solubilization of phenanthrene that may be due to the low concentration of HPCD. But, when the concentration of HPCD solution was increased to 10%, the electroosmotic flow decreased which resulted in a low soil–solution–contaminant interaction. In some manner, if the electroosmotic flow is increased in the tests with high concentrations of HPCD, a significant removal of phenanthrene may be achieved.

Fig. 5b shows the normalized phenanthrene concentration in the soil after the termination of the electrokinetic tests with deionized water, 1% HPCD, and 10% HPCD. In the deionized water test, the normalized concentration of phenanthrene is found to be lower than one in most parts of the soil and there is a slight increasing trend from the anode to the cathode. The lower normalized concentration values may be as a result of lower actual initial concentration (448 mg kg⁻¹) as compared to the target initial concentration (500 mg kg⁻¹). The phenanthrene mobilization was not significant in this test due to very low solubility of phenanthrene in water. The maximum phenanthrene mobilization was observed in the test with 1% HPCD solution. The normalized concentration near the anode was around 0.7 and it increased gradually to 1.6 in the soil section near the cathode. This mobility may be due to partial solubilization of phenanthrene and also due to the increased soil–solution–contaminant interaction resulted from increased electroosmotic flow. Moreover, the pH values were low in the entire soil specimen which could have caused the clay particles to have an open structure and hence there was a high interaction between the solution and phenanthrene. However, the concentration of the HPCD solution was not sufficient enough to cause significant phenanthrene solubilization to occur. In the test with 10% HPCD, even though only one pore volume was flushed, significant mobilization of phenanthrene was observed in the soil near the anode because of the high concentration. Moreover, the low pH values near the anode may have resulted in open structure of the clay particles that may have resulted in the high interaction between the solution, soil and the contaminant. The normalized concentration of phenanthrene at the section near the anode was 0.5 and increased to a value of 1.35 in the second section and then remained close to 1 in all the remaining sections. Although, when compared to 1% HPCD, the concentration was sufficient enough for the solubilization to occur, but mobilization remained minimal because of the low soil–solution–contaminant interaction due to low electroosmotic flow. If the electroosmotic flow is sustained, then significant removal of phenanthrene may be possible.

Based on the experimental results, the selected cyclodextrin enhanced phenanthrene migration from anode to cathode; however, it did not remove phenanthrene completely from the soil into the cathode solution either due to low electroosmotic flow or due to low solubilization.

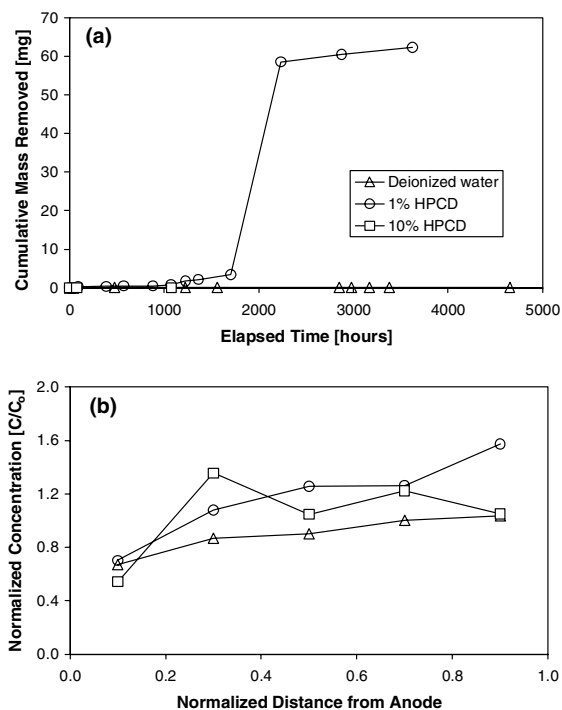


Fig. 5. (a) Cumulative phenanthrene mass removal and (b) normalized phenanthrene concentration profiles.

Moreover, in β -cyclodextrin, larger cavities are created by the arrangement of two β -cyclodextrin molecules in a head to head fashion. The head to head dimers are arranged side by side in layers. But, the stacking is not always linear, and frequently lateral displacement is observed so that the cavity formed by one dimer is closed on both ends by adjacent dimers (Szejtli, 1988). As HPCD is a derivative of β -cyclodextrin, the cavity may be insufficient to accommodate the phenanthrene molecules due to this lateral displacement.

3.4. Nickel removal

Fig. 6a shows the cumulative mass of nickel removed in the three tests: baseline, 1% HPCD, and 10% HPCD tests. It can be observed from these results that there was no significant removal of nickel in all the three tests. The removal was close to zero in baseline and the test with 10% HPCD. In the case of 1% HPCD, the removal was slightly more, which was about 5.6 mg. The poor removal may be due to the low HPCD concentration that was not sufficient to complex with nickel in 1% HPCD test. In addition, the high pH conditions that existed near the cathode region may be responsible for the precipitation of nickel in the soil itself inhibiting its removal into the cathode solution.

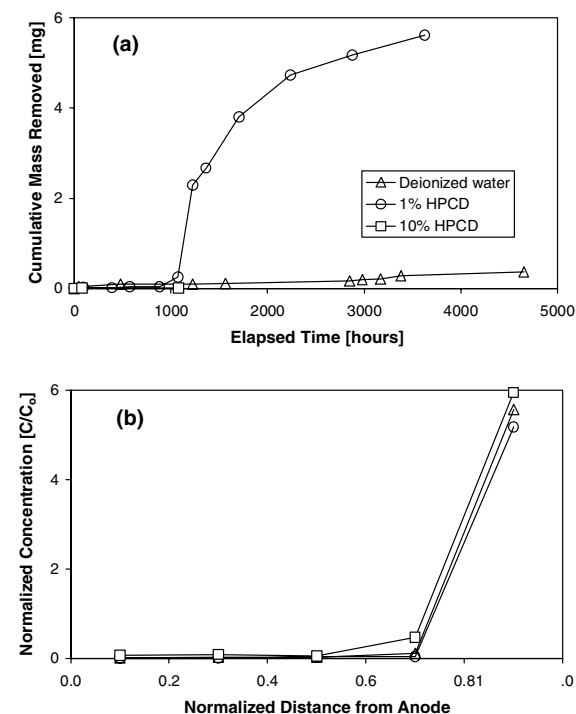


Fig. 6. (a) Cumulative nickel mass removal and (b) normalized nickel concentration profiles.

Fig. 6b shows the nickel concentration in the soil sections after the termination of the electrokinetic tests with deionized water, 1% HPCD, and 10% HPCD. The mobilization of nickel was significant in all the tests. In the baseline test, normalized nickel concentration was about 0.01 in the four sections from the anode and it increased to 5.57 in the last soil section near the cathode. Nickel exists as cations (Ni^{2+} ions) under low pH conditions; therefore, it electromigrated towards the cathode. The complete removal of nickel into the cathode did not occur because of the precipitation of Ni as $\text{Ni}(\text{OH})_2$ under the high pH conditions that existed in the soil section near the cathode. In both tests with HPCD, nickel migrated towards the cathode due to electromigration. In the test with 1% HPCD, the normalized concentration of nickel was zero in the first two sections and then gradually increased to 0.04 in the fourth section and it increased to 5.18 in the section near the anode. The reason for the incomplete removal may be the low concentration of HPCD that may not be sufficient to complex with nickel and remove it. Also, the reaction retention time may not be sufficient to remove nickel. Even though the pH of whole soil section near the cathode is about 4, the high pH (10–12) conditions in the cathode and in the soil in the vicinity of cathode cause nickel to precipitate. In the case of the test with 10% HPCD, normalized nickel concentration was 0.06 at the soil section near the anode and it reduced to 0.05 at the middle section and then drastically increased to 5.95. The low electroosmotic flow and hence the low soil–solution–contaminant interaction and also the existence of the high pH conditions near the cathode may have inhibited the complete removal of nickel into the cathode.

4. Conclusions

The purpose of this study was to evaluate the potential of cyclodextrins for the simultaneous removal of co-existing heavy metals and PAHs from soils having low permeability using electrokinetics. Based on the results of a series of laboratory experiments, the following conclusions can be drawn:

- The electric current in the test with deionized water was lower than in the test in which 1% HPCD was used. This may be because of the more number of ions available in the case of 1% HPCD. However, in spite of more number of ions available in 10% HPCD when compared to 1% HPCD, the electric current was low.
- The electroosmotic flow was found to depend on the electrical current values in all the tests. The electroosmotic flow was high in the 1% HPCD test followed by deionized water and 10% HPCD tests corresponding

to the current values in the respective tests. The electroosmotic flow is directly proportional to dielectric constant and indirectly proportional to the viscosity of the solution. 1% HPCD will have a higher dielectric constant and a lower viscosity than 10% HPCD. Consequently, the electroosmotic flow in 1% HPCD test was greater than the electroosmotic flow in 10% HPCD test.

- In spite of maintaining high pH in anode by addition of 0.01 M NaOH, the soil pH reduced near the anode and increased near the cathode. The pH values in the test with 1% HPCD were lower than the other tests due to high electroosmotic flow that allowed faster migration of H^+ ions towards cathode and inhibited electromigration of OH^- ions into the soil from cathode.
- The migration of phenanthrene occurred from anode to cathode in all the tests. The phenanthrene mass removal was high in the case of 1% HPCD test when compared to the baseline and 10% HPCD tests. The high electroosmotic flow and hence more number of flushed pore volumes have aided the interaction between the soil, HPCD and phenanthrene. The overall removal was not high because of the low concentration of the HPCD solution. Though the concentration of HPCD in the test with 10% HPCD was high, the low electroosmotic flow and hence less number of pore volumes flushed were not sufficient for the solubilization of phenanthrene because of the less interaction between the soil, HPCD and phenanthrene. In the test with deionized water, the solubilization of phenanthrene could not occur because of the hydrophobic characteristic of phenanthrene, though there was high electroosmotic flow and hence more interaction between the solution and the contaminant.
- There was a similar and significant mobilization of nickel from anode to cathode in all the tests. Nickel exists as cation under low pH conditions and it was able to electromigrate towards the cathode. The complete removal of nickel into the solution was retarded because of the precipitation of nickel as a result of the high pH conditions that existed in the soil adjacent to the cathode.

Overall, this study showed that sustained higher electroosmotic flow with higher concentration HPCD may be needed to increase phenanthrene removal efficiency. Simultaneously, reducing the soil pH near the cathode may be needed to increase nickel removal efficiency.

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