



Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil

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Abstract

Polycyclic aromatic hydrocarbon (PAH)-contaminated soils exist at numerous sites, and these sites may threaten public health and the environment because many PAH compounds are toxic, mutagenic, and/or carcinogenic. PAHs are also hydrophobic and persistent, so conventional remediation methods are often costly or inefficient, especially when the contaminants are present in low permeability and/or organic soils. An innovative technique, electrokinetically enhanced in situ flushing, has the potential to increase soil–solution–contaminant interaction and PAH removal efficiency for low permeability soils; however, the electrolysis reaction at the anode may adversely affect the remediation of low acid buffering capacity soils, such as kaolin. Therefore, the objective of this study was to improve the remediation of low acid buffering soils by controlling the pH at the anode to counteract the electrolysis reaction. Six bench-scale electrokinetic experiments were conducted, where each test employed one of three different flushing solutions, deionized water, a surfactant, or a cosolvent. For each of these solutions, tests were performed with and without a 0.01 M NaOH solution at the anode to control the pH. The test using deionized water with pH control generated a higher electroosmotic flow than the equivalent test performed without pH control, but the electroosmotic flow difference between the surfactant and cosolvent tests with and without pH control was minor compared to that observed with the deionized water tests. Controlling the pH was beneficial for increasing contaminant solubilization and migration from the soil region adjacent to the anode, but the high contaminant concentrations that resulted in the middle or cathode soil regions indicates that subsequent changes in the soil and/or solution chemistry caused contaminant deposition and low overall contaminant removal efficiency.

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1. Introduction

Polycyclic aromatic hydrocarbon (PAH) contamination is a problem at numerous sites throughout the United States partly because conventional remediation technologies are often inefficient or costly for PAH-contaminated soils (USEPA, 2000). Specifically, many

of the conventional techniques have difficulties treating heterogeneous subsurface environments that contain clayey and/or organic soils with low permeability. In situ soil flushing with surfactants/cosolvents has shown great promise for PAH-contaminated soils with a hydraulic conductivity of at least 10^{-5} cm/s in magnitude, but the likelihood of success decreases when lower permeability soils are present (Roote, 1997). Thus, for the present study, the in situ flushing and electrokinetic techniques have been integrated in an innovative remediation technique known as electrokinetically enhanced in situ soil flushing, and this technique has a great potential to

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improve the remedial efficiency for PAH-contaminated subsurface environments possessing low permeability soils.

The in situ flushing process first entails drilling one or more injection and extraction wells up and down gradient of the contaminated zone. The selected flushing solution is then pumped below the surface via the injection well so that it flows by gravity, or with applied pressure, down gradient towards the contaminated region. Once within the contaminated zone, it is essential that flushing solution interacts with the contaminants and solubilization occurs. The contaminant-laden solution then flows further down gradient to the extraction well where it is withdrawn, treated using common wastewater techniques, and then possibly recycled back to the subsurface (Abdul et al., 1992; Pinto and Moore, 2000; Lee et al., 2001). The electrokinetically enhanced in situ flushing process basically involves the installation of electrodes into the injection and extraction wells and the application of a low voltage gradient across the designated anode and cathode electrodes. The electrically induced contaminant transport mechanism of electroosmosis greatly improves soil–solution–contaminant interaction through low permeability soils (Casagrande, 1949). However, low pH conditions occur in low buffering soils as a result of the migration of acid generated at the anode due to the electrolysis reaction. The low pH soil conditions impede electroosmosis and, hence, removal efficiency.

The present laboratory investigation was undertaken to examine the effects of using a low concentration alkaline (0.01 M NaOH) flushing solution to counteract the electrolysis reaction at the anode and enhance electroosmotic flow in low acid buffering soils. Six bench-scale electrokinetic experiments were conducted using a low buffering kaolin soil spiked with phenanthrene as the representative PAH. Each test employed one of three different flushing solutions, deionized water, a surfactant, or a cosolvent, with and without pH control. The effects of the pH control solution were then assessed by comparing the test results, in particular, the tests were evaluated by comparing the electrical current, electroosmotic flow and cumulative mass removal that occurred during test operation, as well as the pH and residual contaminant concentrations that existed in the soil at the conclusion of testing.

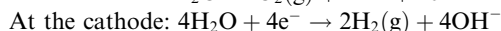
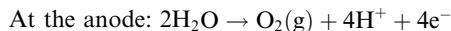
2. Background

A comprehensive review of the physico-chemical processes that are involved in electrokinetics has been provided in several previous studies, such as those by Eykholt and Daniel (1994), Yeung (1994), Acar et al. (1995), and Alshawabkeh and Bricka (2000). Furthermore, although electrokinetics is commonly used for toxic metal contamination, researchers, such as Acar

et al. (1992), Bruell et al. (1992) and Shapiro and Probst (1993), have performed laboratory investigations and have found that electrokinetics can be successfully used for the remediation of soluble organic contaminants, such as benzene, toluene, and phenol.

Clayey soils that are difficult to treat with hydraulic flushing alone are considered to be suitable soils for electrokinetically enhanced flushing. Initially, it should be recognized that due to isomorphic substitution or broken bonds, negative charges are commonly present on clay mineral surfaces. These negative charges may be balanced by adsorbed cations and associated anions that are present as salt precipitates, and, when the particle surface is covered with water, the precipitated salts go into solution (Mitchell, 1993). Once they are dissolved in the solution, the concentration of ions may be initially high near the particle surface, so the ions diffuse away in the direction of decreasing concentration gradient. However, the negative electrical field originating from the particle surface counteracts the diffusion process, and the cations and anions distribute themselves in a diffuse double layer configuration (Mitchell, 1993).

When an electric potential is applied electrolysis of water occurs at the electrodes according to the following reactions:



As seen from these equations, the electrolysis reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. The primary contaminant transport mechanisms that occur during electrokinetics are *electromigration*, *electroosmosis*, and *electrophoresis*. *Electromigration* describes the transport of ionic species present in the pore fluid. This process is largely responsible for generating the electrical current, and it includes the migration of H^+ and OH^- towards the oppositely charged electrode. Moreover, under an electric potential, electroosmotic flow (*electroosmosis*) is produced because the locally existing excess ions migrate in a plane parallel to the particle surface towards the oppositely charged electrode, and, as they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces (Eykholt, 1992). Electroosmosis depends on the net amount of ionic migration towards an electrode location, and, in low permeability clayey soils, the net ion migration may be high and it could significantly affect the decontamination process. The following Helmholtz–Smoluchowski (H–S) equation is often used to estimate the average electroosmotic flow velocity (v_{eo}) (Eykholt and Daniel, 1994):

$$v_{\text{eo}} = -\frac{D\varepsilon_0\zeta}{\eta}E_x \quad (1)$$

According to this equation, the flow velocity is proportional to the electrical gradient (E_x), zeta potential (ζ), and dielectric constant (D), and it is inversely proportional to the viscosity (η). The (ϵ_0) term represents the permittivity of vacuum (8.854×10^{-12} C/V m), and the dielectric constant and viscosity are properties of the pore fluid. The zeta potential depends on several factors, including the charge on the particle surface and the conductivity of the pore solution. The zero point of charge (ZPC) refers to the pH at which the net charge on the particle surface is zero. Generally, when the pH is below its ZPC, a soil has a positive zeta potential and the electroosmotic flow occurs towards the anode. Conversely, when the pH is above the ZPC, the soil has a negative zeta potential and the electroosmotic flow occurs towards the cathode. Alternately, the electroosmotic flow velocity is given by:

$$v_{eo} = K_e E_x \quad (2)$$

where K_e is referred to as the electroosmotic conductivity. Finally, *electrophoresis* is the migration of charged colloids, but, in a compact soil system, electrophoresis is less important since larger colloid-sized particles are typically restrained from movement.

Although the electrokinetically enhanced in situ flushing technique has great potential, the effectiveness of the process depends on soil–solution–contaminant chemistry. By observing the H–S equation, it can be seen that changes in the surface charge of the soil particles and changes in the pore fluid properties (such as conductivity, dielectric constant, and viscosity) influence the electroosmotic flow. In addition, the electrical gradient may not be uniform through the soil, so the electroosmotic flow is generally not uniform spatially or temporally (Eykholt and Daniel, 1994). Therefore, the average electroosmotic conductivity (K_e) through the soil commonly varies with time, and, as a result of physico-chemical changes, the electroosmotic flow may cease or reverse in direction. Furthermore, soils are variable and complex substances, both structurally and compositionally (Mitchell, 1993), and contaminant chemistry, desorption and solubilization reactions, as well as the mass transport mechanisms that occur during electrokinetics may complicate the process.

The electrolysis reactions affect the remediation process because the ionic products (H^+ and OH^-) may electromigrate and/or they may be transported by electroosmotic advection towards the oppositely charged electrode location. Thus, an acidic (H^+) front of solution may move from the anode towards the cathode, and/or an alkaline (OH^-) front of solution may move from the cathode towards the anode. The rate of electromigration could be affected by ionic mobility, and, since hydrogen ions are smaller and have 1.76 times the ionic mobility of hydroxyl ions, the acidic front generally moves faster

through the soil (Alshwabkeh and Bricka, 2000). In addition, the reaction kinetics, or the rate of the electrolysis reactions at the electrodes could affect the generation and migration of the hydrogen and/or hydroxyl ions. For low acid buffering clayey soils, such as kaolin, the inflow of H^+ ions has the effect of causing the charge on the mineral surface to become more positive, which decreases the electroosmotic flow towards the cathode. Shapiro and Probst (1993) and Schultz (1997) have found that adding a pH control solution to the anode reservoir helps to counteract or neutralize the electrolysis reaction at the anode, and the result is a higher and more sustained electroosmotic flow and greater contaminant removal.

During electrokinetically enhanced in situ flushing, there are two fundamental requirements for PAH removal from low permeability soils. The first is that there needs to be sufficient soil–solution–contaminant interaction, and the second is that the flushing solution must be capable of solubilizing the contaminant. Saichek (2002) conducted batch tests that indicated that surfactants/cosolvents were capable of enhancing phenanthrene solubilization, but subsequent bench-scale electrokinetic tests with these solutions revealed that contaminant migration was occurring but the actual amount of contaminant removal was limited. It was hypothesized that controlling the pH at the anode would improve soil–solution–contaminant interaction and removal efficiency.

3. Materials and methods

3.1. Materials

Table 1 shows the mineralogy and properties of the kaolin soil used in this investigation. Kaolin basically consists of the kaolinite mineral and it has a hydraulic conductivity of 1×10^{-8} cm/s. Kaolin is often used for electrokinetic laboratory experiments because it has a low organic content, it is fairly nonreactive, and it has a low cation exchange capacity. It is important to remember, however, that clay soils usually contain a variety of other substances that are present in smaller or trace amounts and are not clay minerals, and these substances include organic matter, iron oxides, quartz and feldspars, oxides and hydroxides of aluminum and manganese, oxides of titanium, and carbonates, principally calcite (Greenland and Hayes, 1978). Twelve random samples of the kaolin soil were analyzed by an acid digestion procedure followed by an inductive coupled plasma–mass spectrophotometry (ICP–MS) analysis, and it was revealed that the kaolin possessed appreciable amounts (>3500 mg/kg) of aluminum and calcium and lesser amounts (about 250 mg/kg on

Table 1
Properties of kaolin

Mineralogy	Kaolinite 100% Muscovite: trace Illite: trace
Particle size distribution (%) (ASTM D 422)	
Gravel	0
Sand	4
Silt	18
Clay	78
Specific gravity (ASTM D 854)	2.6
Hydraulic conductivity (cm/s)	1.0×10^{-8}
Organic content (%)	Near 0
pH (ASTM D 4972)	4.9
Cation exchange capacity (meq/100g) (ASTM D 9081)	1.0–1.6
USCS classification (ASTM D 2487)	CL

average) of metals such as iron, magnesium, sodium, and zinc.

As observed in Table 1, the kaolin used in this investigation had a negligible amount of organic matter, but Schwarzenbach et al. (1993) found that the sorption of neutral organic chemicals to mineral surfaces could occur when the amount of soil organic matter was low. Researchers have hypothesized that the electrical charge of the mineral surface affects sorption behavior, even when the organic contaminant molecules are uncharged, because the mineral surface may exhibit attractive dispersion, or London–van der Waals forces (Schwarzenbach et al., 1993; Stumm and Morgan, 1996). Moreover, when the organic contaminant possessed more functional groups with dipoles or hydrogen bonding capabilities, stronger bonding was observed on mineral surfaces, such as silica (Schwarzenbach et al., 1993). Furthermore, Luthy et al. (1997) identified a number of mechanisms responsible for the adsorption of hydrophobic organic contaminants to soils, and, for inorganic surfaces, these researchers suggest that mass transfer is inhibited because the contaminants adsorb into the microporous regions of mineral matrices and/or into the interlayer surfaces of swelling clay minerals.

Phenanthrene, a neutrally charged three-ring PAH (98% pure, $C_{14}H_{10}$; molecular weight = 178.2), was selected to be a representative PAH compound, and it has an aqueous solubility of 1.1 mg/l and a $\log K_{ow}$ of 4.57 at 25 °C (Schwarzenbach et al., 1993). Three different flushing solutions, deionized water (baseline solution), 3% Tween 80 (polyoxyethylene (20) sorbitan monooleate), and 40% ethanol (C_2H_5OH) were used in this study. An alkaline (0.01 M NaOH) solution was used to control the pH in the anode reservoir. Saichek (2002) provided a basis for the selection and properties of these surfactants and cosolvents, and it should be noted that

relative to many organic liquids, water has a high dielectric constant of 78.54 at 25 °C, whereas organic liquids, such as ethanol (dielectric constant of 24.3 at 25 °C), are generally not as polarized and have lower dielectric constants (Weast et al., 1984). A total of six electrokinetic experiments were performed. The first set of three tests was conducted using three flushing solutions without pH control. The second set of three tests was conducted using the same flushing solutions, but with a pH control in the anode reservoir.

3.2. Electrokinetic reactor

The electrokinetic reactor used in this study was similar to that used in previous electrokinetic research (Reddy and Parupudi, 1997; Reddy and Shirani, 1997; Reddy et al., 1997). A schematic diagram of the overall electrokinetic test setup and the electrokinetic cell is shown in Fig. 1. The reactor simulates 1-D contaminant transport under the combined influences of electrical, hydraulic and chemical gradients.

The reactor consists of a cell, two electrode compartments (containing slotted graphite electrodes), an anode electrode reservoir, a cathode sample bottle, a power supply, a multimeter (Protek Model B-845), and peripherals, such as C-Flex tubing (Cole Parmer Instrument Company), wiring, and stands. The reactor cell was made of Plexiglas and it had an inside diameter of 6.2 cm (cross-sectional area = 30.2 cm²) and a length of 19.1 cm. Gas vents were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape. For all the experiments, the power supplies used were either Protek DC models 3006 or 3033 or a Hewlett-Packard DC model 6205B.

3.3. Testing procedure

For all the electrokinetic tests, the soil was artificially contaminated (spiked) with phenanthrene at a target concentration of 500 mg/kg (mass of phenanthrene/mass of dry soil), which represents the typical PAH concentrations found near source zones of contaminated sites (USEPA, 2000). Approximately 1.1 kg of dry kaolin was spiked for each electrokinetic test (including some extra soil for the determination of the initial phenanthrene concentration). Initially, the phenanthrene required to yield the target concentration was measured and then completely dissolved in about 500 ml of hexane. Hexane was used because of the low solubility of phenanthrene in water. The hexane–phenanthrene mixture was subsequently mixed with the measured amount of soil, and additional hexane was added so that the soil–hexane–phenanthrene mixture could be easily stirred and blended homogeneously. The mixtures were stirred with stainless steel spoons, and all mixing operations were performed within glass beakers. The soil–

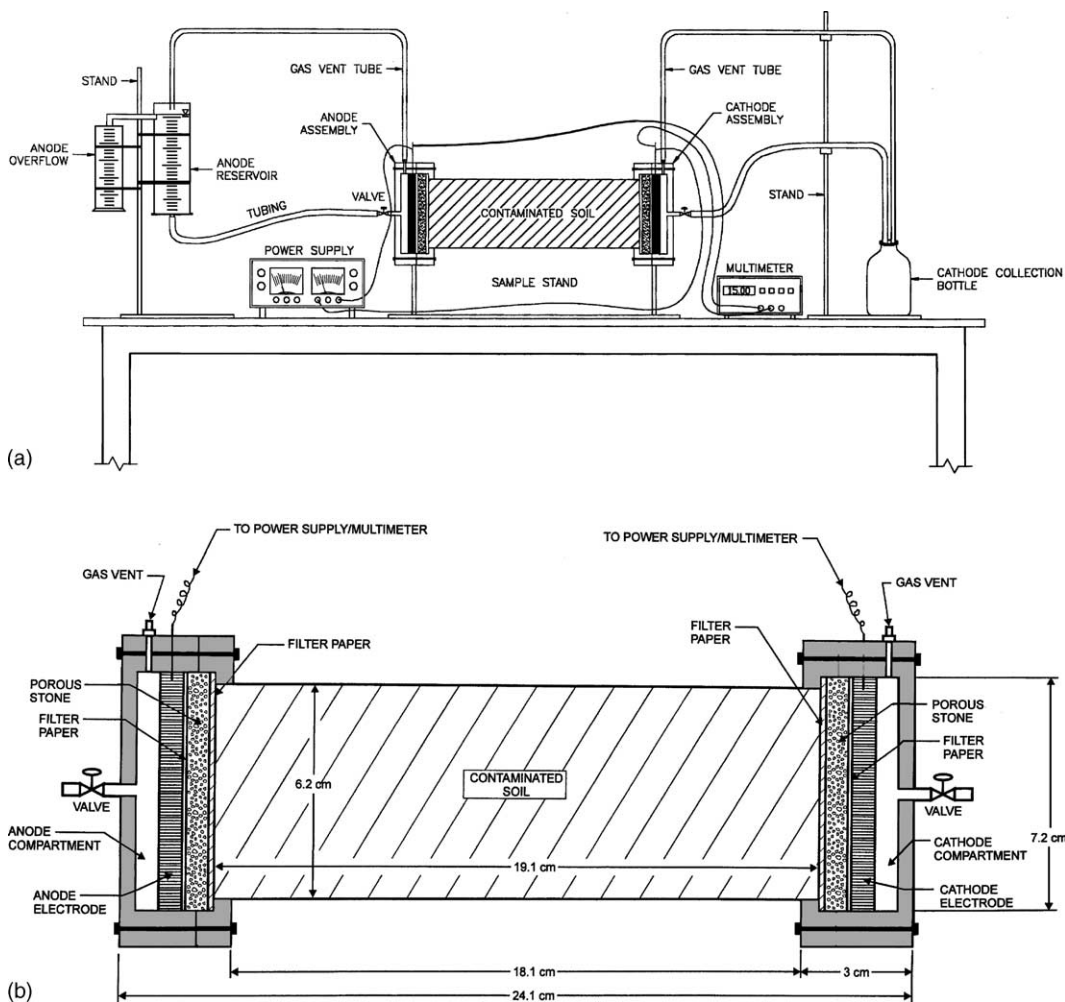


Fig. 1. Schematic of electrokinetic reactor: (a) overall test setup and (b) electrokinetic cell.

hexane–phenanthrene mixture was then placed beneath a ventilation hood for nearly a week until the hexane completely evaporated and the contaminated soil was dry. A sample was taken to determine the actual initial concentration of phenanthrene in the soil, since a portion of the contaminant volatilizes along with the solvent (hexane).

After the phenanthrene-contaminated soil was dry, it was thoroughly mixed with a measured amount of deionized water in a glass pan, so that the soil water content would simulate field conditions. The target water content for the kaolin soil was 35%. The moist contaminated soil was then placed into the electrokinetic cell in layers, and each layer was tamped into the cell using an aluminum pestle so that the amount of void space was minimized. Once the soil was fully packed into the cell, the reactor assembly was completed, the peripheral equipment was attached, the anode and cathode

electrode compartments as well as the anode reservoir were filled with solution, and a constant voltage gradient of 1.0 VDC/cm was used for all the tests conducted in this study. At the start of testing, the cathode compartment was filled with deionized water and the anode compartment and reservoir were filled with the appropriate flushing solution.

During the testing, the electrical current and the inflow volume and effluent volume at the anode and cathode were measured periodically, and samples of the effluent were taken so that the phenanthrene concentration could be measured. The tests were run until the current decreased and became stable, the effluent volume reduced or stabilized, and the phenanthrene concentration in the effluent was stable. At the conclusion of testing, the soil was extruded from the electrokinetic cell and divided into five 4 cm sections along the length of the cell to analyze the spatial distribution of the pH as

well as the residual phenanthrene remaining in the soil. After sectioning, the soil from each 4 cm section was mixed and a representative sample was obtained for the determination of moisture content, soil pH, and phenanthrene concentration. Soil pH measurements were determined using a soil to water ratio of 1:1 as described in ASTM method D 4972. Generally, 10 ml of deionized water was added to 10 g of soil, and the pH was measured using a Digi-Sense digital pH meter that was calibrated using standardized pH solutions. Water contents were determined using ASTM method D 2216.

3.4. Chemical analysis

For the chemical analysis of the soil, a dry representative sample weighing 10 g was thoroughly mixed with about 10 g of Na_2SO_4 , and the mixture was placed into a Whatman cellulose extraction thimble. The phenanthrene was then extracted using a Soxhlet apparatus according to the procedure outlined in USEPA test method 3540C (USEPA, 1986). The solution used in the Soxhlet extraction process was a 1:1 mixture of hexane and acetone. After the extraction was completed, HPLC analyses were performed on the liquid samples. The soil usually contained a high concentration of phenanthrene (300–800 mg/kg), so the solvent–phenanthrene liquid samples obtained from the Soxhlet extraction could be directly analyzed. The liquid (effluent) samples from the electrokinetic tests were analyzed by first extracting the phenanthrene from the aqueous (surfactant/cosolvent) solution into a solvent. The phenanthrene was extracted using a triple liquid–liquid extraction procedure using a total volume of approximately 50 ml of dichloromethane. The extract volume was subsequently reduced using a Kuderna-Danish concentrator, and the solvent was exchanged to methanol for injection into the HPLC.

A Hewlett-Packard Model 1100 HPLC equipped with an Alltech Econosphere reverse-phase C18 column (250 × 4.6 mm, 5 μm particle size) and a diode array UV detector was used. The detector wavelength was set at 254 nm. Before injection into the HPLC, the samples were filtered through a 0.22 μm particle retaining Cameo 13F Teflon, polytetrafluoroethylene (PTFE), membrane. Each sample was injected via a manual injector with a 20 μl sample loop. A mixture of water and methanol, 25:75, was used as the mobile phase at a constant flow rate of 1.0 ml/min. The HPLC was calibrated using four external standards (phenanthrene) prior to performing chemical analyses, and the detection limit was 0.01 mg/l.

3.5. Quality control

Throughout the electrokinetic testing, the Plexiglas reactors and reservoirs were either specifically constructed for these tests, or they were previously used reactors that had been thoroughly washed. The elec-

trodes, tubing, and connecting pins or hose clamps were all new for each test. Furthermore, all the glassware, such as vials and sample bottles, were new from the manufacturer and certified to be clean. All the testing equipment, such as the multimeters, power supplies, and pH meters, were in good condition and were calibrated, and a conscious effort was made to ensure that the chemicals used as solvents or in analyses were new from the manufacturer and that they were fresh and high-grade (HPLC) purity. The deionized water was tested to verify that it was had a low (<2 $\mu\text{S}/\text{cm}$) electrical conductivity.

Phenanthrene was used as an external standard for calibration, and the standards for the HPLC analyses were prepared in two different concentration ranges, where each series contained at least four standard solutions that covered an order of magnitude in concentration or more. The linearity of the calibration graph was always checked, and the average regression coefficient (R^2) was 0.996. Sample blanks, without contamination, were injected regularly to ensure that the system remained uncontaminated. Duplicate standard samples were commonly injected to certify a uniform response, and to ensure that the calibration graph and the baseline remained stable. The syringe was rinsed with solvent several times between sample injections to eliminate cross-contamination.

3.6. Mass balance

After the electrokinetic tests were completed, a mass balance was conducted for the phenanthrene in the system and compared to the phenanthrene spike. There was at least an 80% agreement between observed and expected mass balance values. Discrepancies in the mass balance may have been caused by uneven contaminant distribution within the soil, detection limitations in the chemical analyses, or contaminant adsorption to the electrokinetic equipment, such as the Plexiglas chambers, the electrodes, porous stones, tubing, and/or sample bottles. Volatilization of phenanthrene along with the solvents during the extraction procedures may have also occurred.

4. Results and discussion

4.1. Electrical current

Fig. 2 shows the changes in the electrical current that occurred during the electrokinetic experiments. The current values generally reached a peak near or at the start of testing when the quantity of ions in the pore solution was greatest due to the dissolution of salts that were associated with the dry soil particles (Mitchell, 1993). As the ions electromigrated towards the elec-

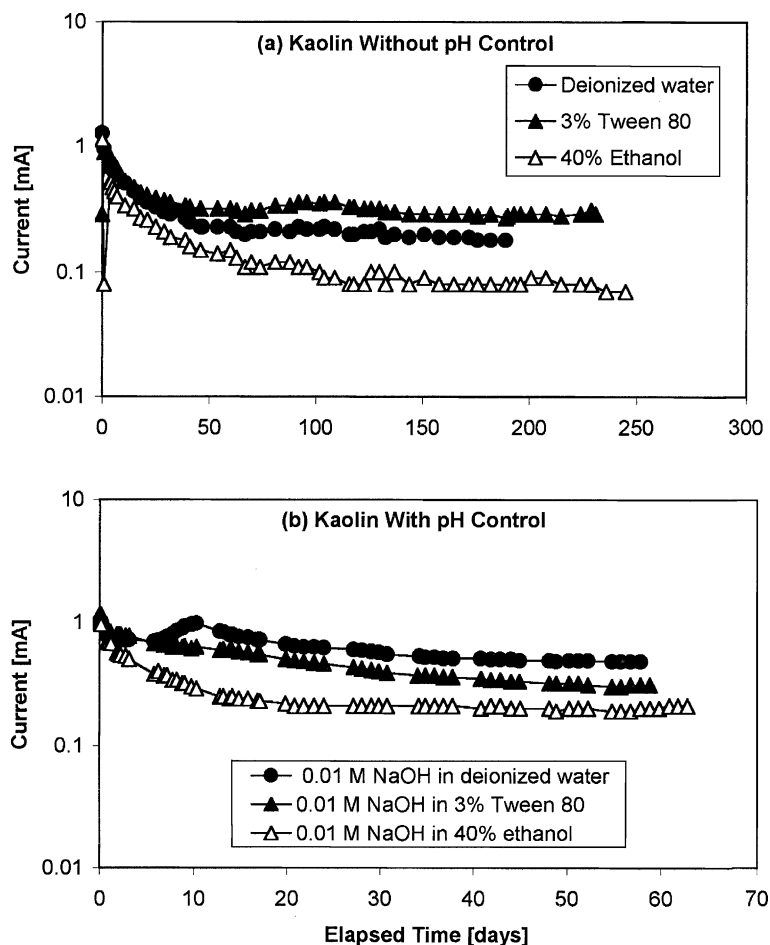


Fig. 2. Comparison of current with and without pH control.

trodes, however, the current gradually declined, and several other researchers have also observed similar behavior (Eykholt, 1992; Pamukcu, 1994; Grundl and Michalski, 1996). After approximately 50 days, a more stable or residual current value was reached. Comparing the results of the tests performed with and without pH control, it can be observed that the tests employing the 0.01 M NaOH solution commonly had slightly higher current values, and this is most likely a result of the additional ions introduced by the NaOH electrolyte. When the Na^+ and OH^- ions were introduced, the OH^- ions neutralized some of the H^+ ions generated at the anode by the electrolysis reaction (e.g. forming water, H_2O), while Na^+ ions electromigrated towards the cathode, consequently increasing the current.

It is interesting to observe in Fig. 2 that all six of the tests, with and without pH control, had an initial peak current value of approximately 1.0 mA. This indicates that the 0.01 M NaOH concentration was too weak to produce a substantial current increase. It was evident, however, that the pH control solution slightly increased

the current, especially when the deionized water solution was employed. When deionized water was used, after about 50 days, the residual current values between the equivalent tests run with and without the NaOH solution were about 0.49 and 0.23 mA, respectively (Fig. 2). In contrast to the deionized water tests, the differences in residual current between the equivalent tests run with and without the NaOH solution with the 3% Tween 80 and 40% ethanol solutions were minor. After about 50 days, there was no difference between the current values for the Tween 80 tests, and the ethanol test with pH control had a current that was only 0.05 mA higher than the equivalent test without pH control. The low dielectric constant for the 40% ethanol solution and a lower amount of ion dissociation may explain why the current was less in this solution than in the other two solutions, deionized water and 3% Tween 80 (Fig. 2).

The analysis of the 3% Tween 80 solution was complicated by surfactant chemistry and the presence of micelles. Although Tween 80 is a nonionic and neutrally charged surfactant, several investigators have

determined that nonionic surfactant molecules may acquire charges and/or become protonated (Rosen, 1989; Edwards et al., 1994; Ko et al., 1998b). As seen in Fig. 2(a), the Tween 80 test performed without pH control had current values that were generally about 0.1 mA higher than the values in the equivalent deionized water test. This suggests that surfactant molecule adsorption to the mineral surface reduced the adsorption of mobile ions, such as H^+ , Al^{3+} , or Ca^{2+} , thereby allowing these ions to produce a higher current. Moreover, surfactant molecule adsorption displaces and releases ions that had been previously adsorbed to the surface. Conversely, in the test using 3% Tween 80 with pH control, the Na^+ and OH^- ions adversely affected the current compared to the equivalent deionized water test. This is attributed to the reduction of the critical micelle concentration (CMC) of the nonionic surfactant, and/or the increase of the aggregation number, which commonly occurs following the addition of an electrolyte (Attwood and Florence, 1983). The introduction of 0.01 M NaOH reduced the polarity of the aqueous solution, thereby increasing micelle formation (micellization) and reducing surfactant adsorption. This depolarization effect occurs because water molecules are attracted to, and hydrate, electrolyte ions, so there are less water molecules available to interact with each other. Greater micellization or less surfactant adsorption would cause mobile ions, such as Na^+ , H^+ , or Ca^{2+} , to adsorb to the mineral surface, resulting in a lower amount of ions in solution and a reduced electrical current. Furthermore, bulk liquid phase surfactant molecules (micelles) would contribute to reducing the current by partially neutralizing some of the mobile ions in solution. Another consideration is that research has shown that elevating the electrolyte concentration may cause the current, or conductivity, of a solution to decrease due to interionic interactions (Hamann et al., 1998).

In Fig. 2(b) it can be seen that the test using deionized water with pH control had a small rise in current after it had been decreasing over the first five days. The induced electroosmotic flow and pH reduction near the anode may have caused the kaolin to flocculate during this time, producing a more open soil structure (Lambe and Whitman, 1969) that facilitated additional salt dissolution and, after a few days, an increased current.

4.2. Electroosmotic flow

As observed in Fig. 3, the largest difference in electroosmotic flow occurred between the equivalent deionized water tests, and this correlates to the electrical current values in Fig. 2. After around 50 days, the deionized water test without pH control accumulated about 400 ml of outflow, but the test with pH control generated over 1430 ml. Moreover, analogous to the current, the difference in electroosmotic flow between

the equivalent 3% Tween 80 and 40% ethanol tests with and without pH control was minor compared to the difference between the deionized water tests (Fig. 3).

Initially, all six tests exhibited their highest flow rates during the first week or so when the current was high, then the electroosmotic flow reduced along with the current. Considering all the tests in Fig. 3, the deionized water and 3% Tween 80 flushing solutions had a higher cumulative electroosmotic flow than the equivalent tests with 40% ethanol, and this is attributed to the lower dielectric constant of ethanol. According to H-S theory, the electroosmotic flow velocity is directly proportional to the dielectric constant.

In comparison to the deionized water tests, the tests using the surfactant solution showed a reduced cumulative electroosmotic flow due to the greater viscosity and the lower dielectric constant of Tween 80. Surfactant sorption to the mineral surface could also disrupt electroosmotic flow. After the surfactant molecules adsorb to the mineral surface, cations, such as H^+ , are capable of bonding with the adsorbed surfactant molecules, thereby causing the mineral surface to become more positively charged. Generally, a more positively charged surface translates to a more positive zeta potential and a reduced electroosmotic flow towards the cathode.

Research has shown that electrolytes reduce the CMC (Attwood and Florence, 1983) and have a depolarizing effect on the solution that results in greater micellization and/or less surfactant adsorption. Consequently, as shown in Fig. 3, after around 50 days, the flow in the 3% Tween 80 test without pH control was noticeably less than the corresponding test with pH control. Greater surfactant adsorption occurred without pH control, and this produced a more positively charged mineral surface and a reduction in electroosmotic flow towards the cathode.

4.3. Cumulative mass in solution

Fig. 4 shows the cumulative mass of phenanthrene measured in the effluent. As seen in this figure, compared to the initial mass of approximately 500 mg, phenanthrene removal was low for all the tests. The tests that were conducted with pH control were operated for about a fourth of the time period that tests without pH control were run, but, during the first 50 days of testing, the electroosmotic flow in the controlled tests was greater than it was in the uncontrolled tests, especially for the test employing deionized water. By observing Figs. 3 and 4, it can be seen that the higher electroosmotic flow and greater soil-solution interaction did not result in greater contaminant removal, so there was not adequate phenanthrene solubilization. The only test to show progressive contaminant removal was the 40% ethanol test without the 0.01 M NaOH solution, where a

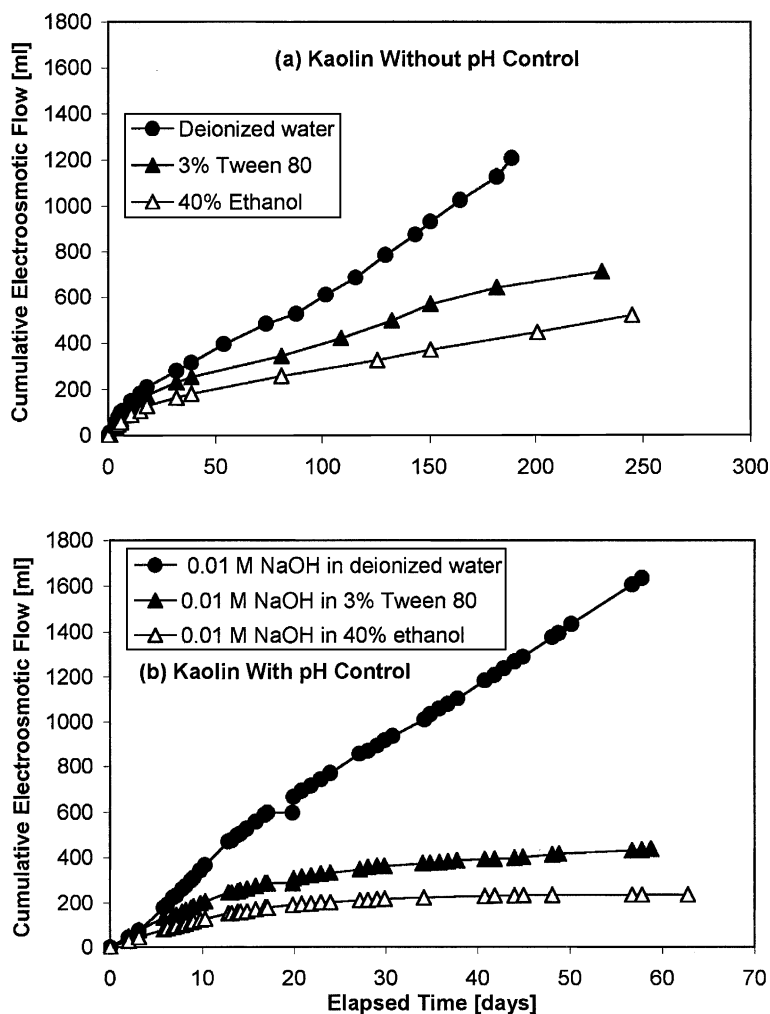


Fig. 3. Comparison of electroosmotic flow with and without pH control.

breakthrough was seen after about 126 days of operation.

As observed in Fig. 4, the phenanthrene concentration commonly increased in the last solution sample that was collected, especially in the ethanol test without pH control. The last effluent sample included the solution drained from the cathode compartment, and this relatively high phenanthrene concentration resulted from the draining process at the conclusion of testing. In the last effluent sample of the experiments that used the 40% ethanol solution, the concentration reached 1.7 and 5.2 mg/l in the tests with and without pH control, respectively, but for both the 3% Tween 80 tests and the deionized water test with pH control, the concentration in the last sample was less than the solubility of phenanthrene in water.

The 3% Tween 80 solution exhibited an unexpectedly small amount of phenanthrene removal, due to the low

concentration. Although the concentration was above the CMC, several investigators have found that surfactant adsorption may continue well beyond the CMC (Pennell et al., 1993; Adeel and Luthy, 1995; Ko et al., 1998a), and the phenanthrene then partitions to the sorbed surfactant molecules. Additionally, inadequate soil–solution–contaminant interaction and/or the kinetics, or reaction rate, was not sufficient to produce solubilization or phenanthrene micellization (Grimberg et al., 1995; Yoem et al., 1996; Lowe et al., 1999; Patterson et al., 1999).

Although the 40% ethanol solution had the lowest cumulative electroosmotic flow and, therefore, probably the least amount of soil–solution–contaminant interaction, this solution accomplished the greatest phenanthrene removal, especially in the test conducted without pH control. This is due to the cosolvency and lower surface tension, which increased phenanthrene solubility. Nevertheless, the quantity of phenanthrene that

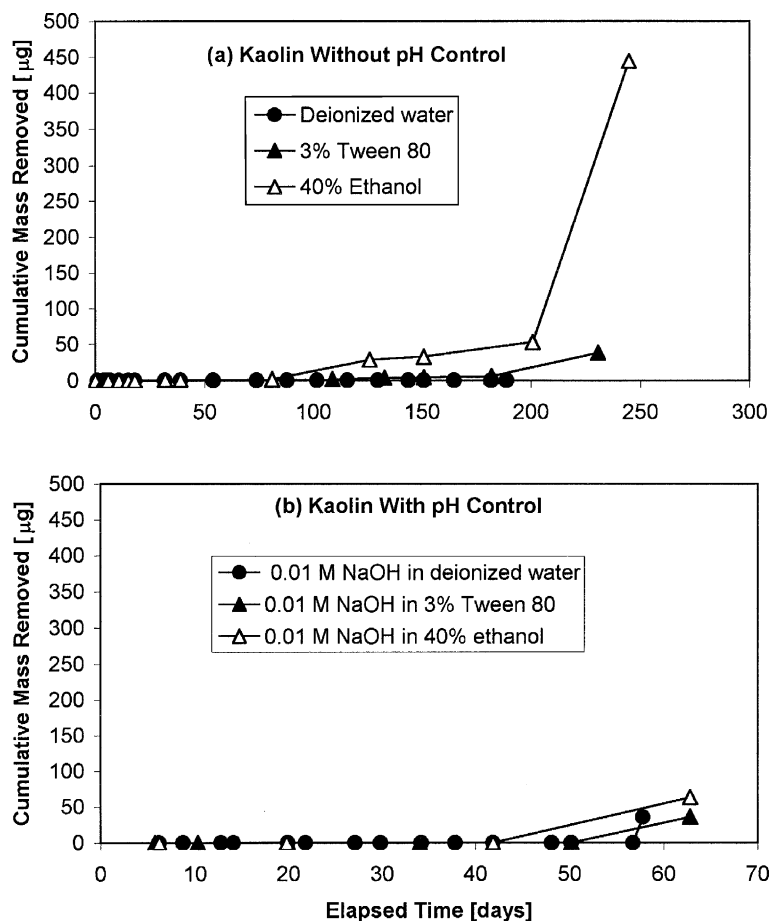


Fig. 4. Comparison of phenanthrene mass removal with and without pH control.

was removed in the ethanol test was negligible compared to what was expected based on the batch test results reported by Saichek (2002). It is important to understand that during electrokinetics the soil basically remains stationary and the solution travels through the soil by the transport mechanism of electroosmosis. The applied electrical gradient produces physico-chemical effects that alter the mass transport conditions and soil-solution-contaminant interaction. Changes in properties such as pH, ion concentration, electrical gradient, pore pressure, viscosity, and mineral surface charge greatly affected contaminant removal, which was substantially lower than the removal measured in batch tests where the soil slurry was shaken mechanically (Saichek, 2002).

4.4. Comparison of pH

The electrolysis reaction at the anode and the low buffering capacity of kaolin caused the tests that were

operated without pH control to experience a higher H^+ ion concentration (lower pH) in the anode compartment, and this low pH solution was transported into the soil towards the cathode via electromigration and electroosmosis (Acar et al., 1995). Moreover, in the tests conducted without pH control, the H^+ ions migrated through the soil all the way to the cathode region, which is evident because acidic pH values occurred along the length of the soil profiles. As observed in Fig. 5(a), the pH values varied from a low of around 3 near the anode to a high of about 5 near the cathode. Conversely, the tests conducted with pH control had somewhat higher pH values that ranged from a low of 3.6 near the anode to a high of 7.8 near the cathode.

The electrolysis reaction at the anode generates a greater concentration of H^+ ions when the electroosmotic flow is slower, because the solution has a longer retention time in the anode compartment. As seen in Fig. 5(a), compared to the deionized water test, the tests using 3% Tween 80 and 40% ethanol had lower pH

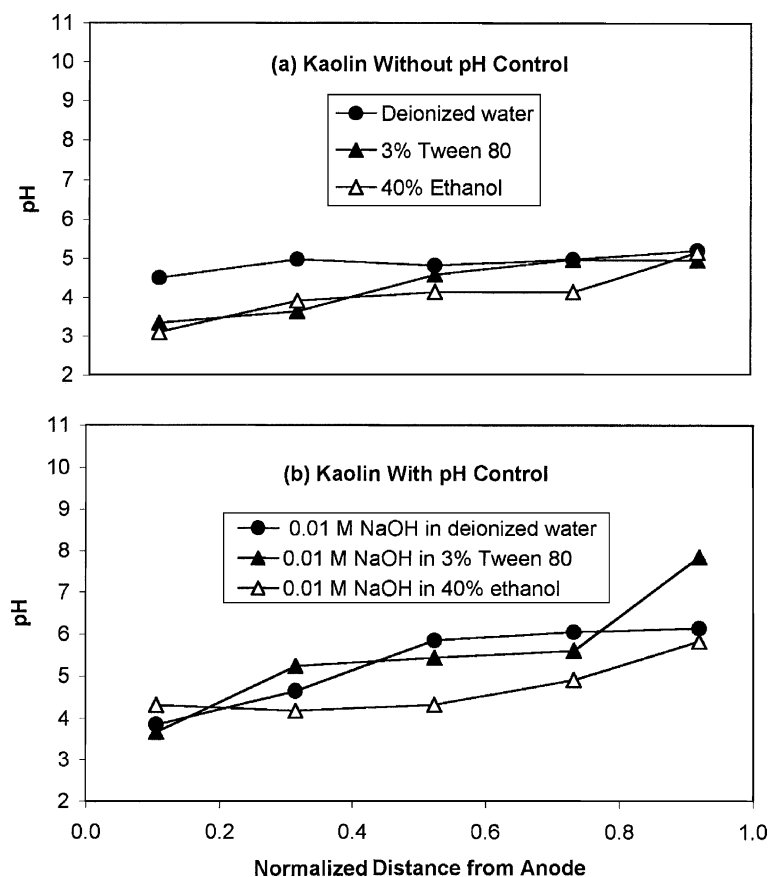


Fig. 5. Comparison of pH with and without pH control.

values near the anode, and Fig. 3(a) shows that both of these tests had a lower amount of electroosmotic flow. Furthermore, OH^- ions are generated due to the electrolysis reaction at the cathode, and they electromigrate towards the anode in the opposite direction of the flow. Thus, when the flow is lower, the OH^- ions are capable of electromigrating further and having a greater effect on the pH near the cathode. The lower mobility of the OH^- ions compared to H^+ ions is also a factor (Acar et al., 1995). As seen in Fig. 5(b), a pH value of about 8 was measured near the cathode in the test using 3% Tween 80, and, as seen in Fig. 3(b), this test had a much lower electroosmotic flow than the equivalent deionized water test, which had a pH value near 6 in the cathode region. The test using 40% ethanol was less affected by OH^- electromigration, because OH^- ion migration was inhibited by the low dielectric constant. In addition, the soil was more consolidated near the cathode, and clogged pore spaces reduced OH^- migration. It should also be recognized that H^+ and OH^- ions may react together during the electrokinetic process to form water (Dzenitis, 1997), and, therefore, the neutralization of OH^- ions near the cathode often keeps the pH low or closer to neutral.

The pH of the 0.01 M NaOH solution was 12, so the pH near the anode should have increased in the controlled tests due to the neutralization of H^+ at the anode. As shown in Fig. 5, this was not the case, because the test with the highest electroosmotic flow was the deionized water with pH control test and it had a pH of only around 4 near the anode, which was actually lower than the pH of 4.5 that was measured near the anode in the equivalent test without pH control. Moreover, the tests using 3% Tween 80 and 40% ethanol with pH control had pH values that were only slightly higher than the corresponding tests without pH control (Fig. 5). Therefore, a more concentrated pH control solution or a solution circulation process should be used to counteract the electrolysis reaction at the anode.

The pH near the anode in the deionized water test operated with pH control was lower than in the equivalent test operated without pH control (Fig. 5), but the electroosmotic flow in the controlled test was considerably higher (Fig. 3). The controlled test with the higher flow should have maintained a higher pH, but both deionized water tests experienced a substantially higher

flow than the equivalent surfactant and cosolvent tests. There are other considerations besides the flow, such as the kinetics of the electrolysis reaction that can affect the pH. Ideally, graphite electrodes are supposed to be inert and permit electron transfer without entering into the reaction, but the electrode material commonly forms bonds with the species in solution, and oxide formation as well as species adsorption onto the electrodes occurs (Brett and Brett, 1993). In other words, the electrolysis reaction at the anode, or the generation of H^+ ions, probably decreases over time, and this is important because the deionized water test without pH control was run for approximately four times as long as the equivalent test with pH control. The reduction in electrical current affects the rate of electrolysis, and, as seen in Fig. 2, at the conclusion of testing, the current in the deionized water test without pH control was about 0.2 mA, whereas the current at the end of the equivalent controlled test was 0.5 mA. Therefore, although the electroosmotic flow in the controlled test was higher than it was in the uncontrolled test (Fig. 3), the electrolysis reaction at the anode in the controlled test was generating H^+ ions at a faster rate, so it is reasonable that the pH near the anode in the controlled test was lower than in the uncontrolled test.

In addition, there are other factors to consider for the discrepancy between the lower pH near the anode and the high electroosmotic flow in the controlled deionized water test as opposed to the equivalent uncontrolled test. Dzenitis (1996) explains that the magnitude of the electroosmotic flow depends on the local electric field strength (or local voltage gradient = E_x). Dzenitis (1996) shows that the H^+ and OH^- ions react to form water in a region near the cathode, and the water may lower the conductivity of the pore solution in that region, which produces a relatively large voltage gradient. Consequently, by H-S theory, a greater electroosmotic flow velocity occurs in that low conductivity region. Comparing the pH of the deionized water tests in Fig. 5, the pH in the soil from the middle of the electrokinetic reactor to the cathode end is noticeably higher in the controlled test. Therefore, this high pH and low conductivity region may have been the driving force responsible for the higher electroosmotic flow. In addition, at a low pH, the kaolin particles near the anode could have been flocculated and produced a more open pore structure (Lambe and Whitman, 1969), and this could have allowed the flow to more easily penetrate into the higher pH region toward the middle of the soil profile.

4.5. Comparison of phenanthrene concentration

Fig. 6 shows a comparison of the residual phenanthrene concentration profiles from anode to cathode at the conclusion of the electrokinetic experiments. Fig. 6(a) shows that the deionized water test without pH

control exhibited minimal phenanthrene migration, and this was expected since phenanthrene is hydrophobic and nearly insoluble in water. However, the deionized water test with pH control caused some contaminant mobilization, especially near the anode region. The low solubility of phenanthrene and the high amount of contaminant mobilization suggests that solubilization was not responsible for transport, especially considering that the solubility of phenanthrene in water is roughly 1.1 mg/l at 25 °C (Schwarzenbach et al., 1993). Although approximately 1.6 l of cumulative electroosmotic flow occurred, based on the aqueous solubility, this would not have been nearly enough to produce the amount of contaminant migration that was measured. It may have been possible, however, for the deionized water to flush poorly adsorbed phenanthrene particles towards the cathode due to the high flow volume and the flushing action through the small pore spaces. Moreover, since the soil in the deionized water test with pH control had a lower pH near the anode than the equivalent test without pH control, the soil in the anode region could have been more flocculated and had a more open structure that was more susceptible to flushing. In addition, the phenanthrene was probably weakly adsorbed to kaolin because it has a low organic content.

The electroosmotic flow rate is a function of many variables, including the zeta potential and electrical gradient, so the flow is generally not uniform throughout the sample (Eykholt and Daniel, 1994; Eykholt, 1997). This could benefit some soil sections with high flow rates and greater soil–contaminant–solution interaction, such as near the inlet, or anode region, while other sections may receive contaminants from the soil at the inflow end, such as sections near the cathode. In Fig. 6, it looks as if the greater amount of soil–solution–contaminant interaction that occurs near the anode during electrokinetics may be beneficial for phenanthrene mobilization in kaolin, and this is evident in all the tests except for the test using deionized water. Fig. 6(a) shows that the increased interaction near the anode improved phenanthrene migration in the 40% ethanol test considerably, because it had a clean soil section adjacent to the anode. It seems that the contaminant that was removed near the anode was then distributed uniformly throughout the remainder of the soil profile. Furthermore, this 40% ethanol test was run for a longer duration and had a greater amount of cumulative electroosmotic flow than the corresponding test with pH control, and this may partially explain the greater contaminant migration from the anode region. The lower amount of phenanthrene solubilization and migration in the 40% ethanol test with pH control could have partly been a result of the NaOH, because salts typically lower the solubility of a hydrophobic organic contaminant in a cosolvent (Schwarzenbach et al., 1993; Valsaraj, 2000).

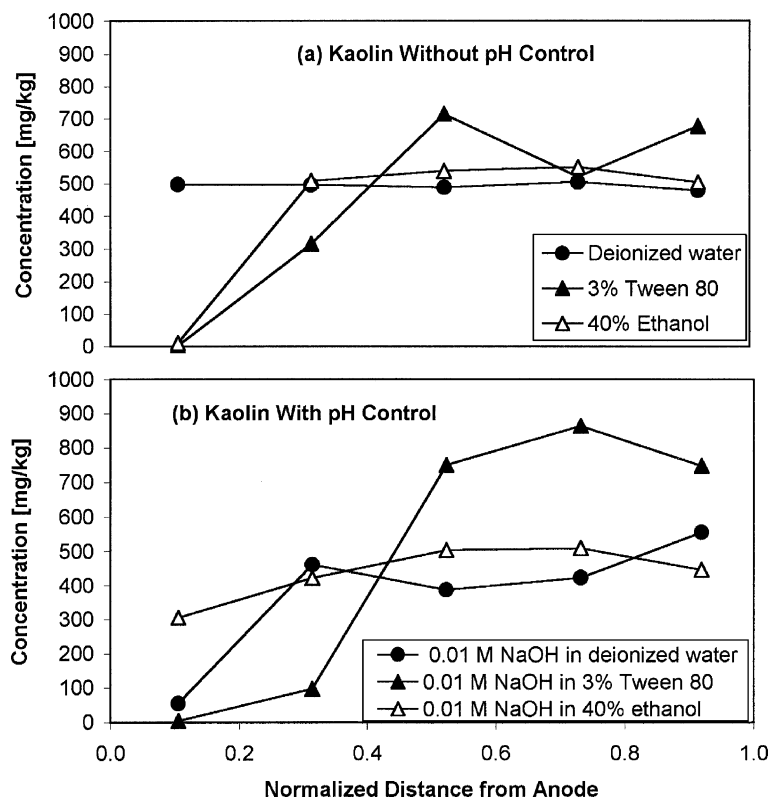


Fig. 6. Comparison of residual phenanthrene in soil with and without pH control.

The 3% Tween 80 solution showed fairly strong evidence of producing phenanthrene solubilization and migration towards the cathode in both of the tests, with and without pH control, but both these tests had very low actual contaminant removal (Fig. 6). The 3% Tween 80 test in Fig. 6(a) shows phenanthrene concentrations that were low near the anode, high in the middle section, and high at the cathode end. The high flow near the anode seems to have solubilized phenanthrene, allowing it to migrate toward the middle section, but then there was contaminant deposition or inadequate electroosmotic flow to mobilize the contaminant completely out of the soil or into the cathode reservoir. The 3% Tween 80 test with pH control had phenanthrene concentrations that were low near both sections closest to the anode, but then the concentration greatly increased towards the middle and end sections of the soil profile. Again, it was evident that there was partial phenanthrene solubilization near the anode, but then sorption occurred or there was not enough flow to remove the contaminant completely from the soil. With the 3% Tween 80 solution, changes in the soil and/or solution chemistry that occurred near the middle and cathode regions are probably responsible for the low contaminant removal. Overall though, the pH control solution

was advantageous for either increasing the electroosmotic flow and/or for mobilizing the phenanthrene towards the cathode, and this was most evident in the test employing the surfactant solution, 3% Tween 80.

5. Conclusions

The objective of this laboratory investigation was to attempt to improve soil–solution–contaminant interaction and removal efficiency by controlling the pH near the anode with 0.01 M NaOH along with the flushing solution during electrokinetics. One soil type, kaolin, and three flushing solutions, deionized water, 3% Tween 80, and 40% ethanol were used in the different tests with and without pH control. The parameters that were measured during testing included the electric current, cumulative electroosmotic flow, and cumulative mass removal, and, after each test was concluded, the pH and residual contaminant concentration were measured along the soil profile. The main conclusions drawn from the results of this investigation are as follows:

1. The concentration of the pH control solution (0.01 M NaOH) may have been too low, since the tests performed with and without control started with nearly the

same amount of electrical current and resulted in similar pH soil profiles after the tests were concluded. It was evident however, that the pH control solution affected the electrokinetic process, because, during the first 60 days of testing, the current was generally higher in the tests that employed pH control. Comparing the tests performed with and without the NaOH solution, the greatest improvement was observed with the deionized water solution, where the electroosmotic flow increased by over a liter in the first 50 days of testing. However, the flow difference was not nearly as great when the NaOH solution was used in combination with the surfactant or cosolvent solution.

2. The controlled deionized water test exhibited a greatly improved electroosmotic flow over the deionized water test without control, but it was surprising that the pH in the soil near the anode was actually lower in the test using NaOH. The duration of the test without pH control was longer, so a reduction in the rate of the electrolysis reaction at the anode allowed the pH to increase. Moreover, the driving force for the electroosmotic flow may be related to the higher pH and lower conductivity regions located toward the cathode region of the soil profile, and the low pH near the anode may cause the soil particles to flocculate and form a more open structure (Lambe and Whitman, 1969) that allows the solution to penetrate to these higher pH and low conductivity regions.

3. Compared to the deionized water and 3% Tween 80 solutions, the lower dielectric constant of the 40% ethanol solution resulted in a reduced electrical current and less electroosmotic flow. The tests performed with the 3% Tween 80 flushing solution exhibited a unique behavior that was attributed to the chemistry of the surfactant molecules as well as to the possible charge that may be acquired by these molecules. The NaOH solution reduced the polarity (dielectric constant) of the solution, and this resulted in a lower electrical current compared to deionized water. Moreover, the sorption of surfactant molecules at the mineral surface and the subsequent adsorption of cationic species caused the mineral surface to become more positively charged, consequently lowering the electroosmotic flow. It was suggested that adding NaOH to the surfactant lowered the CMC (produced more micellization and/or less surfactant adsorption), and this resulted in an electroosmotic flow that was higher than in the equivalent test without NaOH.

4. It was evident that the greater amount of soil–solution–contaminant interaction occurring in the soil adjacent to anode was beneficial for contaminant solubilization and migration or mobilization due to flushing action, but due to changes in the soil and/or solution chemistry near the middle and cathode regions, overall contaminant removal was low for all the tests. However, the 3% Tween 80 solution with pH control exhibited

encouraging evidence of phenanthrene solubilization and migration.

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