

# Cosolvent-enhanced Desorption and Transport of Heavy Metals and Organic Contaminants in Soils during Electrokinetic Remediation

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**Abstract** Numerous sites are contaminated with both heavy metals and polycyclic aromatic hydrocarbons (PAHs) and the technologies to treat such mixed contaminants are very limited. Electrokinetic remediation has the potential to remediate mixed contaminants in soils, including low permeability soils; however, the efficiency of this technology depends on the extracting solution employed. Previous studies on electrokinetic remediation have focused on the removal of heavy metals and organic compounds when they exist individually in clayey soils. In the present study, the feasibility of using cosolvents to enhance the electrokinetic removal of PAHs from clayey soils in the presence of heavy metals is investigated. A series of laboratory electrokinetic experiments was conducted using kaolin soil spiked with phenanthrene and nickel at concentrations of 500 mg/kg each to simulate typical field mixed contamination. Experiments were performed using *n*-butylamine (cosolvent) at concentrations of 10 and 20% and deionized water, each mixed with 0.01 M NaOH solution and circulated at the anode to maintain alkaline conditions. A periodic voltage gradient of

2 VDC/cm in cycles of 5 days on and 2 days off was applied in all the tests. During the initial stages when the soil pH was low, nickel existed as a cation and electromigrated towards the cathode. However, as the soil pH increased due to hydroxyl ions generated at the cathode and also flushing of high pH *n*-butylamine solution from the anode, nickel precipitated with no further migration. Phenanthrene was found migrating towards the cathode in proportion to the concentration of *n*-butylamine. The extent of phenanthrene removal was found to depend on both the electroosmotic flow and the concentration of *n*-butylamine, but the presence of nickel did not influence the transport and removal of phenanthrene.

**Keywords** Soil · Clays · Solubilization · Electrokinetics · Heavy metals · PAHs · Phenanthrene · Nickel · Cosolvent · Remediation

## 1 Introduction

Numerous sites are contaminated with heavy metal and organic contamination (USEPA 1996a, b). Urgent remediation of these sites is required to protect public health and the environment. Solidification/stabilization, soil washing/flushing, and bioremediation have been the most common technologies used to treat soils contaminated with heavy metals and PAHs (Sharma and Reddy 2004). Treatment trains combining several technologies in a series (e.g., flushing followed by

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bioremediation) have also been employed to address multiple contaminants existing in soils. However, these technologies fail in low permeability soils because of the difficulty in delivery of the reactive agents required for remediation. Electrokinetic remediation involving the installation of electrodes into multiple wells/drains within a contaminated zone and the application of a low direct current electric potential (Acar et al. 1995; Saichek and Reddy 2005; Reddy and Saichek 2004) has the potential to be applicable under such conditions. Ideally, the contaminants migrate toward the electrodes due to transport processes such as electromigration, electroosmosis, and electrophoresis. When contaminants reach the wells/drains, the contaminant-laden fluids are removed and treated. Although implementation is simple, the transport processes and geochemistry that occur within the soil during electrokinetic treatment are complex and dependent on system variables such as soil type, contaminant type, treatment time, electrolyte solution, and applied electric potential (Acar et al. 1995; Saichek 2001; Reddy and Saichek 2004).

Previous research has shown that electrokinetic remediation has the potential to remove heavy metals (Reddy and Chinthamreddy 2003, 2004; Reddy et al. 2003) and PAHs (Reddy and Saichek 2004) from soils. Though the efficiency of electrokinetic remediation was tested when these contaminant groups exist individually, no studies have investigated the feasibility of using electrokinetic remediation for mixed contamination. Because of the different nature of the contaminant groups, extracting solutions must be carefully selected to remove both the contaminant groups simultaneously. A comprehensive research program has been undertaken at the University of Illinois at Chicago (UIC) to develop enhanced electrokinetic remediation technology that is able to remediate mixed contamination in difficult subsurface conditions, including low permeability and heterogeneous conditions. A systematic evaluation of different extracting solutions including cyclodextrins, surfactants, cosolvents, weak acids and chelates is being conducted. Maturi (2004) and Maturi and Reddy (2006) performed batch experiments and bench-scale electrokinetic experiments and found that cyclodextrins are not very effective for the simultaneous removal of heavy metals and organic compounds from soils using electrokinetics. This paper presents an evaluation using cosolvents to enhance electrokinetic remediation, specifically to determine the efficiency of cosolvents for the removal of PAHs in the

presence of heavy metals and to determine the consequent effects on the mobility of heavy metals during cosolvent flushing.

Generally, cosolvents have molecular structures that are polarized allowing them to mix well with water, but they are also organic in nature making them mix better with hydrophobic organic compounds (HOCs) (Saichek and Reddy 2005; Saichek 2001). Cosolvency phenomena refers to the changes in the behavior, including the solubility, sorption equilibrium, kinetics and transport velocity of solute chemicals upon the addition of one or more organic solvents (cosolvent) to an aqueous solution. Research has shown that cosolvents exhibit the ability to significantly enhance the solubilization of the number of HOCs including PAHs (Saichek and Reddy 2005; Saichek 2001; Li et al. 2000). A cosolvent increases the solubility of a HOC by lowering the interfacial tension of the mixture (Saichek and Reddy 2005; Saichek 2001).

In a previous study conducted at UIC (Li et al. 2000), several batch desorption experiments were conducted using different cosolvents (acetone, tetrahydrofuran, and *n*-butylamine) to remove phenanthrene from glacial till soil. All the batch experiments were conducted using 20% concentration for all the selected cosolvents. In comparison to the other selected cosolvents, *n*-butylamine was found to be the most effective for desorption of phenanthrene. It was also reported that *n*-butylamine had water-cosolvent interactions that could favor phenanthrene solubility. Li et al. (2000) conducted additional bench-scale electrokinetic experiments using 20% *n*-butylamine as the extracting solution to remove phenanthrene from the glacial till soil. A significant migration of phenanthrene was achieved using *n*-butylamine. Subsequently, Maturi (2004) conducted a series of batch desorption experiments using kaolin soil spiked with phenanthrene and nickel at a concentration 500 mg/kg each. The results showed that about 46% of phenanthrene was removed from the soil using 20% *n*-butylamine; however, the removal of nickel was very low. The batch experiments do not represent the in-situ conditions and thus electrokinetic bench-scale experiments were recommended to assess the actual performance of *n*-butylamine under in-situ conditions.

This paper presents a series of bench-scale electrokinetic experiments conducted to investigate the

feasibility of using *n*-butylamine for the removal of PAHs in the presence of heavy metals from low permeability kaolin soil using electrokinetics. The transport of heavy metals was also evaluated while observing the removal of phenanthrene. The optimization of concentration of *n*-butylamine and the effect of test duration on the removal of phenanthrene were assessed.

## 2 Experimental Methodology

### 2.1 Materials and Methods

Kaolin was selected as model low permeability soil. Its composition and properties are summarized in Table 1. Phenanthrene (C<sub>14</sub>H<sub>10</sub>), 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 ( $K_{ow}$ ), and vapor pressure that are similar to other PAHs including acenaphthene, fluoranthene, and fluorene. Although higher molecular weight and more carcinogenic PAHs such as benzo(*a*) pyrene may have higher  $K_{ow}$  values and lower aqueous solubilities, it was hypothesized that since the parent structures are similar, phenanthrene would be an adequate representative compound that would give a general indication of the PAH behavior. All PAHs are hydrophobic and phenanthrene has an aqueous solubil-

ity of 1.1 mg/L 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 in contaminated sites. The major sources of nickel contamination in the soils are the metal plating industry, combustion of fossil fuels, and nickel mining and refining. Nickel (Ni) is a transition element with the atomic number 28 and an atomic weight of 58.69. In low pH regions, nickel exists in the form of the nickelous ion (Ni<sup>+2</sup>). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide (Ni(OH)<sub>2</sub>), which is a stable compound (Pourbaix 1978). Based on the previous studies conducted with different cosolvents, *n*-butylamine was shown to be effective for desorption/solubilization of phenanthrene and, as such, it was selected for this study.

### 2.2 Electrokinetic Test Setup

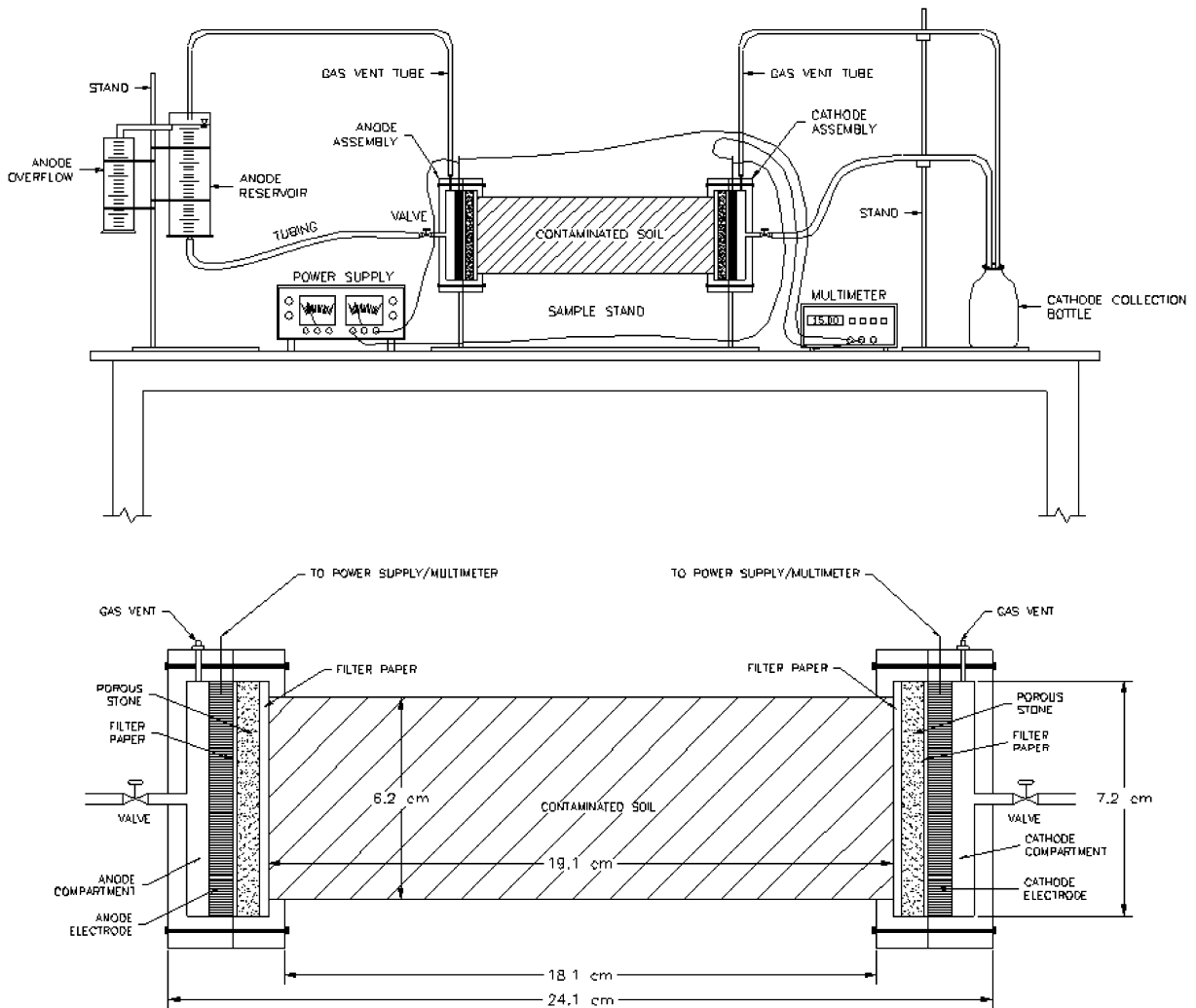
Figure 1 shows the schematic of the electrokinetic test setup used in this study (Reddy et al. 1997; Reddy and Saichek 2003). The setup consisted of a cell; two electrode compartments; an anode electrode reservoir; a peristaltic pump to circulate the solution in the anode reservoir in order to maintain neutral pH; 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 a 6.2 cm inside diameter and a 19.1 cm length, which was supported on a raised aluminum stand. Each electrode compartment was also made of Plexiglas® and contained Whatman® filter paper, a porous stone, and a perforated graphite electrode. The filter paper was placed between the soil and the porous stone, all of which 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.

### 2.3 Testing Program

A total of four electrokinetic tests were conducted with variables shown in Table 2. One test was conducted using deionized water as an extracting solution to serve as a baseline test. A second test was conducted using 10% *n*-butylamine as an extracting solution.

**Table 1** Properties of kaolin soil

Property	Result
Mineralogy (X-ray diffraction)	Kaolinite 100% Muscovite: trace Illite: trace
Particle size distribution (ASTM D422)	
Gravel (>4.75 mm) [%]	0
Sand (>0.075 mm) [%]	4
Silt (>0.005 mm) [%]	18
Clay (<0.005 mm) [%]	78
Specific gravity (ASTM D854)	2.54
Hydraulic conductivity [cm/s] (ASTM D5084)	1.0 × 10 <sup>-8</sup>
Organic content [%] (ASTM D2974)	Near 0
pH (ASTM D4972)	4.9
Cation exchange capacity [meq/100 g] (ASTM D9081)	1.0–1.6
USCS classification (ASTM D2487)	CL



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

The third and fourth tests were performed using 20% *n*-butylamine with different test durations. Tests were conducted under a periodic voltage application of 2 VDC/cm with a cycle of 5 days of continuous vol-

tage application followed by 2 days of “down-time” where the voltage was not applied to allow for kinetic chemical reactions to occur (Saichek and Reddy 2005; Saichek 2001). To maintain near neutral pH at the

**Table 2** Bench-scale electrokinetic testing program

Test	Soil	Contaminants	Anode solution	pH control solution	Voltage gradient (VDC/cm)	Mode of voltage application	Duration (days)
1	Kaolin	Nickel – 500 mg/Kg; Phenanthrene – 500 mg/Kg	Deionized water	0.01 M NaOH	2	Periodic (5 days on/2 days off)	193
2	Kaolin	Nickel – 500 mg/Kg; Phenanthrene – 500 mg/Kg	10% <i>n</i> -butylamine	0.01 M NaOH	2	Periodic (5 days on/2 days off)	151
3	Kaolin	Nickel – 500 mg/Kg; Phenanthrene – 500 mg/Kg	20% <i>n</i> -butylamine	0.01 M NaOH	2	Periodic (5 days on/2 days off)	37
4	Kaolin	Nickel – 500 mg/Kg; Phenanthrene – 500 mg/Kg	20% <i>n</i> -butylamine	0.01 M NaOH	2	Periodic (5 days on/2 days off)	151

anode, 0.01 M NaOH was recirculated in the anode reservoir using a peristaltic pump. The duration of the testing with 10% *n*-butylamine and 20% *n*-butylamine (denoted as long) was 150 days (3,600 h), while the duration of the test using deionized water was 190 days (4,560 h). The duration of the test with 20% *n*-butylamine was 37 days (888 h) and helped examine the effects of test duration on the transport and removal of contaminants.

#### 2.4 Testing Procedure

Approximately 1,200 g of kaolin was used for each test. Kaolin was spiked with phenanthrene at an initial target concentration of 500 mg/kg. This concentration was based on typical PAH concentrations found near source zones at contaminated sites (USEPA 2000). Initially, the phenanthrene required to yield the target concentration was measured and then completely dissolved in 500 mL of hexane. The hexane–phenanthrene mixture was subsequently combined with the measured amount of soil and with additional hexane so that the soil–hexane–phenanthrene mixture could be easily blended homogeneously. The mixtures were stirred with stainless steel spoons in glass beakers to ensure uniform distribution of phenanthrene in the soil. The soil–hexane–phenanthrene mixture was then placed in a ventilation hood for nearly a week until the hexane evaporated completely and the contaminated soil was dry. Occasional stirring was necessary during the drying period to increase the rate of drying and further ensure uniform phenanthrene distribution. After drying, a soil sample was taken to determine the actual initial concentration of phenanthrene in the soil using the Soxhlet extraction procedure in accordance with the USEPA test method 3540C (USEPA 1996a; Reddy and Saichek 2003).

The phenanthrene-spiked kaolin was then spiked with nickel at a target concentration of 500 mg/kg. The required amount of nickel chloride was dissolved in de-ionized 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 the soil was adjusted to 35% by adding deionized water. The initial nickel concentration in the soil was measured based on the USEPA acid digestion procedure followed by analysis with an atomic absorption spectrophotometer (USEPA 1996a; Reddy and Chinthamreddy 2003, 2004).

The moist soil was placed into the electrokinetic cell in uniform layers. 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 reservoirs were attached to the cell and the anode reservoir was filled with flushing solution (deionized water, 10% *n*-butylamine, or 20% *n*-butylamine). The flushing solution at the anode reservoir was mixed with 0.01 M NaOH and circulated using a peristaltic circulation pump to maintain neutral pH conditions. The cathode compartment was initially filled with deionized water. A periodic DC voltage gradient of 2 VDC/cm in cycles of 5 days on and 2 days off was applied.

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. At the completion of each test, the reservoirs 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 used for the analysis of nickel and phenanthrene concentrations. From each soil section, 10 g of soil was taken and mixed with 10 mL of a 0.01 M CaCl<sub>2</sub> solution in a glass vial. The soil-solution mixtures were shaken thoroughly by hand for several minutes and the solids were allowed to settle for an hour. These soil-solutions were then used to measure the soil pH and electrical conductivity. The pH of the aqueous solutions collected near the cathode was measured. The moisture content of each soil section was determined in accordance with ASTM D2216.

#### 2.5 Chemical Analysis

The phenanthrene concentration in the soil was determined using the Soxhlet extraction procedure in accordance with USEPA test method 3540C followed by analysis using Gas Chromatography (GC) (USEPA 1996a). The GC used was an Agilent Model 6890 GC equipped with a Flame Ionization Detector (FID). The injection volume of 1 µL was injected via an auto-injector at an inlet temperature of 250°C. The column used on the GC was a J&W Scientific (Folsom, CA)

DB-5, 30 m×0.32 mm×25  $\mu$ m. The carrier gas was nitrogen at a constant pressure of 25-psi. The oven temperature ramped from 100 to 250°C at 18°C/min for 1.5 min and then held at 250°C till the end of the run time. The instrument was calibrated using 2-fluorobiphenyl as an external standard. The calibration range was from 1 to 40 mg/L. The extraction efficiency was calculated based on a surrogate concentration obtained from the GC. The final phenanthrene concentration in the original soil extract was determined.

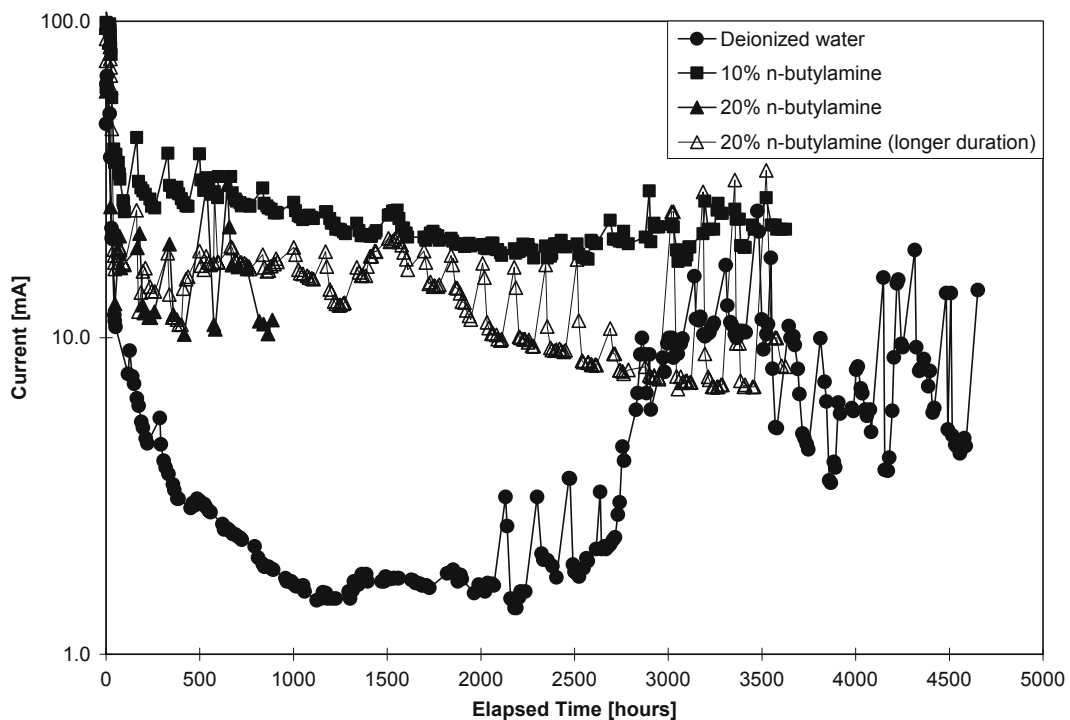
The liquid samples collected at the cathode were analyzed for phenanthrene after performing liquid–liquid extraction. The extraction procedure consisted of placing 1 mL of the contaminated supernatant in a conical flask using a syringe. The sample was then diluted in a ratio of 1:10 with water. The conical flask was shaken thoroughly before transferring the diluted sample into a test tube when 200  $\mu$ L of 2-fluorobiphenyl was added. Subsequently, 2 mL of methylene chloride was added to the test tube. The test tube was hand shaken for 5 min. The methylene chloride phase and the aqueous phase were then allowed to separate. Of the methylene chloride phase 1–2 mL were placed into a 2 mL autosampler vial using a syringe. The sample was then run on the GC.

The nickel concentration in the soil was determined by the acid digestion in accordance with USEPA 3050 procedure followed by analysis using an atomic absorption spectrophotometer (AAS) in accordance with the USEPA method 7520 (USEPA1996a). The liquid samples collected near the cathode from the electrokinetic tests were tested directly using AAS for the nickel concentration in accordance with the USEPA method 7520.

### 3 Results and Analysis

#### 3.1 Current

Figure 2 shows the comparison of current variation with elapsed time for the tests conducted using deionized water, 10% *n*-butylamine, and 20% *n*-butylamine as extracting solutions and with all other variables consistent. The same trend in the variation was observed in all tests. In general, the current values initially increased to a maximum value within a short time and then reduced and stabilized within 100 h of the test initiation. High current was measured due to the partial solubilization of salt precipitates



**Fig. 2** Effect of *n*-butylamine concentration on current

resulting in higher ionic concentration in pore-water (Mitchell 1993; Saichek and Reddy 2005; Saichek 2001). However, with increased elapsed time, these ions are depleted as they electromigrate into the electrodes (Saichek and Reddy 2005; Saichek 2001). At the same time, ions constantly generated near the anode had high mobility and were transported through the soil due to different transport processes including electromigration and electroosmosis (Acar et al. 1995). The initial higher current in the tests may also be attributed to the inflow of acidic solution that lowers the pH of the soil leading to additional mineral dissolution and a higher current (Saichek and Reddy 2005; Saichek 2001). Due to the changes in the solution chemistry and periodic voltage application, there were fluctuating trends in the current variation. During the “downtime” period when electric potential was not applied, additional ions entered into the solution leading to an increase in the current values when the voltage was reapplied after 2 days of “downtime.”

The current values were higher in the 10% *n*-butylamine test than in those with 20% *n*-butylamine. The higher current in the 10% *n*-butylamine test may be due to the presence of a greater number of mobile ions when compared with the 20% *n*-butylamine test. Generally, the dielectric constant is low for cosolvents and it decreases with an increased concentration of cosolvent (Saichek and Reddy 2005; Saichek 2001). The dielectric constant of the non-aqueous solutions is generally one-third the dielectric constant of water (Reddy and Saichek 2002; Weast et al. 1984). It is known that the dielectric constant is directly related to the dissociation of the ions and hence a lower dielectric constant was one of the reasons for lower current in 20% *n*-butylamine test when compared with the 10% *n*-butylamine test. Both tests with 20% *n*-butylamine had similar current values with slight fluctuations, demonstrating the repeatability of the test results. Though the dielectric constant of water is very high, the current in the test with deionized water was the least when compared with the other three tests conducted with *n*-butylamine as the extracting solution. This may be because a lower number of ions participated in the electrolysis reaction and because of the rapid depletion of ions in the test with water compared to the tests with *n*-butylamine. The current in the tests with deionized water, 10% *n*-butylamine, and 20% *n*-butylamine (longer duration) increased slightly after 3,000 h due to added fresh stock solutions.

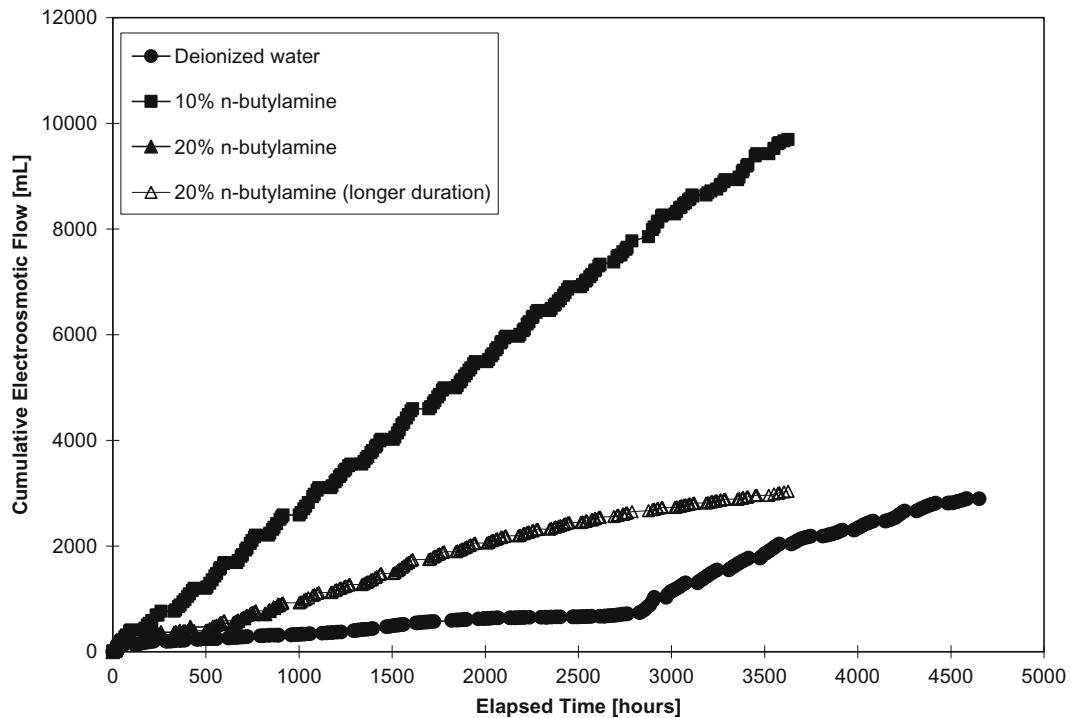
### 3.2 Electroosmotic Flow

Figure 3 shows the cumulative electroosmotic flow in the baseline of deionized water, 10% *n*-butylamine, and 20% *n*-butylamine tests. The fluctuations in the flow variation were due to the application of electric potential in a periodic mode and also due to the replenishment of anode and cathode reservoirs with fresh stock solutions at different time periods. Table 3 summarizes the equivalent number of pore volumes flushed in each of the tests. Approximately 11 pore volumes of flow was observed in both the deionized water and 20% *n*-butylamine (longer duration) tests, while 37 and 3 pore volumes of flow were observed in the 10% *n*-butylamine and 20% *n*-butylamine (shorter duration) tests, respectively. The maximum electroosmotic flow was measured in the 10% *n*-butylamine test and it was consistent with the high current generated in this test (Fig. 2).

It should be noted that 20% *n*-butylamine possesses a lower dielectric constant as compared to 10% *n*-butylamine and deionized water which should cause low electroosmotic flow according to the Helmholtz–Smoluchowski theory (H–S theory) (Saichek 2001). However, the higher ionic strength of 20% *n*-butylamine as compared to deionized water resulted in higher flow in the 20% *n*-butylamine test. The higher ionic strength and relatively higher dielectric constant of 10% *n*-butylamine as compared to 20% *n*-butylamine resulted in higher current values and higher electroosmotic flow in the 10% *n*-butylamine test. Though deionized water has a high dielectric constant, the test with deionized water as an extracting solution resulted in a low electroosmotic flow because of low ionic strength.

### 3.3 Soil pH Distribution

The initial pH of the soil was 4.9 (Table 1). Figure 4 shows the change in the soil pH from the anode to the cathode at the end of testing for all tests conducted in this study. When voltage potential is applied to the electrokinetic cell, an electrolysis reaction occurs in the electrodes, and  $H^+$  and  $OH^-$  ions are generated at the 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 migrates through the soil towards the cathode by electromigration and



**Fig. 3** Effect of *n*-butylamine concentration on electroosmotic flow

electroosmotic flow, lowering the pH of the soil (Acar et al. 1995). For the test with deionized water, the pH value was 1.6 near the anode and gradually increased to 6.4 towards the cathode. The low 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 (Saichek and Reddy 2005; Saichek 2001). Additionally,  $OH^-$  ions generated by the electrolysis reaction at the cathode electromigrate into the soil in the opposite direction of electroosmotic flow and increase the soil pH in the region near the cathode or neutralize the migrating  $H^+$  ions. This creates a low

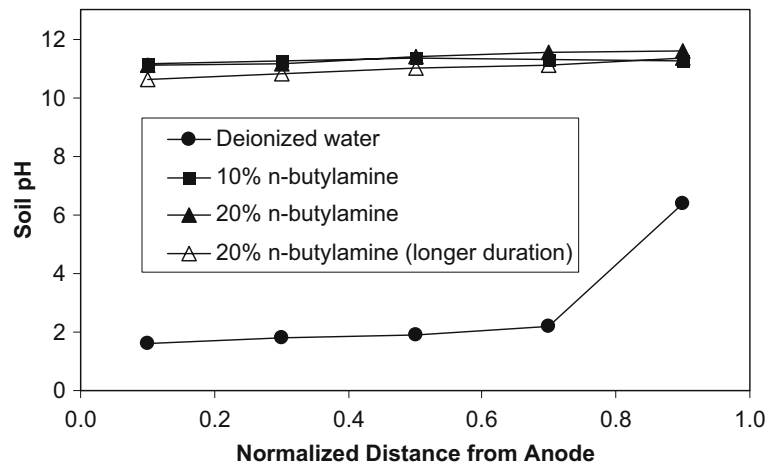
conductivity region with a somewhat neutral pH near the cathode (Saichek and Reddy 2005; Saichek 2001; Dzenitis 1996).

The variation of soil pH in the *n*-butylamine tests was significantly different than that found in the deionized water test. A uniformly high soil pH in the range of 10.6–11.6 was observed in all the tests in which *n*-butylamine was used. The high soil pH in these tests was attributed to the flushing of highly alkaline *n*-butylamine (>11) solution through the soil. The acid generated at the anode by electrolysis reactions was buffered by the *n*-butylamine solution. The slightly higher pH conditions near the cathode were attributed to the transport of hydroxyl ions from the cathode into the soil.

**Table 3** Initial soil conditions and number of pore volumes flushed

Test	Extracting solution	Water content (%)	Dry density ( $g/cm^3$ )	Void ratio	Porosity (%)	Total cumulative flow (mL)	Number of pore volumes flushed
1	Deionized water	32.5	1.37	0.90	47.4	273	10.6
2	10% <i>n</i> -butylamine	35.2	1.39	0.83	45.2	260	37.2
3	20% <i>n</i> -butylamine	35.0	1.36	0.87	46.5	268	3.3
4	20% <i>n</i> -butylamine (longer duration)	39.0	1.30	0.96	49.0	283	10.8

**Fig. 4** Effect of *n*-butylamine concentration on pH of soil



### 3.4 Removal of Phenanthrene

Figure 5a shows the phenanthrene removal from the soil in deionized water, 10% *n*-butylamine, and 20% *n*-butylamine tests. As seen from these results, removal of phenanthrene in all four tests was very low. Deionized water was ineffective in removing phenanthrene due to the hydrophobic nature of phenanthrene limiting solubilization into pore-water.

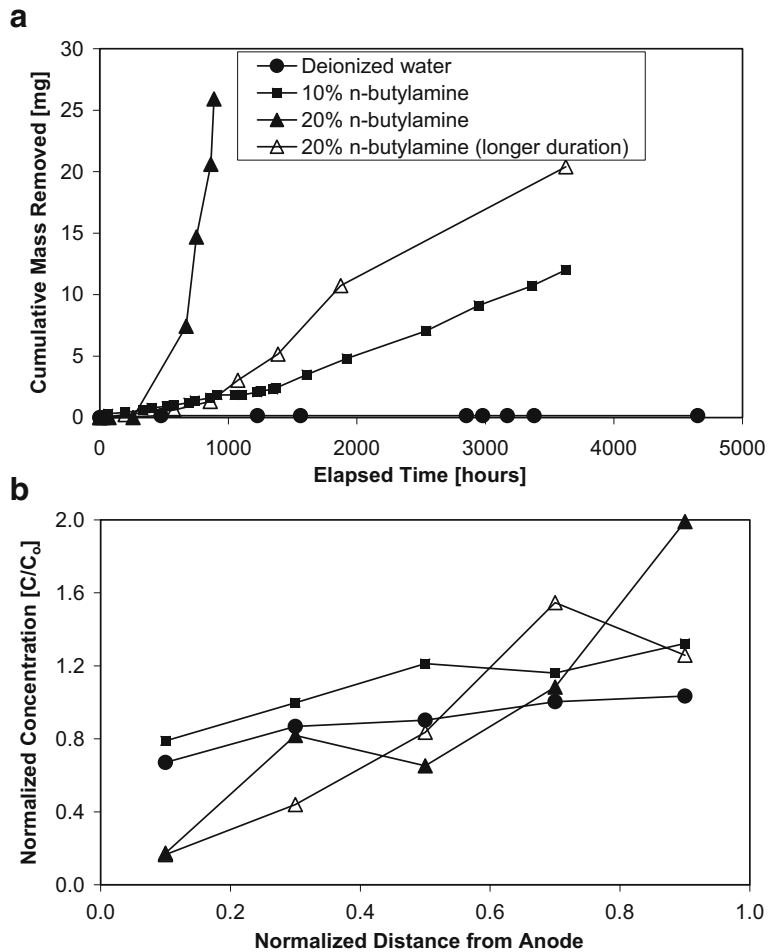
The removal of phenanthrene in the *n*-butylamine tests was dependent on the concentration of *n*-butylamine used and the amount of electroosmotic flow that occurred. The 20% *n*-butylamine test showed greater removal of phenanthrene than the 10% *n*-butylamine test due to increased solubilization of phenanthrene. However, the use of 20% *n*-butylamine yielded a lower electroosmotic flow as compared to that observed with the use of 10% *n*-butylamine, resulting in a limited removal of phenanthrene at the end of testing. The increase in test duration with 20% *n*-butylamine did not have a significant influence on the removal of phenanthrene from the soil. The amount of phenanthrene removed as compared to the initial total mass loaded into the soil was insignificant and the differences in the mass removal were mainly attributed to the heterogeneities in the contaminant distribution in the small soil specimens used for chemical analysis.

Figure 5b shows the residual phenanthrene concentrations in the soil (normalized with respect to the initial phenanthrene concentration) for tests with deionized water, 10% *n*-butylamine, and 20% *n*-butylamine. The phenanthrene concentrations in the baseline test increased slightly from anode to cathode,

indicating trends in transport of phenanthrene towards the cathode. The low transport of phenanthrene can be attributed to its very low aqueous solubility, resulting in a low availability of mass for electroosmotic advective transport. The 10% *n*-butylamine test results indicate that transport of phenanthrene occurred towards the cathode; however, it was lower than that observed in the 20% *n*-butylamine tests. The lower mobility in the 10% *n*-butylamine test as compared to the 20% *n*-butylamine tests may be due to the lower solubilization of phenanthrene at lower concentrations of *n*-butylamine. The 20% *n*-butylamine test conducted for a shorter duration also demonstrated a better mobility of phenanthrene when compared to that observed in the 10% *n*-butylamine test. These results show that longer test duration increased the mobility of phenanthrene towards the cathode due to increased solubility and advective transport of phenanthrene. However, the electroosmotic flow decreased in the 20% *n*-butylamine test, causing low total removal of phenanthrene from the soil at the end of testing. Therefore, the challenging task to increase the efficiency of removal is to optimize the concentration of *n*-butylamine that will result in increased solubilization of phenanthrene as well as provide sustained or increased electroosmotic flow.

Li et al. (2000) performed an electrokinetic bench-scale test on a glacial till soil spiked with 26 mg/kg of phenanthrene. The extracting solution used was 20% *n*-butylamine and the test was conducted under a constant electric potential of 1 VDC/cm. The duration of the test was 3,000 h which is comparable to the 20% *n*-butylamine (longer duration) test conducted in the present study. However, the soil type, the initial

**Fig. 5** **a** Cumulative phenanthrene mass removal, **b** Normalized phenanthrene concentration profiles in the soil sections



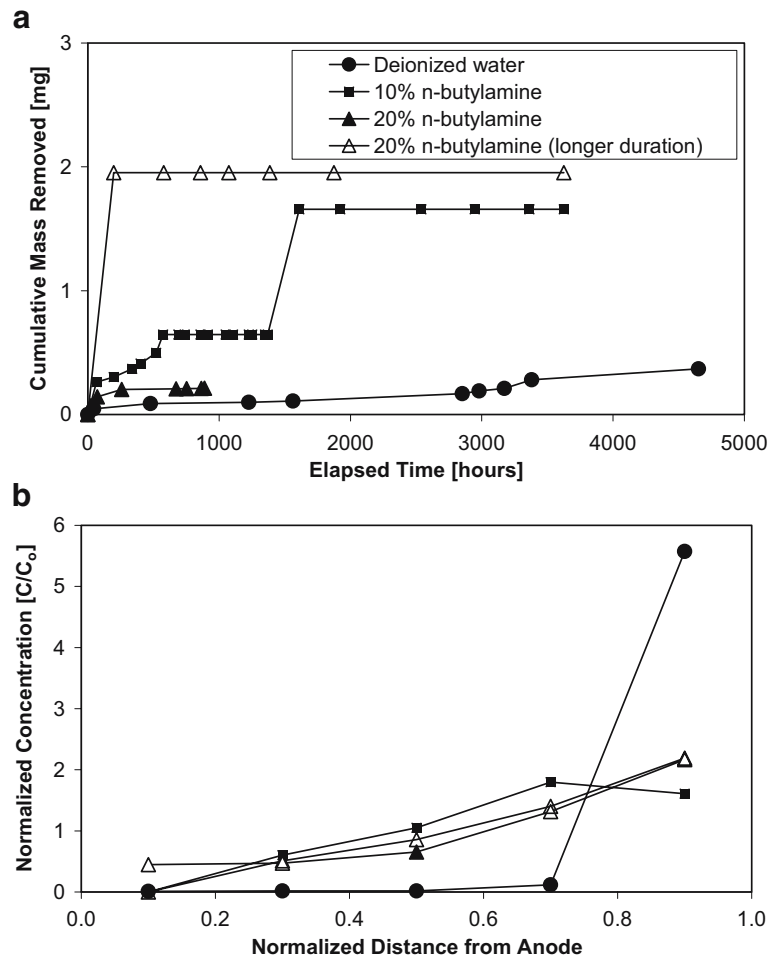
phenanthrene concentration, and the voltage potential were all different in the present study as compared to that used in Li et al. (2000). In the present study, the kaolin soil spiked with 500 mg/kg of phenanthrene was used and the test was conducted under a periodic voltage potential of 2 VDC/cm. In both studies, approximately 10 pore volumes of flow was generated and significant migration of phenanthrene towards the cathode occurred with most of the phenanthrene accumulated in the soil sections close to the cathode. Li et al. (2000) reported about 43% of the added 26 mg/kg phenanthrene removed with the solution. Glacial till contains about 2% organic matter. Phenanthrene sorption onto the organic matter may have caused low solubilization and removal of phenanthrene with such a soil. In contrast, only 7% of phenanthrene was removed completely into the solution in the present study. Kaolin soil does not contain organic matter and the low removal may be attributed to the

high initial mass of phenanthrene present in the soil and more electroosmotic flow and/or the higher concentration of *n*-butylamine may result in a greater mass removal. Overall, these results indicate that the extent of phenanthrene removal depends on the soil composition and the system controls such as magnitude and mode of applied electric potential.

### 3.5 Removal of Nickel

Figure 6a shows the nickel removal from the soil. Figure 6b shows the residual nickel concentration (normalized with respect to the initial concentration) in the soil after the completion of the electrokinetic tests using deionized water and *n*-butylamine as extracting solutions. These results show that the removal of nickel from the soil was insignificant in all the tests. However, the mobilization of nickel was significant in the baseline test. In the baseline test,

**Fig. 6** **a** Cumulative nickel mass removal, **b** Normalized nickel concentration profiles in the soil sections



normalized nickel concentration was about 0.009 throughout the sample except near the cathode where it increased to 5.57. Significant nickel mobilization in this test may be attributed to low pH conditions that caused nickel to exist as a cation and electromigrate towards the cathode. However, the complete removal of nickel into the cathode did not occur due to precipitation of Ni as  $\text{Ni}(\text{OH})_2$  under the high pH conditions that existed in the soil near the cathode. During the initial stages, when the soil pH was low prior to flushing with *n*-butylamine solution, nickel existed as a cation and migrated towards the cathode because of electromigration. However, flushing of highly alkaline *n*-butylamine solution increased the soil pH throughout, causing nickel to precipitate and retard any migration towards the cathode.

Chinthamreddy (1999) conducted an electrokinetic baseline test using kaolin soil spiked with 500 mg/kg

of nickel alone. A constant voltage potential of 1 VDC/cm was applied and the duration of the test was about 250 h. For the baseline test in the present study, the soil type and the initial phenanthrene concentration were the same; however, a periodic voltage potential of 2 VDC/cm was applied for a total duration of about 4,700 h. Because of the low voltage potential, the current and the electroosmotic flow were lower in the Chinthamreddy (1999) study as compared to those observed in this study. Nevertheless, the significant migration of nickel towards the cathode and the subsequent accumulation within the soil near the cathode was similar to that observed in this study. The accumulation of nickel near the cathode was attributed to the formation of nickel precipitates (e.g.,  $\text{Ni}(\text{OH})_2$ ) due to high pH conditions existing near the cathode due to electrolysis reactions. The results of Chinthamreddy (1999) and the present

study suggest that the migration of nickel is not affected by the presence of phenanthrene in the soil.

#### 4 Conclusions

A series of bench-scale electrokinetic experiments was conducted using low permeability kaolin soil spiked with phenanthrene and nickel each at 500 mg/kg under a periodic voltage application of 2.0 VDC/cm in cycles of 5 days on and 2 days off. The specific objective of these experiments was to assess the effectiveness of using *n*-butylamine (cosolvent) as an extracting solution for the enhanced removal of PAHs in the presence of heavy metals from soils having low permeability using electrokinetics. The following conclusions can be drawn from this study:

1. The electric current decreased as the concentration of the cosolvent increased. The electroosmotic flow was found to be in agreement with the electrical current values in all the tests. The electroosmotic flow was highest in the 10% *n*-butylamine test followed by the 20% *n*-butylamine and deionized water tests corresponding to the current values in the respective tests. The increased number of ions in the *n*-butylamine led to higher current values and higher electroosmotic flow as compared to the deionized water.
2. The entire soil pH increased to greater than 10 due to the flushing of highly alkaline *n*-butylamine solution. The soil pH decreased to less than 2 near the anode and increased to greater than 6 near the cathode due to electrolysis of water at the electrodes.
3. The residual phenanthrene concentrations increased from the anode to the cathode, demonstrating that phenanthrene migrated towards the cathode. The extent of migration was dependent on the *n*-butylamine concentration and the amount of electroosmotic flow. In the tests with 20% *n*-butylamine, the mobilization of phenanthrene was higher than in the other two tests. The migration of phenanthrene in the deionized test was low because of the hydrophobic nature of phenanthrene that was unable to solubilize phenanthrene. The slight migration that had occurred was because of the electroosmotic flow that flushed phenanthrene towards the cathode. The actual phenanthrene removal at the cathode was consistent with the

residual concentrations measured in the soil, i.e., highest in the 20% *n*-butylamine test followed by 10% *n*-butylamine and deionized water tests. The solubility of phenanthrene increases, but the electroosmotic flow decreases with an increase in the concentration of *n*-butylamine; therefore, a careful optimization of the concentration of *n*-butylamine is required to achieve high removal efficiencies.

4. Nickel migrated from anode to cathode in the test with deionized water and accumulated near the cathode region due to precipitation under high pH conditions. The migration of nickel was not significant in tests with *n*-butylamine due to increased pH conditions throughout the soil as a result of the high initial pH of *n*-butylamine solution. Therefore, immobilization rather than removal of metals was observed within the soil with the use of *n*-butylamine.

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