

Surfactant-enhanced Electrokinetic Remediation of Mixed Contamination in Low Permeability Soil

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Abstract: Thousands of sites are contaminated with both heavy metals and organic compounds and these sites pose a major threat to the environment. Very few technologies, such as soil washing/flushing and stabilization/solidification, are available to remediate these sites; however, all these technologies are ineffective under low permeability and heterogeneous soil conditions. Previous studies have shown that electrokinetic remediation has potential to remove heavy metals and organic compounds when they exist individually in clayey soils. In the present study, the feasibility of using surfactants in electrokinetic remediation was evaluated to remove the PAHs in the presence of heavy metals from clayey soils. Kaolin was selected as a model clayey soil and it was spiked with phenanthrene and nickel at a concentration of 500 mg/kg-dry each to simulate typical mixed contamination. Bench-scale electrokinetic tests were performed using deionized water and two different surfactants, Igepal CA-720 and Tween 80, at 3% and 5% (in weight) each at the anode. These solutions at the anode were circulated and were buffered with 0.01 M NaOH to maintain neutral pH conditions. A periodic voltage gradient of 2 V/cm (with 5 days on and 2 days off cycles) was applied for all the tests. There was a significant migration of phenanthrene towards cathode in all the tests. Among all the extracting solutions used, complete removal of phenanthrene was observed using 5% Igepal CA-720. In case of Tween 80, the low electroosmotic flow limited the delivery of Tween 80 into the soil and therefore,

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limiting the phenanthrene solubilization and transport. It was observed that solubilization, electroosmotic flow, and concentration of the extracting solution are the critical factors that contribute to the removal of phenanthrene. Nickel electro-migrated as cation towards the cathode and precipitated in the soil near the cathode due to high pH in all tests. Overall, nickel migration pattern was not affected by the presence of phenanthrene and the extracting solutions used in this study.

Keywords: Clays, electrokinetic remediation, heavy metals, mixed contamination, nickel, PAHs, phenanthrene, soils, surfactants

INTRODUCTION

Over 300,000 sites with potential contamination have been reported to state or federal authorities over the past few years that still require remediation at an estimated cost of over \$200 billion (1). About 70 to 80% of these sites are found to contain contaminated soils. About 41% of the Superfund sites and most of the Department of Energy sites contain soils contaminated by both toxic heavy metals and organic compounds. The soils with mixed contaminants pose a risk to public health and the environment and their remediation has been challenging. Solidification/stabilization and soil washing/flushing have been the most common technologies to treat the soils contaminated with heavy metals and polycyclic aromatic hydrocarbons (PAHs). Treatment trains combining several treatment technologies concurrently or in sequence (e.g., flushing followed by bioremediation) have also been employed to address multiple contaminants existing in soils. However, these technologies fail when low permeable soils are encountered because of the difficulty in the hydraulic delivery of the reactive agents required for the remediation.

Previous research has shown that electrokinetic remediation has potential to remove either heavy metals (2–4) or PAHs (5) from soils. Electrokinetic remediation is a technique where electrodes are placed across the contaminated soil to employ a very low direct current (DC) electric potential to transport the contaminants into electrodes. If the contaminants are ionic compounds, they are transported to the oppositely charged electrode by electromigration. In addition, electroosmotic flow (EO flow) provides driving force for the movement of contaminants. Therefore, removal of soluble contaminants is aided by EO flow. A single capable technology such as electrokinetic remediation to remediate both heavy metals and PAHs can make remediation process simple and efficient. However, because of the different nature of the heavy metals and the PAHs, solubilizing solutions must be carefully selected to remove both the contaminant groups simultaneously.

The use of surfactants to enhance removal of organic compounds from soils during electrokinetic remediation has been investigated by several researchers (6–11). Compounds such as BTEX (benzene, toluene, ethylbenzene, xylenes), PAHs (naphthalene, 2-methylnaphthalene, and phenanthrene), hexachlorobenzene (HCB), and DDT were used as model organic contaminants to evaluate the ability of several surfactants in the removal of organic pollutants from soils. The different surfactants investigated include Tween 80, Igepal, cetyltrimethylammonium bromide (CTAB), APG (alkyl polyglucoside), Brij 30 (polyoxyethylene-4-lauryl ether), SDS (sodium dodecyl sulfate), and SDBS ($C_{18}H_{29}NaO_3S$). In general, Tween 80 yielded good results in phase distribution tests due to its ability to solubilize organic compounds: HCB and DDT; however, the removal was lower in the electrokinetic test due to the interaction of the surfactant with the soil surface (7,9). Similar results were found with CTAB; this surfactant also retards the movement of hydrophobic organics compared with an electrokinetic experiment with no surfactant (8). On the other hand, SDBS showed a lower interaction with the soil, and DDT was removed by electromigration towards the anode due to the positive charge of the micelles formed by SDBS (9). APG, Brij 30 and SDS were tested for the removal of phenanthrene in electrokinetic tests (6). APG can be suitable for EK operations at field scale due to the low toxicity, possible degradation and the reasonably high electroosmotic flow that yielded a removal of about 75%, whereas Brij 30 needed the addition of acetate buffer to achieve a high electroosmotic flow. SDS was less effective, around 50% removal.

Surfactants lower the interfacial surface tension and increase solubility of hydrophobic organic compounds (HOCs) in aqueous solution through a process called micellar solubilization (11,12). In order to reduce the surfactant adsorption to the soil and optimize contaminant transport during the electrokinetic remediation, only nonionic surfactants are considered suitable to use. Nonionic surfactants are often good for solubilization of PAHs and they are relatively nontoxic (12,14). Generally, surfactants are of very low toxicity to mammals, but the aquatic organisms may be more sensitive, and toxicity usually increases with an increasing hydrophobic nature of the surfactant molecule (12,15).

Surfactant molecules or monomers which have a distinct structure that is composed of two separate groups. The head is polar and hydrophilic, or attracted to the water phase, while the tail group is non-polar and hydrophobic (12,13). The ionic charge of the polar head section is commonly used to classify surfactants, and the four major types of charge are negative, positive, negative and positive, and no apparent charge, which corresponds to anionic, cationic, zwitterionic, and nonionic surfactants, respectively (12,16). For nonionic surfactants, the polar head

section is often composed of a polyoxyethylene (POE) group, and the tail section may be much more varied but usually consists of a long hydrocarbon chain. Surfactants are classified according to the balance between the hydrophilic and hydrophobic, or lipophilic, portions of the molecule. A lipophilic substance is one with a high affinity for fatty or organic solvents and it is essentially a hydrophobic substance (12,13). Surfactants with a high hydrophile-lipophile balance (HLB) number are more soluble in water, and a low HLB indicates the surfactant is more soluble in an organic solvent (12,17). Surfactants increase PAH solubility through micellar solubilization. The formation of micelles begins at a specific surfactant concentration termed the critical micelle concentration (CMC), where the physical properties of the solution, such as interfacial tension, electrical conductivity, and light scattering behavior, often change due to the existence of micelles (12,16). For micelles in aqueous surfactant solutions above the CMC, the hydrophilic head groups are directed towards the aqueous phase and the hydrophobic tails are directed towards the interior region. The interior of the micelle thus becomes a hydrophobic region suitable for a HOC, and when both micelles and a HOC are present, the HOC molecules partition, or solubilize, into the micelles (12).

A comprehensive study to develop an enhanced electrokinetic remediation that is effective for soils contaminated with both PAHs and heavy metals has been initiated at the University of Illinois at Chicago (UIC). The specific objective of this paper is to present the results of an investigation that determined the feasibility of using surfactants for the removal of PAHs in the presence of heavy metals using electrokinetics. Based on a series of bench-scale electrokinetic experiments, the transport of heavy metals while removing PAHs was studied, and the effect of surfactant concentration on the removal of PAHs was also investigated.

EXPERIMENTAL PROGRAM

Electrokinetic Test Setup

The electrokinetic test setup used in this study was similar to that used in previous electrokinetic research at UIC (18). Figure 1 shows the electrokinetic test setup, and it 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, cathode sample collection flask, a power supply, wiring, stands, and tubing such as C-Flex and M-Flex from Cole-Palmer (Vernon Hills, IL). C-Flex tubing was used to make the connections to the cell and also for the gas-vents,

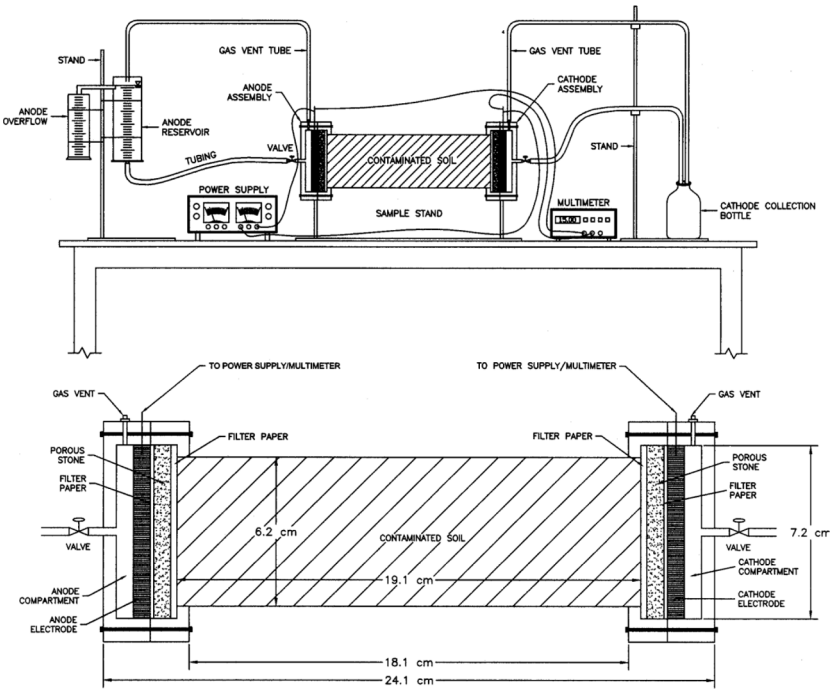


Figure 1. Electrokinetic test setup.

while M-Flex tubing was used for the circulation pump. The electrokinetic cell was made of Plexiglas[®] with 6.2 cm inside diameter and 19.1 cm length, and it was supported on a raised aluminum stand. Each electrode compartment was also made of Plexiglas[®] and contained Whatman filter paper, a porous stone, and a perforated graphite electrode. The filter paper was placed between the soil and the porous stone and both were placed in front of the electrode. Gas vents were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape.

Materials

Soil

Kaolin was selected as the model soil for the present study as it represents a low permeability soil. The composition and properties of this soil are summarized in Table 1. The colloidal laboratory grade kaolin was

Table 1. Properties of kaolin soil

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)	2.54
Hydraulic Conductivity (cm/s)	1.0×10^{-8}
Organic Content (%)	Near 0
PH (ASTM D 4972)	4.9
Cation Exchange Capacity (meq/100 g) (ASTM D 9081)	1.0–1.6
USCS Classification (ASTM D 2487)	CL

obtained from VWR Scientific Products (West Chester, PA) and the manufacturer was EM Science (Gibbstown, NJ). Kaolin mainly consists of the kaolinite mineral.

Contaminants

Phenanthrene ($C_{14}H_{10}$), a neutral organic compound that contains three aromatic rings, was selected as a representative PAH. It has environmental properties such as aqueous solubility, octanol-water partition coefficient (K_{ow}), and vapor pressure that are similar to other PAHs, such as 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 solubility of 1.1 mg/L at 25°C (19).

Nickel was selected as a representative heavy metal as it is one of the most prevalent heavy metals found at contaminated sites. The major sources of nickel contamination in the soil are the metal plating industry, combustion of fossil fuels, and nickel mining and refining. Nickel (Ni) is a transition element with atomic number 28 and atomic weight 58.69. In low pH regions, nickel exists in the form of the nickelous ion (Ni^{2+}). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide ($Ni(OH)_2$), which is a stable compound. This precipitate readily

dissolves in acid solutions forming Ni^{2+} , and in very alkaline conditions, nickel exists in the form of stable nickelo-nickelic oxide (Ni_3O_4) that is soluble in acid solutions. Other nickel oxides such as nickelic oxide (Ni_2O_3) and nickel peroxide (NiO_2) are unstable in alkaline solutions and decompose by giving off oxygen. However, in acidic regions, these solids dissolve producing Ni^{2+} (20).

Flushing Solutions

Saichek (21) tested several commercially available surfactants by conducting several batch desorption experiments and found that Igepal CA-720 and Tween 80 are effective for the phenanthrene solubilization. Saichek (21) also conducted several bench-scale electrokinetic tests with Igepal CA-720 and Tween 80 as extracting solutions to remove phenanthrene from kaolin. In the present study, the effectiveness of Igepal CA-720 and Tween 80 for the removal of phenanthrene from kaolin in the presence of heavy metals was investigated. The chemical formula of Igepal CA-720 is $4-(\text{C}_8\text{H}_{17})\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{11}\text{CH}_2\text{CH}_2\text{OH}$, and its molecular weight is 734.97 g/mol. Tween 80 is the common name of a chemical compound called Polyoxyethylene-(20)-sorbitan-monooleate, with chemical formula $\text{C}_{64}\text{H}_{124}\text{O}_{26}$ and molecular weight 1310 g/mol.

Testing Program

The testing program for the present study is shown in Table 2. A total of five electrokinetic tests were conducted. One test was conducted using deionized water as an extracting solution, which served as a baseline test. Two tests were conducted using Igepal CA-720 at 3% and 5% (by weight) concentration each. The remaining two tests were conducted using Tween 80 at 3% and 5% (by weight) concentrations each. These tests were performed mainly to observe the efficiency of surfactants, Igepal CA-720 and Tween 80, to solubilize and remove phenanthrene. The transport of nickel while observing the solubilization of phenanthrene was also studied. The effect of concentration of both the surfactants on the removal of phenanthrene and transport of nickel was also studied. A periodic or pulsed voltage application of 2 V/cm and a 0.01 M NaOH buffer was used in all the five tests. The periodic voltage application consisted of a cycle of five days of continuous voltage application followed by two days of "down time," where the voltage was not applied in order to allow time for the mass transfer, or the diffusion of the contaminant from the soil matrix, to occur and also to balance the dual objectives of generating

Table 2. Bench-scale electrokinetic testing program

Test	Soil	Contaminants	Anode solution	Buffering solution	Voltage gradient (V/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	3% Igepal CA-720	0.01 M NaOH	2	Periodic (5 days on/2 days off)	131
3	Kaolin	Nickel-500 mg/kg; Phenanthrene-500 mg/kg	5% Igepal CA-720	0.01 M NaOH	2	Periodic (5 days on/2 days off)	148
4	Kaolin	Nickel-500 mg/kg; Phenanthrene-500 mg/kg	3% Tween 80	0.01 M NaOH	2	Periodic (5 days on/2 days off)	68
5	Kaolin	Nickel-500 mg/kg; Phenanthrene-500 mg/kg	5% Tween 80	0.01 M NaOH	2	Periodic (5 days on/2 days off)	193

high electroosmotic flow while providing adequate time for mass transfer and contaminant removal (5). Furthermore, it also resulted in the additional benefit of saving in electric power consumption. All the tests were conducted for about 150 days except the test in which 3% Tween 80 was used. This test was stopped after 69 days because of significant reduction in the electroosmotic flow.

Testing Procedure

Approximately 1200 g of kaolin was used for each test. Kaolin was spiked with phenanthrene at an initial target concentration of 500 mg/kg. This concentration was based on typical PAH concentrations that is found near source zones at contaminated sites (22). Initially, the phenanthrene that is required to yield the target concentration was measured and then completely dissolved in about 500 mL of hexane. Hexane was used because phenanthrene has an extremely low solubility 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 in glass beakers. The motivation for this mixing technique was to ensure that the phenanthrene would be distributed evenly throughout the soil. The soil-hexane-phenanthrene mixture was then placed beneath a ventilation hood for nearly a week until hexane completely evaporated 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. A portion of the contaminant may volatilize along with the solvent. Therefore, a soil sample was taken to determine the actual initial concentration of phenanthrene in the soil using Soxhlet extraction procedure in accordance with the USEPA (United States Environmental Protection Agency) test method 3540C (23,24).

After loading of kaolin with phenanthrene, the soil was spiked with nickel at a target concentration of 500 mg/kg. A required amount of nickel chloride was dissolved in deionized water and then added to the soil. The soil and solution were mixed homogeneously and air-dried in a fume hood for a week. The final moisture level of soil was adjusted to 35% by adding of deionized water. The initial nickel concentration in soil was measured based on the USEPA acid digestion procedure followed by analysis with atomic absorption spectrophotometry (23,24).

The moist soil was then placed into the electrokinetic cell in layers, and each layer was compacted uniformly using a stainless steel tamper, so that the amount of void space was minimized. Once the cell was full

with soil, the sides and the outer part of the cell were completely cleaned. Then, the anode and the cathode compartments and reservoirs were attached to the cell, and the anode reservoir was filled with appropriate flushing solution. The flushing solution at the anode reservoir was buffered with 0.01 M NaOH and was 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 V/cm 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. The tests were run until the current greatly decreased, the effluent volume significantly reduced, or it appeared that the phenanthrene and nickel in the effluent concentrations had reached a steady state condition.

At the completion of each test, the 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 was used to analyze nickel and phenanthrene concentrations. From each soil section, 10 g of soil was taken and mixed with 10 mL of a 0.01 M CaCl₂ solution in a glass vial. The soil-solution mixture was shaken thoroughly by hand for several minutes and the solids were allowed to settle for an hours. This soil-solution was then used for measuring the soil pH. The pH of the aqueous solutions collected at the cathode was also measured. The moisture content of each soil section was also determined in accordance with the ASTM (American Society for Testing and Materials) method D2216.

Phenanthrene and Ni mass balance was checked for each experiment based on the initial total mass in the soil sample, the mass removed in the effluent, and the mass remaining in the soil. The discrepancy in mass balance was found to be $\pm 5\%$, which is often acceptable in electrokinetic testing. The discrepancy is attributed to experimental variations associated with the preparation of the kaolinite experiment, the heterogeneous distribution of the contaminants within the soil sections, and the analytical procedure.

Chemical Analysis

Phenanthrene Analysis

The phenanthrene concentration in the soil was determined using Soxhlet extraction procedure in accordance with the USEPA test method 3540C

(23). A dry representative soil sample weighing 10 g was thoroughly mixed with about 10 g of dry Na_2SO_4 (Fisher Scientific, Pittsburgh, PA), and the mixture was placed into a Whatman cellulose extraction thimble. The phenanthrene was then extracted using a Soxhlet apparatus consisting of a 250 mL flask, a Soxhlet extraction tube, and a bulb-type Allihn condenser. The solution used in the Soxhlet extraction process was 190 mL of a 1:1 mixture of methylene chloride and acetone (Fisher Scientific), and the process was operated at 4–6 cycles/h for at least 24 h. After the extraction was completed, the volume of the solvent remaining in the Soxhlet extraction tube and flask was measured, and analysis by Gas Chromatography (GC) was performed on a sample of the liquid. The soil was usually highly contaminated with phenanthrene, so the solvent-phenanthrene liquid samples obtained from the Soxhlet extraction could be directly analyzed using GC without performing a concentrating procedure.

The liquid samples collected at the cathode from the electrokinetic tests 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. Then, the sample was diluted in the ratio of 1:10 with water. The conical flask was shaken thoroughly before transferring the diluted sample into a test tube. Then 200 μL of 2-fluorobiphenyl was added. After that 2 mL of methylene chloride was added into the test tube. The test tube was hand shaken at least for five min. Then, the two phases, methylene chloride phase and the aqueous phase, were allowed to separate. Approximately 1 to 2 mL of the methylene chloride phase were taken using a syringe into a 2 mL autosampler vial. The sample was then run on the GC.

The GC used was an Agilent Model 6890 GC equipped with a Flame Ionization Detector (FID). The injection volume was 1 μL , and it 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 \times 0.32 mm \times 25 μm . The carrier gas was nitrogen at 172 kPa (25 psi) constant pressure. The oven temperature ramped from 100°C 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 surrogate concentration obtained from the GC. The final phenanthrene concentration in the original soil extract was determined.

Nickel Analysis

The nickel concentration in the soil was determined by the acid digestion in accordance with USEPA 3050 procedure (23). Approximately 1 to 2 g

of a representative sample from each section was weighed in a conical beaker and then mixed with 10 mL of 1:1 nitric acid (HNO_3). The mixture was stirred thoroughly, the beaker was covered with a watch glass and heated to 95°C , and then it was refluxed for 15 min. The sample was cooled, 5 mL of concentrated HNO_3 was added and again it was refluxed for 30 min. This last step was then repeated once. The conical beaker was then covered with a ribbed watch glass and the sample was allowed to evaporate to 5 mL. The sample was cooled, and 2 mL of deionized water and 3 mL of 30% hydrogen peroxide (H_2O_2) were added. The mixture was warmed to observe the peroxide reaction and heated until the effervescence subsided. The sample was then cooled and the addition of 1 mL H_2O_2 was continued until the effervescence was minimal. The maximum amount of H_2O_2 added was less than 10 mL. The sample was cooled and 5 mL of concentrated HNO_3 and 10 mL of deionized water were added and the mixture was refluxed for 15 min. The sample was centrifuged at 4000 rpm for 30 min to separate the supernatant and then diluted to 100 mL. The supernatant was then analyzed using an atomic absorption spectrophotometer (AAS) to determine the concentration of nickel in accordance with the USEPA method 7520 (23). The liquid samples collected at the cathode from the electrokinetic tests were directly tested using AAS for the nickel concentration in accordance with the USEPA method 7520. Dilution of the liquid samples was done with deionized water when the concentrations were high.

RESULTS AND ANALYSIS

Electric Current

All the tests followed the same trend in the variation of electric current with some fluctuations (Fig. 2). Initially, the electric current was high in all the tests. The high initial values are due to the presence in the kaolinite specimen of ionic species that are mobilized under the effect of the electric field and migrate towards the opposite charged electrode; but over time these ions are depleted as they electromigrate and move into the electrode chambers (12) and a decreasing in the current intensity is observed. The electric current intensity followed this pattern until 500 h. After that, there were fluctuations in the current, which was due to the changes in the solution chemistry and application of periodic voltage. The chemistry of the interstitial solution of the soil is changed by the flushing solutions (surfactants and NaOH) at the anode, and the electrochemical split of water. H^+ ions are constantly being generated at the anode. The buffering solution in the anode (0.01 M NaOH) was

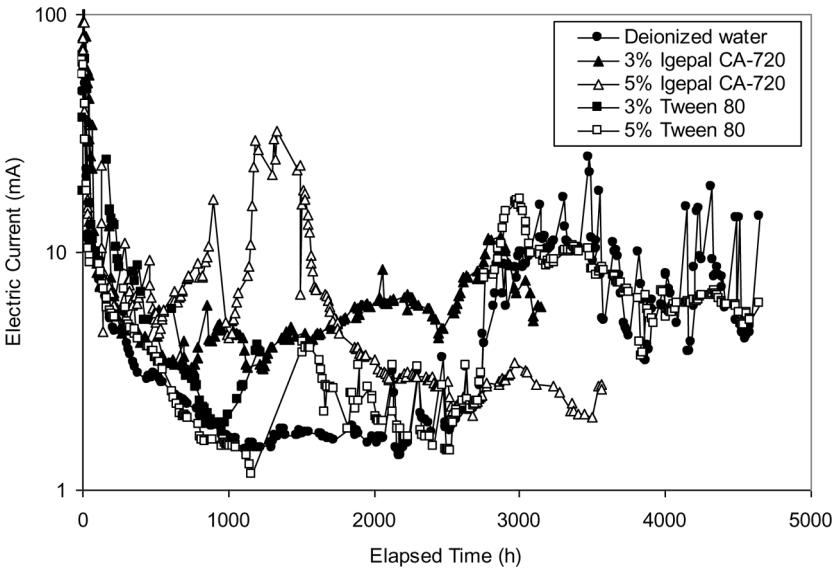


Figure 2. Effect of surfactant concentration on electric current.

not enough to neutralize the electrogenerated H^+ ions and the pH in the anode reached acid pH values. H^+ ions have a high mobility and move into the soil due to the electrokinetic transport mechanisms of electromigration and electroosmosis (26). The acidification of the sample provokes the dissolution of precipitated salts and favors the desorption of adsorbed ionic compounds to the soil surface (12,25). The result is the increasing of the current intensity. Furthermore, the use of surfactants modified the interaction between the soil and the interstitial solution and the zeta potential, affecting the electroosmotic flow. Variations in the electroosmotic flow also affected to the supply of ionic species to the soil from the anode, provoking changes in the electric current intensity. But the main reason for the fluctuation in the electric current is the application of the periodic voltage. The “down time” give to the system enough time for reaction and mass transfer, providing more free ions that can electromigrate when the potential is on. It explains the fast fluctuations observed in most of the experiments.

The current values were in the same range in almost all the tests. In general, Igepal CA-720 had higher current values than Tween 80 during most part of the test. The higher current in Igepal CA-720 tests when compared to the tests with Tween 80 may be due to the low dielectric constant of Tween 80 solution. The dielectric constant is directly related to the ion dissociation and hence a lower dielectric constant was the one

of the reasons for a lower current in Tween 80 tests when compared to the Igepal CA-720 tests. Though water has high dielectric constant, the current in the test with water during most part of the test duration was the least when compared to the other four tests conducted with surfactants as the extracting solution. This may be because of the lower number of ions that participated in the electrolysis reaction in the test with water compared to the tests with surfactants. The current in the tests with deionized water slightly increased after 3000 h, and was more than the current in the tests with surfactants, which may be due to replenishing with fresh stock solutions (deionized water in the cathode and 0.01 M NaOH in the anode).

Electroosmotic Flow

The cumulative electroosmotic flow in the baseline (deionized water), 3% Igepal CA-720, 5% Igepal CA-720, 3% Tween 80, and 5% Tween 80 tests is shown in Figure 3 and Table 3. The tests with deionized water, 5% Igepal CA-720, and 5% Tween 80 had 9 to 10 number of pore volumes flushed. The number of pore volumes flushed in 3% Igepal CA-720 and 3% Tween 80 tests were 15.1 and 3.8, respectively. The maximum cumulative electroosmotic flow was observed in the test with 3% Igepal CA-720 corresponding to the high current values in the test (Fig. 3). The dielectric constant of 3% Igepal CA-720 is expected to be higher than that of 5% Igepal CA-720 as the dielectric constant decreases with

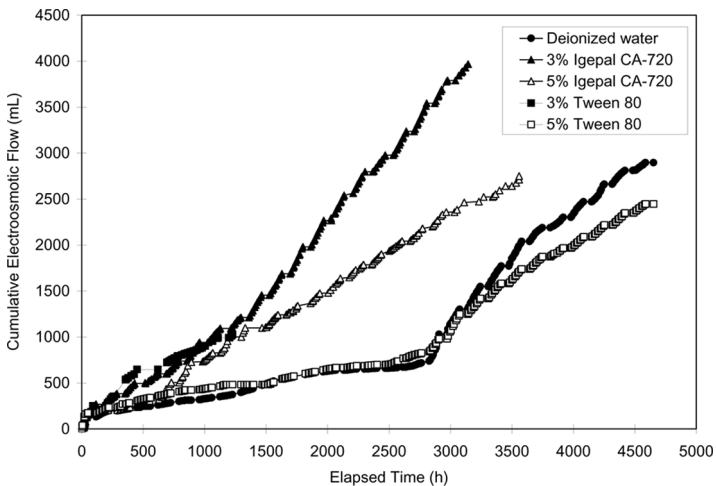


Figure 3. Effect of surfactant concentration on electroosmotic flow.

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

Test	Extracting solution	Water content (%)	Dry density (g/cm ³)	Void ratio	Porosity (%)	Pore volume (mL)	Number of pore volumes flushed
1	Water	32.47	1.367	0.901	47.4	273.2	10.6
2	3% Igepal CA-720	34.79	1.381	0.839	45.6	262.9	15.1
3	5% Igepal CA-720	34.78	1.384	0.835	45.5	262.3	10.5
4	3% Tween 80	34.95	1.358	0.871	46.5	268.3	3.8
5	5% Tween 80	35.66	1.351	0.881	46.8	269.9	9.1

concentration of the surfactant. Hence, the electroosmotic flow was high in 3% Igepal CA-720 test. However, electroosmotic flow was low in 3% Tween 80 test than 5% Tween 80 test. The electroosmotic flow in Igepal CA-720 tests was generally higher than in the Tween 80 tests. Though the current values were in the same range in all the tests, the difference in the viscosity may be the reason for the difference in the electroosmotic flow between the Igepal CA-720 and Tween 80 tests. During most part of the test duration, the test with deionized water as an extracting solution had the minimum electroosmotic flow among all the tests. But, the electroosmotic flow was more than that in 5% Tween 80 after 3000 h. This flow behavior is attributed to the corresponding current variations, as shown in Figure 3. The electroosmotic flow is directly proportional to the dielectric constant according to the Helmholtz-Smoluchowski theory (H-S theory). Though the dielectric constant of deionized water is high, the low dissolution of ions and relative movement of the ions may be responsible for the low electroosmotic flow.

Soil pH

When voltage potential is applied to the electrokinetic cell, electrolysis reactions take place and H⁺ and OH⁻ ions are generated at anode and cathode, respectively. This results in a high pH at the cathode and a low pH at the anode despite the use of a buffering solution (0.01 M NaOH). During the course of testing, the acidic solution generated at the anode gradually moves through the soil towards the cathode by electromigration and electroosmotic flow, and this lowers the pH of the soil (26).

The measured pH variation in all tests is compared in Figure 4. For the test with deionized water, the pH value in the soil was 1.6 near the anode and then gradually increased to 6.4 towards the cathode. The pH of the Igepal CA-720 tests ranged from 2.9–3.2 near the anode region

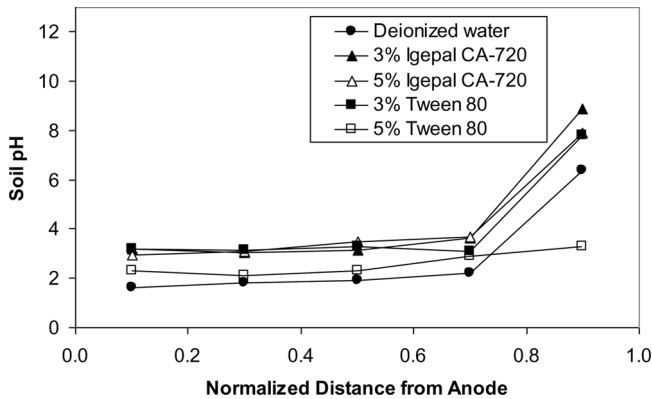
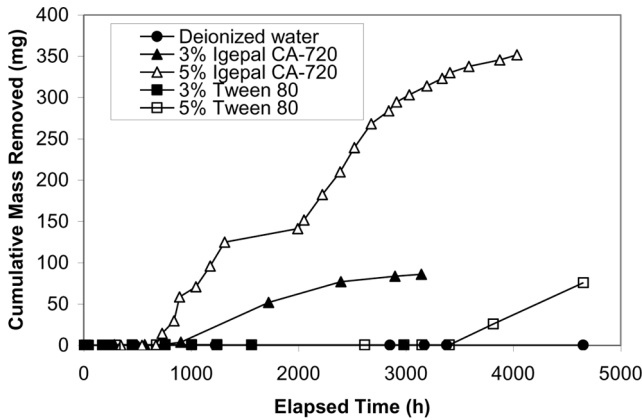


Figure 4. Effect of surfactant concentration on pH of soil.

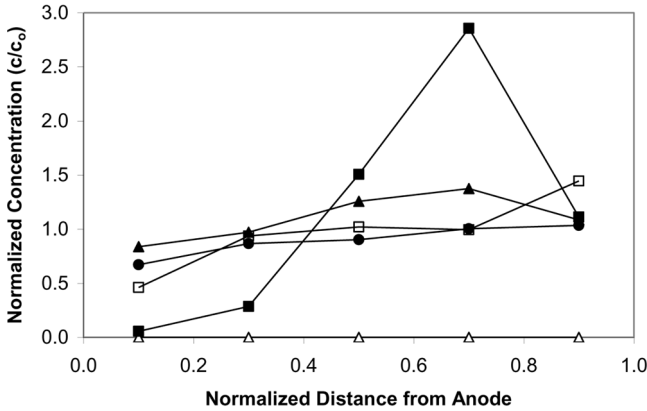
and from 7.9–8.9 near the cathode region. The pH in both tests was almost the same in the corresponding soil sections. The low pH in the region near the anode indicates a greater H^+ concentration and a more positively charged mineral surface. When the mineral surface becomes positively charged, the zeta potential becomes positive, and by H-S theory, the electroosmotic flow towards the cathode is reduced. Additionally, OH^- ions generated by the electrolysis reaction at the cathode may electromigrate into the soil sample against the electroosmotic flow and increase the pH in the region near the cathode or neutralize the migrating H^+ ions. This may cause a low conductivity region with a somewhat neutral pH to exist near the cathode (21,27). As shown in Fig. 4, the pH was 3.17 in the section near the anode and the cathode region had a much higher pH of 7.8 in the test in which 3% Tween 80 was used. In the test with 5% Tween 80, the pH values were lower in the entire soil specimen, which ranged from 2.3–3.3. The low pH conditions may be due to the longer duration of the experiment since the electroosmotic flow was lower than in the others test. The longer treatment time allowed H^+ ions to migrate into the soil and neutralize the OH^- ions in the entire kaolinite specimen. This is possible due to the high ionic mobility of the H^+ ion (about twice the ionic mobility of OH^-). The pH values in all the soil sections for the baseline test were lower than in the surfactant tests. In most part of the soil, Igepal CA-720 tests had higher pH values than the baseline and Tween 80 tests.

Removal of Phenanthrene

As seen in Figure 5(a), Igepal CA-720 tests had higher removal of phenanthrene than the tests in which Tween 80 was used, although the latter



(a)



(b)

Figure 5. (a) Cumulative phenanthrene mass removal, (b) Normalized phenanthrene concentration profiles in the soil sections.

has a lower critical micelle concentration (CMC) and a higher hydrophile-lipophile balance (HLB). Among the Igepal CA-720 tests, 5% Igepal CA-720 test resulted in a complete removal of phenanthrene, whereas 3% Igepal CA-720 only yielded a removal of 20% of initial phenanthrene in the soil. Though the pH values and electroosmotic flow were slightly lower in the 5% Igepal CA-720 test than the 3% Igepal CA-720 test, higher removal may be due to the availability of more number of micelles at a higher concentration that mobilized and transported phenanthrene more effectively.

The test in which 5% Tween 80 was used did not have a significant removal of phenanthrene. This may be due to the low pH values in the

soil specimen. It is known that the oxyethylene (polar) group binds to the protonated soil particle surface at lower pH (28,29). Therefore, at a low pH, less amount of surfactant will be available for the solubilization of phenanthrene. Moreover, the number of pore volumes flushed, and hence the electroosmotic flow, was low in both the Tween 80 tests, causing the low removal of phenanthrene.

Deionized water used in the baseline test was ineffective in removing phenanthrene into the solution due to the hydrophobic nature of phenanthrene that did not allow it to get solubilized into water.

Figure 5(b) shows the normalized phenanthrene concentration in the soil sections after they were extruded from the cells after the completion of the electrokinetic tests with deionized water, 3% Igepal CA-720, 5% Igepal CA-720, 3% Tween 80, and 5% Tween 80 solutions. The normalized phenanthrene concentration with respect to the initial phenanthrene concentration in the soil did not vary significantly in the baseline test, but the phenanthrene concentration slightly increased from anode towards cathode, indicating transport of phenanthrene in the soil. This transport may be mainly attributed to the electroosmotic flushing effect because phenanthrene is hydrophobic and relatively insoluble in water. The maximum phenanthrene mobilization and removal was observed in the test with 5% Igepal CA-720 solution when compared to all the other tests. In this test, the phenanthrene concentration was zero in all the soil sections. The high concentration and hence more number of available micelles, soil-solution-contaminant interaction and duration of the test were the reasons for the complete removal of phenanthrene. In the test with 3% Igepal CA-720 solution, the normalized concentration near the anode was around 0.8 and it increased gradually to 1.37 in the fourth soil section, which is at about 0.7 units of normalized distance from anode. Later, the normalized phenanthrene concentration decreased slightly to a value of 1.08 in the soil section near the cathode. These results with Igepal CA-720 3% may be attributed to a low concentration of the surfactant used, resulting in a lower number of micelles which may not have been sufficient for the significant solubilization of phenanthrene.

The test with 3% Tween 80 showed a significant reduction of the concentration of phenanthrene in the first and second sections (close to the anode), but the transported phenanthrene was concentrated in the third section. The test with 5% of Tween 80 showed a slight decrease in concentration in the first section and the corresponding accumulation in the last section close to the cathode. Tween 80 has a lower critical micelle concentration (CMC) and a higher hydrophile-lipophile balance (HLB). Although these properties favor the solubilization of phenanthrene, shorter duration and low electroosmotic flow may be the reasons for the poor removal of phenanthrene. In the case of 5% Tween 80 solution,

low pH values that allowed the adsorption of the Tween 80 solution to the soil may be one of the reasons for the low removal of phenanthrene.

In an earlier study at UIC, Saichek (21) conducted an electrokinetic bench-scale study to remove phenanthrene from kaolin spiked with phenanthrene alone using deionized water as an extracting solution. A concentration of 500 mg/kg-dry was employed for phenanthrene and the spiking procedure was the same as in the present study. A continuous voltage potential of 1 V/cm was applied to the test and the test duration was about 4080 h. In the present study, a periodic voltage of 2 V/cm was applied and the duration of the test was about 4652 h. In both the tests 0.01 M NaOH buffer solution was used at the anode. Because of the periodic application of voltage, the current and hence the electroosmotic flow values were higher in the present study than in the Saichek (21) study. Also, the number of mobile ions may have increased due to the presence of nickel that may have contributed to an increase in the current and the electroosmotic flow. In both the investigations, it was observed that migration and removal of phenanthrene was negligible with deionized water due to phenanthrene's hydrophobicity.

A comparison was made between the 3% Tween 80 test conducted by Saichek (21) and that conducted with 3% Tween 80 in the present study. It should be noted that a continuous voltage potential of 1 V/cm was applied and the test duration was about 1200 h in the case of Saichek (2001) study. The current and the electroosmotic flow values were high in the present investigation due to an increased voltage potential and pulsed voltage application. The presence of nickel may be another reason for the increased current values because of the presence of more number of mobile ions. The migration pattern of phenanthrene was similar in both the cases.

The test with 3% Igepal CA-720 in the present study was compared to the test conducted by Saichek (21) using the same extracting solution. Saichek (21) used 0.1 M NaOH buffering solution at anode and applied continuous voltage gradient for a total time duration of about 2880 h. The current and the electroosmotic flow increased in the present study and this may be due to the presence of nickel. The phenanthrene removal in both the tests was comparable. The migration in the present study was more because of the increased electroosmotic flow and test duration. A comparison was also made between both the studies for the test with 5% Igepal CA-720. All the variables were same except the duration in both the tests. The test conducted by Saichek (21) was conducted for a longer duration. The current and the electroosmotic flow values were high in the present study. Although, the duration was less in the present study, the presence of nickel may be the possible reason for the increased current and electroosmotic flow values. The removal and migration of phenanthrene were higher than that found in Saichek (21) test. The

complete removal of phenanthrene was observed in the present study using 5% Igepal CA-720.

Removal of Nickel

Figure 6(a) shows the cumulative mass of nickel removed in the five tests: deionized water, 3% Igepal CA-720, 5% Igepal CA-720, 3% Tween 80, and 5% Tween 80 tests. It can be observed from these results that there was no significant removal of nickel in all the tests. The removal was close to zero in baseline test and in the tests with Tween 80 solutions.

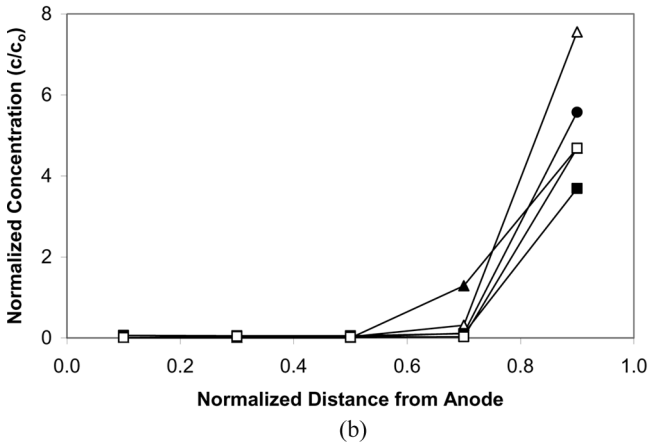
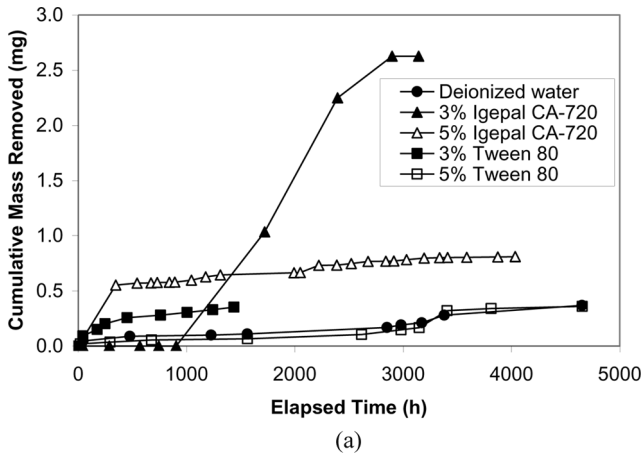


Figure 6. (a) Cumulative nickel mass removal, (b) Normalized nickel concentration profiles in the soil sections.

The tests in which Igepal CA-720 solutions were employed had a slightly higher removal of nickel when compared to Tween 80 and deionized water tests, but the nickel removal in the 3% Igepal CA-720 test was only 1.4% of the initial mass present in the soil, which is very low. This removal can be attributed to the high electroosmotic flow that flushed nickel into the solution. The higher pH conditions that existed near the cathode region may have inhibited the removal of nickel into the cathodic solution in all the tests except the test with 5% Tween 80. Though, the pH values were low in the entire soil specimen, the metal was retained in the last section close to the cathode and the electroosmotic flow was not sufficient enough to flush nickel out of the soil.

Figure 6(b) shows the nickel concentration in the soil sections after they were extruded from the cells after the completion of the electrokinetic tests with deionized water, 3% Igepal CA-720, 5% Igepal CA-720, 3% Tween 80, and 5% Tween 80 solutions. The mobilization of nickel was significant in all the tests. Normalized nickel concentration was almost zero till the middle of the soil specimen and the concentration increased significantly in the soil section near the cathode. It seems that the nickel mobilization in these tests was a result of existence of nickel as cation and their electromigration towards the cathode. The complete removal of nickel into the cathode may not have occurred because of the possible precipitation of Ni as $\text{Ni}(\text{OH})_2$ under the high pH conditions that existed in the soil section near the cathode. Although the soil in the Tween 80 test had low pH conditions, nickel was retained in the section near the cathode. This result may be due to precipitation of nickel due to the high pH in a very thin layer close to the cathode. This interpretation is supported by the longer treatment time of this experiment and the significant electroosmotic flow registered. After the test, the soil specimen is divided into five sections, and the fifth section includes the alkaline layer with the precipitated nickel and a portion of the soil with an acidic pH. Prior to analysis, the section is homogenized, so the reported result of pH corresponds to the average value in this section that includes two zones: one acidic and the other alkaline.

In an earlier study at UIC, Chinthamreddy (30) conducted an electrokinetic baseline test using kaolin soil spiked with 500 mg/kg of nickel alone. A voltage potential of 1 V/cm was applied and the duration of the test was about 250 h. In the present study, the baseline test conditions are the same in that the soil, the contaminant and the contaminant concentration used were the same as in the test conducted by Chinthamreddy (30). However, periodic voltage potential of 2 V/cm was applied in the present test and the test duration was about 4700 h. Because of the low voltage potential in Chinthamreddy (30) test than in the present test, the current and the electroosmotic flow were low in the former when

compared to the corresponding current and the electroosmotic flow values in the latter test. There was a significant migration of nickel in both the tests and most of the nickel accumulated in the soil near the cathode. Because of the high pH conditions that existed near the cathode, nickel may have precipitated as $\text{Ni}(\text{OH})_2$ in both the cases.

CONCLUSIONS

The objective of this investigation was to evaluate the potential of surfactants in the removal of PAHs in the presence of heavy metals from soils having low permeability using electrokinetics. Surfactants were chosen based on the previous studies that show that they are effective in the removal PAHs (Igepal CA-720 and Tween 80). Nickel and phenanthrene were selected as the representative heavy metal and PAHs, respectively, and kaolin was selected to represent low permeable soil. Based on the results of the experiments, the following conclusions can be drawn:

1. The electric current values were in the same range for all the tests although the lowest values corresponded to the baseline test with deionized water, probably due to the depletion of ions and the relative movement of the ions. In general, the current in the Igepal CA-720 tests were less than the current in the Tween 80 tests. The difference in the dielectric constant of the two solutions may be the reason for difference in the current.
2. The cumulative electroosmotic flow in deionized water was lower than in other tests during most part of the test corresponding to the low electric current values. Though water has high dielectric constant, the depletion of the ions and relative movement of the ions may be the reason for the initial low electroosmotic flow. Generally, the tests with Igepal CA-720 had higher electroosmotic flow than in the tests with Tween 80, which may be due to the difference in the viscosity between the Igepal CA-720 and Tween 80 tests. Also, the electroosmotic flow is decreased with the increasing of surfactant concentration since the dielectric constant decreases according to H-S equation.
3. The pH in the soil after the experiments shows a flat profile at a value below pH 4, except in the last section, close to the cathode, where the pH sharply increased to values between pH 6 and 9; except for the experiment with 5% of Tween, which shows acidic pH values throughout the soil. The lowest pH values corresponded to the baseline experiment with deionized water.
4. Deionized water used in the baseline test was ineffective in removing phenanthrene due to the hydrophobic nature of phenanthrene that

did not allow it to get solubilized into water. However, the concentration profile of phenanthrene into the soil showed its migration from anode to cathode.

5. The migration of phenanthrene was from anode to cathode in all the tests. The phenanthrene removal was high in Igepal CA-720 tests than the tests in which Tween 80 was used. 5% Igepal CA-720 test resulted in a complete removal of phenanthrene, whereas the removal with 3% Igepal CA-720 was only 20%. The complete removal of phenanthrene with 5% Igepal CA-720 was because of the higher concentration and high electroosmotic flow and hence high soil-solution-contaminant interaction. There was a significant mobilization of phenanthrene in 3% Igepal CA-720 test. However, the complete removal was retarded because of the insufficient micelles at that concentration, which were not able to solubilize phenanthrene.
6. The lower migration of phenanthrene in Tween 80 tests when compared to the migration of Igepal CA-720 tests was due to the low electroosmotic flow and hence the low interaction between the soil, solution and the contaminant. The solution properties such as dielectric constant and the viscosity may be responsible for this behavior. Furthermore, the low pH values in the test in which 5% Tween 80 favors that the oxyethylene (polar) group binds to the protonated soil particle surface. Therefore, at a low pH, less amount of surfactant will be available for the solubilization of phenanthrene.
7. There was a mobilization of nickel from anode to cathode in all the tests. There was an accumulation of nickel near the cathode region, which may have occurred because of the precipitation of nickel as a result of high pH conditions. The precipitation of nickel may have retarded the complete removal of nickel. It seems that the removal of nickel is not affected by the presence of phenanthrene and the extracting solutions used in this study, and the discrete results suggest that the extraction of Ni require a modification in the operating conditions to avoid the precipitation of Ni before it reaches the cathode.

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