

Sequential Electrokinetic Remediation of Mixed Contaminants in Low Permeability Soils

Krishna R. Reddy¹; Kranti Maturi²; and Claudio Cameselle³

Abstract: The coexistence of heavy metals and polycyclic aromatic hydrocarbons (PAHs) at many of the contaminated sites poses a severe threat to public health and the environment. Very few technologies, such as soil washing/flushing and stabilization/solidification, are available to remediate such sites; however, these technologies are ineffective and expensive to treat contaminants in low permeability clayey soils. 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 and organic acids sequentially and vice versa during electrokinetic remediation was evaluated for the removal of both heavy metals and PAHs from clayey soils. Kaolin was selected as a model clayey soil and it was spiked with phenanthrene and nickel at concentrations of 500 mg/kg dry each to simulate typical field mixed contamination. Bench-scale electrokinetic experiments were performed with the sequential anode conditioning with: (1) 1 M citric acid followed by 5% Igepal CA-720; (2) 1 M citric acid followed by 5% Tween 80; and (3) 5% Igepal CA-720 followed by 1 M citric acid. A periodic voltage gradient of 2 V/cm (with 5 days on and 2 days off cycles) was applied in all the tests. A removal of about 96% of phenanthrene was observed in the test with 5% Igepal CA-720 followed by 1 M citric acid sequence. Most of the nickel (>90%) migrated from anode to cathode in this test; however, it precipitated in the section very close to the cathode due to the high pH conditions. Conversely, the removal efficiency of nickel was about 96 and 88% in the tests with 1 M citric acid followed by 5% Igepal CA-720 sequence and 1 M citric acid followed by 5% Tween 80 sequence, respectively. However, the migration and removal efficiency of phenanthrene in both of these tests were very low. Overall, it can be concluded that the sequential use of 5% Igepal CA-720 followed by 1 M citric acid may be an effective remedial strategy to remove coexisting heavy metals and PAHs from clayey soils.

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Introduction

Heavy metals and organic compounds are the most prevalent contaminants found at National Priority List (NPL) and Department of Defense (DOD) sites, and they are also present at many sites being investigated under the state and voluntary remediation regulations (U.S. EPA 1996). About 500,000 sites with potential contamination have been reported to state or federal authorities over the past 15 years, with over 217,000 sites requiring urgent remediation. New contaminated sites are continuously being added each year. There are 547 superfund sites and 8,336 DOD sites that are yet to be remediated. About 70% of NPL, Resource Recovery and Conservation Act, DOD, and DOE sites have contaminated soils, groundwater, or both. About 41% of NPL sites

and several DOD and DOE sites require remediation for coexisting heavy metal and organic contamination. Urgent remediation of these sites with mixed contaminants is required to protect public health and the environment.

Soil washing/flushing, bioremediation, and solidification/stabilization technologies have been the most common technologies to treat soils contaminated with both heavy metals and organic compounds. Treatment trains combining several treatment technologies in a series (e.g., flushing followed by bioremediation) have also been used to address multiple contaminants in the soils. These technologies, however, fail when low permeable soils are encountered because of the difficulty with the hydraulic delivery of the reactive agents required for the treatment.

Previous research at the University of Illinois at Chicago (UIC) and other published studies have shown that electrokinetic remediation has the potential to remove either heavy metals (Alshawabkeh et al. 1999; Zagury et al. 1999; Page and Page 2002; Reddy and Chinthamreddy 2003; Sawada et al. 2004; Amrate et al. 2005; Deng and Jennings 2006) or organic compounds (Reddy and Saichek 2004; Ribeiro et al. 2005; Niqui-Arroyo and Ortega-Calvo 2007; Isoaari et al. 2007) from soils. However, the efficiency of electrokinetic remediation was not tested when these contaminant groups coexist. Because of the different nature of the two contaminant groups, suitable extracting solutions should be selected, which could solubilize or form complexes with both the contaminant groups. Batch desorption tests and bench-scale electrokinetic studies were conducted using cyclodextrins and cosolvents to remove both heavy metals and

¹Professor, Dept. of Civil and Materials Engineering, Univ. of Illinois at Chicago, 842 West Taylor Street, Chicago, IL 60607. E-mail: kreddy@uic.edu

²Graduate Research Assistant, Dept. of Civil and Materials Engineering, Univ. of Illinois at Chicago, 842 West Taylor Street, Chicago, IL 60607. E-mail: kranthi_m@rediffmail.com

³Associate Professor, Dept. of Chemical Engineering, Univ. of Vigo, University Campus, Building Fundicion, 36310 Vigo, Spain (corresponding author). E-mail: claudio@uvigo.es

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PAHs (Maturi and Reddy 2006, 2008a,b), and it was concluded that they were not effective for the removal of contaminants completely out of the soil. The effectiveness of surfactants in the removal of PAHs and on the migration of heavy metals has been studied using several batch desorption tests and bench-scale electrokinetics using several commercially available surfactants (Khodadoust et al. 2004, 2005; Maturi et al. 2009), and it was found that 5% Igepal CA-720 and 5% Tween 80 were found to be efficient for the removal of PAHs, specifically phenanthrene. However, as expected, they were found ineffective for the removal of heavy metals. Therefore, to remove heavy metals, other efficient extracting solution should be investigated. Batch desorption tests were conducted using chelating agents and organic acids to determine an efficient extracting solution for the removal of heavy metals (Khodadoust et al. 2004,2005), and it was found that organic acids are more effective than chelants to remove heavy metals from the soil.

The present study is a part of comprehensive study at UIC which is aimed at developing an enhanced electrokinetic remediation process that is effective for the soils contaminated with both PAHs and heavy metals. The main goal of this specific study was to investigate the feasibility of using different flushing solutions and optimization of sequential flushing schemes during electrokinetic remediation for the removal of both PAHs and heavy metals from the soil. Bench-scale electrokinetic experiments were conducted using low permeability kaolin soil spiked with nickel and phenanthrene. All the tests were conducted with the application of 2 V/cm periodic voltage gradient (with 5 days on and 2 days off cycles). Flushing sequences with 1 M citric acid followed by 5% Igepal CA-720, 1 M citric acid followed by 5% Tween 80, and 5% Igepal CA-720 followed by 1 M citric acid were investigated in the present study. These test results helped to assess the removal of mixed contaminants from the soil under applied electric potential.

Experimental Methodology

Electrokinetic Test Setup

The electrokinetic test setup used in this study was similar to that used in previous electrokinetic research at UIC (Reddy et al. 1997). Fig. 1 shows the electrokinetic test setup. The setup consists of a cell, two electrode compartments, an anode electrode reservoir, a peristaltic pump to circulate the solution in the anode reservoir to try to maintain neutral pH conditions, cathode sample collection flask, a power supply, wiring, stands, and tubing such as C-Flex and M-Flex purchased from Cole-Palmer (Vernon Hills, Ill.). C-Flex tubing was used to connect the cell to the cathode and anode reservoirs and also for the gas-vents, while M-Flex tubing was used for the circulation pump. The electrokinetic cell was made of Plexiglas with 6.2 cm inside diameter and 19.1 cm length, and it was supported on a raised aluminum stand. Each electrode compartment was also made of Plexiglas and contained a Whatman filter paper, a porous stone, and a perforated graphite electrode. The filter paper was placed between the soil and the porous stone and both were placed in front of the electrode. Gas vents were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape.

Materials

Soil

Kaolin was selected as the model soil 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 obtained from VWR Scientific Products (West Chester, Pa.) and the manufacturer was EM Science (Gibbstown, N.J.). 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 (Schwarzenbach et al. 1993).

Nickel (Ni) was selected as a representative heavy metal as it is one of the most prevalent heavy metals at many contaminated sites. The major sources of nickel contamination in the soil are metal plating industry, combustion of fossil fuels, and nickel mining and refining. Nickel 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+} (Pourbaix 1974).

Flushing Solutions

In previous studies, the ability of surfactants, cosolvents, cyclodextrins, chelating agents, and organic acids to remove Ni and phenanthrene from kaolin soil was tested (Khodadoust et al. 2004, 2005; Maturi and Reddy 2008a). In general, surfactants, cosolvents, and cyclodextrins yielded better results for phenanthrene removal, whereas chelating agents and organic acids yielded better removal for Ni. The combination of surfactants (Igepal and Tween) and chelating agents or organic acids (EDTA, citric acid) in a sequential extraction was also tested. The best results of the sequential extractions test were obtained with citric acid (1 M) combined with Igepal CA-720 (5%) or Tween (5%). These results formed the basis for the selection of flushing sequence for the electrokinetic experiments reported in this study. EDTA was not selected due to known complications using it in electrokinetic experiments (Reddy et al. 2004).

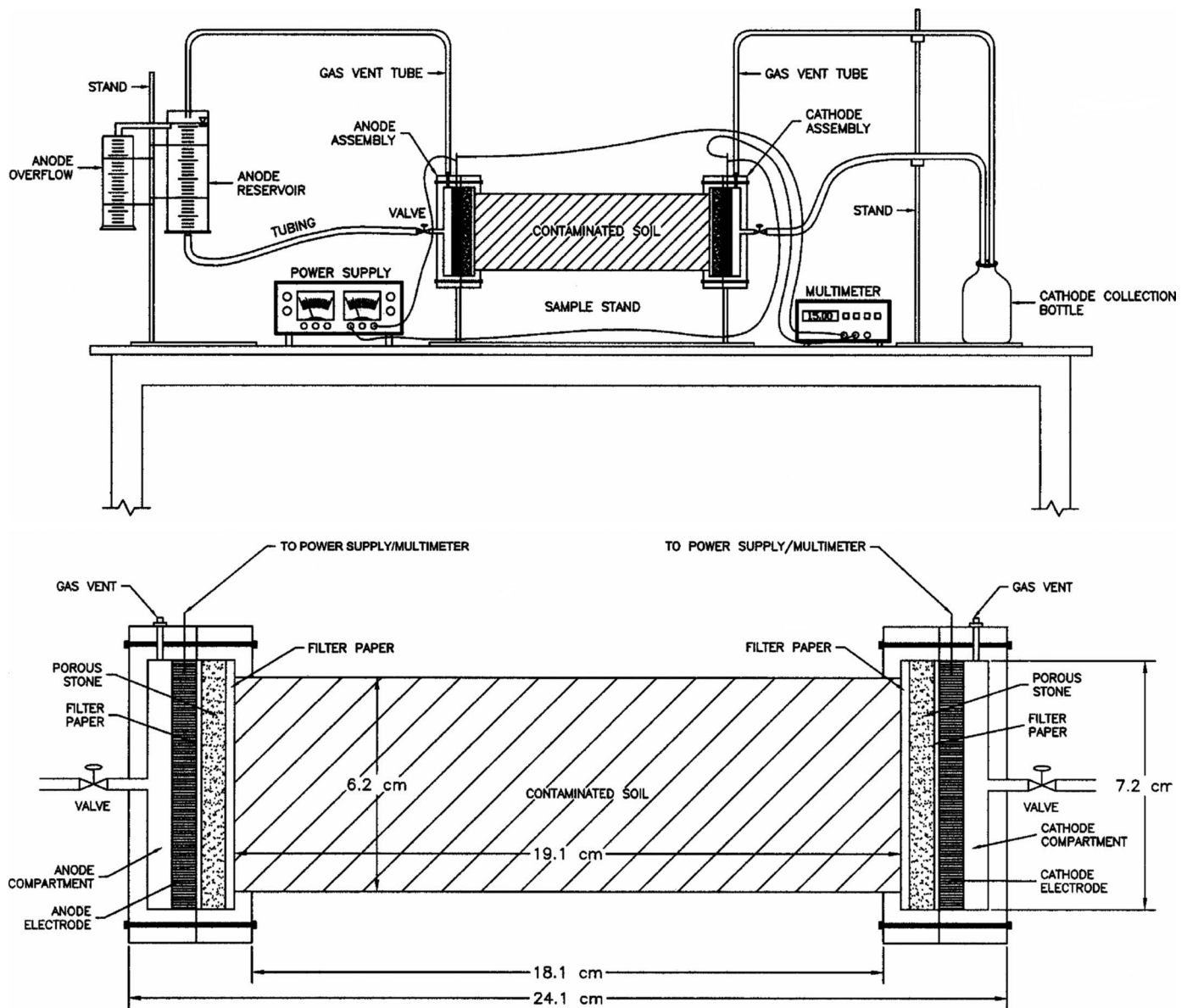


Fig. 1. Electrokinetic test setup and cell details

In this study, 5% Igepal CA-720, 5% Tween 80, and 1 M citric acid were selected as flushing solutions (Khodadoust et al. 2004,2005; Maturi and Reddy 2008a). Tween 80 and Igepal CA-720 were obtained from Aldrich Chemical Company (Milwaukee) and citric acid was obtained from Acros Organics (Morris Plains, N.J.).

Testing Program

A total of three electrokinetic tests were conducted (Table 2) using the following sequences in flushing solutions at the anode: 1 M citric acid followed by 5% Igepal CA-720, 1 M citric acid followed by 5% Tween 80, and 5% Igepal CA-720 followed by 1 M citric acid. These tests were performed mainly to observe the efficiency of the solutions when flushed in sequence to remove both phenanthrene and nickel from the soil. A periodic or pulsed voltage application of 2 V/cm and a 0.01 M NaOH buffer solution at the anode were used in all the three tests. Periodic voltage application consisted of a cycle of 5 days of continuous voltage application followed by two days of “down time,” where the volt-

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
Unified Soil Classification System classification (ASTM D 2487)	CL

Table 2. Bench-Scale Electrokinetic Testing Program

Test	Soil	Contaminants	Anode solution		Buffering solution	Voltage gradient (V/cm)	Mode of voltage application	Duration (days)
			Stage 1	Stage 2				
1	Kaolin	Nickel—500 mg/Kg; Phenanthrene—500 mg/Kg	1 M citric acid 33 days	5% Igepal CA-720 186 days	0.01 M NaOH	2	Periodic (5 days on/2 days off)	Stage 1: 33 Stage 2: 185 Total: 218
2	Kaolin	Nickel—500 mg/Kg; Phenanthrene—500 mg/Kg	1 M citric acid 49 days	5% Tween 80 186 days	0.01 M NaOH	2	Periodic (5 days on/2 days off)	Stage 1: 49 Stage 2: 185 Total: 234
3	Kaolin	Nickel—500 mg/Kg; Phenanthrene—500 mg/Kg	5% Igepal CA-720 194 days	1 M citric acid 46 days	0.01 M NaOH	2	Periodic (5 days on/2 days off)	Stage 1: 183 Stage 2: 45 Total: 238

age was not applied 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 high electroosmotic flow while providing adequate time for mass transfer and contaminant removal. The periodic mode was found to be effective as compared to continuous application of electric potential (Reddy and Saichek 2004); moreover, it also resulted in the additional benefit of saving in electric power consumption. The duration of the citric acid flushing stage ranged from 33 to 49 days and that of surfactant flushing stage ranged from 186 to 194 days.

Testing Procedure

Approximately 1200 g of dry 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 (U.S. EPA 2000). 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 U.S. EPA test method 3540C (U.S. EPA 1986; Reddy and Saichek 2003). After loading of kaolin with phenanthrene, the soil was spiked with nickel at a target concentration of 500 mg/kg. Required amount of nickel chloride was dissolved in deionized water and then added to the soil. The soil and solution were mixed homogeneously and air-dried in a fume hood. The final moisture level of soil was adjusted to 35% by adding of deionized water. The initial nickel concentration in soil was measured based on the U.S. EPA acid digestion

procedure followed by analysis with atomic absorption spectrophotometry (U.S. EPA 1986; Reddy and Chinthamreddy 2003, 2004).

The moist soil was placed into the electrokinetic cell in layers, and each layer was compacted thoroughly using a stainless steel rammer so that the amount of void space was minimized. Once the cell was full with soil, the sides and the outer part of the cell were completely cleaned. Then, anode and 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 1 h. This soil solution was then used for measuring the soil pH and electrical conductivity. The pH and electrical conductivity of the aqueous solutions collected near the cathode were also measured. The moisture content of each soil section was also determined in accordance with ASTM D2216.

Chemical Analysis

Phenanthrene Analysis

The phenanthrene concentration in the soil was determined using Soxhlet extraction procedure in accordance with the U.S. EPA test method 3540C (U.S. EPA 1986). A dry representative soil sample

weighing 10 g was thoroughly mixed with about 10 g of Na₂SO₄ (Fisher Scientific, Pittsburgh), 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, Pittsburgh), 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 near 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 5 min. Then, the two phases, methylene chloride phase and the aqueous phase, were allowed to separate. Approximately 1–2 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 autoinjector at an inlet temperature of 250°C. The column used on the GC was a J&W Scientific (Folsom, Calif.) DB-5, 30 m × 0.32 mm × 25 μm. The carrier gas was nitrogen at 25-psi-constant pressure. The oven temperature ramped from 100 to 250°C at 18°C/min for 1.5 min. and then held at 250°C until 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 U.S. EPA 3050 procedure (U.S. EPA 1986). Approximately 1–2 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 (HNO₃). 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 HNO₃ 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 (H₂O₂) 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 H₂O₂ was continued until the effervescence was minimal. The

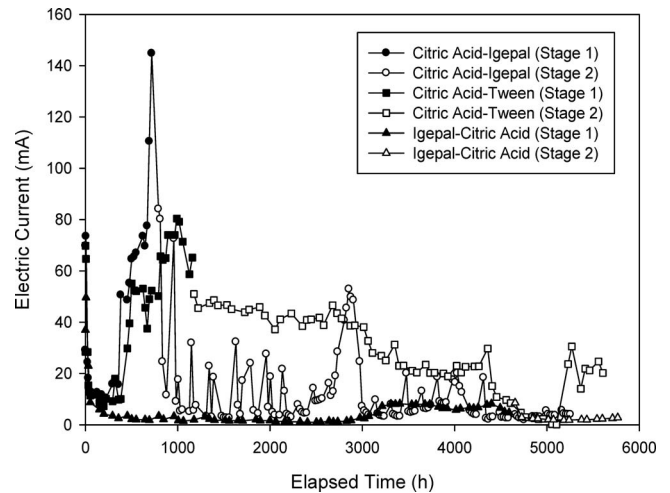


Fig. 2. Effect of flushing sequence on electric current

maximum amount of H₂O₂ added was less than 10 mL. The sample was cooled, and 5 mL of concentrated HNO₃ 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 U.S. EPA method 7520 (U.S. EPA 1986). The liquid samples collected near the cathode from the electrokinetic tests were directly tested using AAS for the nickel concentration in accordance with the U.S. EPA method 7520. Dilution of the liquid samples was done with deionized water when the concentrations were high.

Results and Analysis

Fig. 2 shows the comparison of current variation with elapsed time for all the three tests. There were large fluctuations in the current in all the tests with time. Initially, the current in all the tests was high and then slightly stabilized after 1000 h in the tests in which citric acid was flushed first and 500 h in the test in which Igepal CA-720 was flushed first. During electrokinetics, the fluctuations in current can occur due to different reasons. Initially, high currents result due to the presence of salt precipitates that go into solution (Mitchell 1993; Saichek and Reddy 2005), but over time these ions are depleted as they electromigrate and move into the electrode chambers (Saichek and Reddy 2005). At the same time, ions are constantly being generated at the anode, they have a high mobility, and they move into the soil due to the electrokinetic transport mechanisms of electromigration and electroosmosis (Acar et al. 1995).

The initial higher current in the tests may be attributed to the inflow of acidic solution that lowers the pH of the soil, and this may lead to additional mineral dissolution and a higher current (Saichek and Reddy 2005). The current values did not follow a particular trend in any of the tests. The citric acid-Igepal CA-720 and citric acid-Tween 80 tests, in which citric acid was used first, had high current values when compared to Igepal CA-720-citric acid test, in which Igepal CA-720 was used first. The reason for this may be due to the dissociation of ions in the acid. In citric acid-Igepal CA-720 and citric acid-Tween 80 tests, the current values were comparable during the citric acid flushing stage,

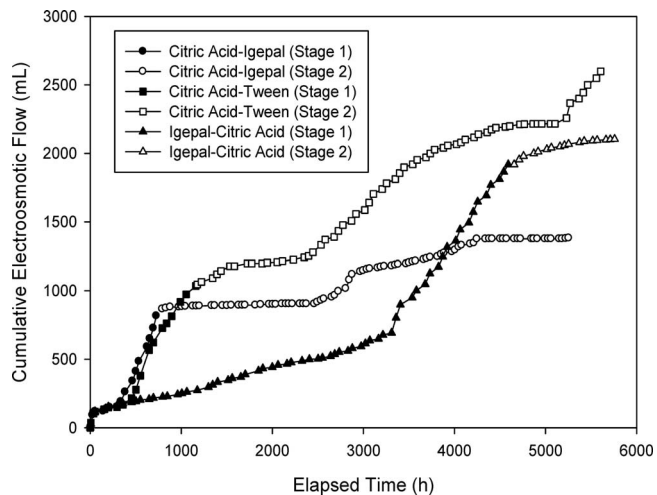


Fig. 3. Effect of flushing sequence on electroosmotic flow

indicating the repeatability of the experiments. During the surfactant flushing stage, citric acid-Tween 80 test had high current values almost throughout the duration of the test when compared to citric acid-Igepal CA-720 test. This may be because of the high dielectric constant of Tween 80 when compared to Igepal CA-720. Igepal CA-720-citric acid test had lower current values throughout the test. After 3000 h, the current values increased slightly, which may be due to addition of fresh stock solutions to the electrode compartments.

Fig. 3 shows the cumulative electroosmotic flow in the three tests and Table 3 summarizes the number of pore volumes flushed in each of the tests. The Igepal CA-720-citric acid and Tween 80-citric acid tests had almost the same number of pore volumes flushed, which were around 9.5. The number of pore volumes flushed in the citric acid-Igepal CA-720 test was 5.49. The maximum cumulative electroosmotic flow was observed in the citric acid-Tween 80 test followed by the experiment with Igepal CA-720-citric acid, and the lowest cumulative electroosmotic flow corresponded to the citric acid-Igepal CA-720 test (Fig. 3). During the citric acid flushing stage, citric acid-Igepal CA-720 and citric acid-Tween 80 tests had comparable current values and also comparable cumulative electroosmotic flow, which shows the repeatability of the experiments. During the citric acid flushing, the flow rate as indicated by the slope of the curves in Fig. 3 was the highest value (Stage 1 in citric acid-Igepal CA 720 and citric acid-Tween 80 tests). Citric acid used as flushing solution in the anode can enter the kaolinite sample by the electroosmotic flow.

Citric acid interacts with the surface of the solid particles and the interstitial solution, resulting in a modification of the zeta potential and a sharp increase in the electroosmotic flow. The same behavior was also reported by Popov et al. (1999) and Nogueira et al. (2007). The increase in the electroosmotic flow during citric acid flushing was also observed under acid conditions. In the second stage, the flushing with a surfactant solution resulted in the decrease in the electroosmotic flow, although this effect was more remarkable with Igepal CA-720 than with Tween 80. Generally, flow observed during the use of Igepal CA-720 was found more than the use of Tween 80, which is consistent with other studies (Maturi et al. 2009). This is because of the differences in the viscosity between the two surfactant solutions, Igepal CA-720 and Tween 80.

Igepal CA-720-citric acid test shows a profile of the cumulative electroosmotic flow rather different than the other two. As it was expected, the electroosmotic flow in the first stage flushing with Igepal CA-720 was lower than the experiment with citric acid-Igepal CA-720, but the reduction in electroosmotic flow in the latter in the second stage resulted in a higher cumulative electroosmotic flow in the Igepal CA-720-citric acid test toward the end of the experiment. The flushing with citric acid in the second stage did not yield the same high electroosmotic flow than in the other two experiments. It was due to the presence of the surfactant into the kaolinite specimen. The surfactant block the interaction of the citric acid with the surface of the kaolinite particles, so there is no modification of the Z-potential and the electroosmotic flow remained low.

Fig. 4(a) shows the soil pH distribution profiles of all the three tests. When voltage potential is applied to the electrokinetic cell, electrolysis reaction takes place, and H^+ and OH^- ions are generated at anode and cathode, respectively. The electrochemical decomposition of water resulted in a high pH near the cathode and a low pH near the anode. The buffering solution used in the anode could only partially neutralize the H^+ ions electrogenerated at the anode electrode, resulting in the acidification of the solution. Generally, the anode pH decreased to acid value (between 2 and 3) and the cathode pH increased to alkaline value (about 11), and they were almost constant during the experiment. The variation of pH in the electrode chambers was approximately the same in all the experiments conducted in this study. During the course of testing, the acidic solution generated at the anode gradually moves through the soil toward the cathode by electromigration and electroosmotic flow, and this lowers the pH of the soil throughout the soil. However, the acidification of the kaolinite specimen was slower than in a conventional electrokinetic ex-

Table 3. Initial Soil Conditions and Number of Pore Volumes Flushed

Test	Anode solution	Water content (%)	Dry density (g/cm^3)	Void ratio	Porosity (%)	Pore volume (mL)	Number of pore volumes flushed
1	1 M citric acid followed by 5% Igepal CA-720	33.0	1.430	0.776	43.7	251.868	Stage 1: 3.4 Stage 2: 2.0 Total: 5.4
2	1 M citric acid followed by 5% Tween 80	33.0	1.408	0.804	44.6	256.925	Stage 1: 4.0 Stage 2: 5.9 Total: 9.9
3	5% Igepal CA-720 followed by 1 M citric acid	35.4	1.538	0.652	39.5	227.453	Stage 1: 8.4 Stage 2: 0.8 Total: 9.2

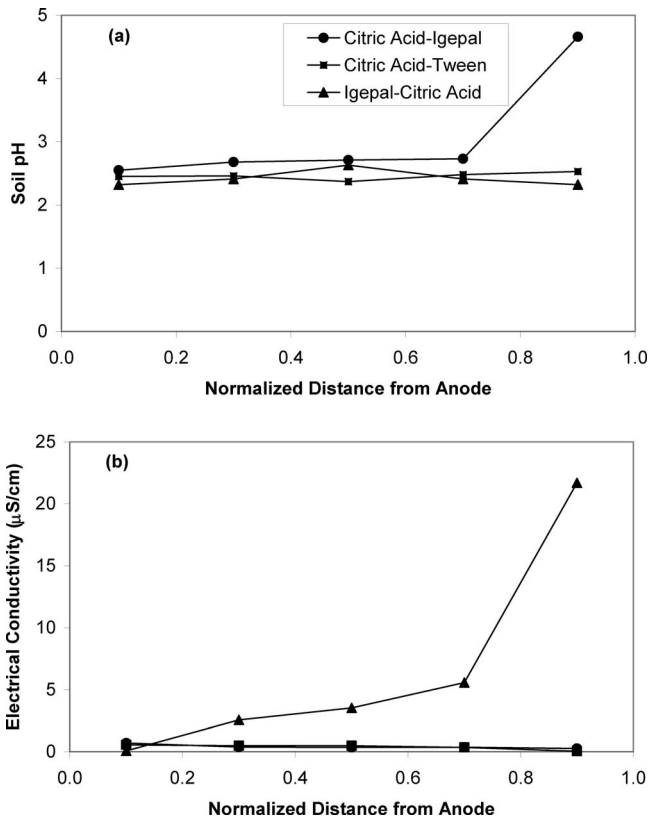


Fig. 4. Effect of flushing sequence on: (a) pH of soil; (b) electrical conductivity of soil

periment with no base at the anode. In the citric acid-Tween 80 test, the pH values were in the range of 2.45–2.53. The Igepal CA-720-citric acid test also had low pH conditions throughout the soil specimen with values ranging between 2.32 and 2.63. Approximately, 9.5 pore volumes of electroosmotic flow was observed in these tests, and the combined transport mechanisms of electroosmosis and electromigration were responsible for the acidic solution generated by the electrolysis reaction at the anode to migrate into the soil and move toward the cathode, and this explains the acidic conditions that existed in the two tests (Acar et al. 1995; Saichek and Reddy 2005). The pH in the citric acid-Igepal CA-720 test was 2.55 at the anode and gradually increased to 4.66 at the region near the cathode. The reduction in the electroosmotic flow toward the end of the test that resulted in a lower electroosmotic flow compared to the other two experiments (5.4 pore volumes flushed) was responsible for the relatively high pH conditions near the cathode. If the electroosmotic flow decreases, a substantial amount of electromigration of OH^- into the soil from the cathode electrolysis reaction could raise the pH near the cathode, and this accounts for the steep increase of pH near the cathode (Saichek and Reddy 2005).

Fig. 4(b) shows the electrical conductivity distribution profiles of all the tests. Conductivity is an indirect measurement of the concentration of ions in the interstitial solution. The actual values of conductivity are also affected by the use of surfactants and citric acid in the tests. Moreover, due to applied electric potential, majority of the ions are transported out of low pH parts of the soil, resulting low conductivity. The results from Fig. 4(b) show that the Igepal CA-720-citric acid test in which 5% Igepal CA-720 was used first had higher conductivity values when compared to the citric acid-Igepal CA-720 and citric acid-Tween 80

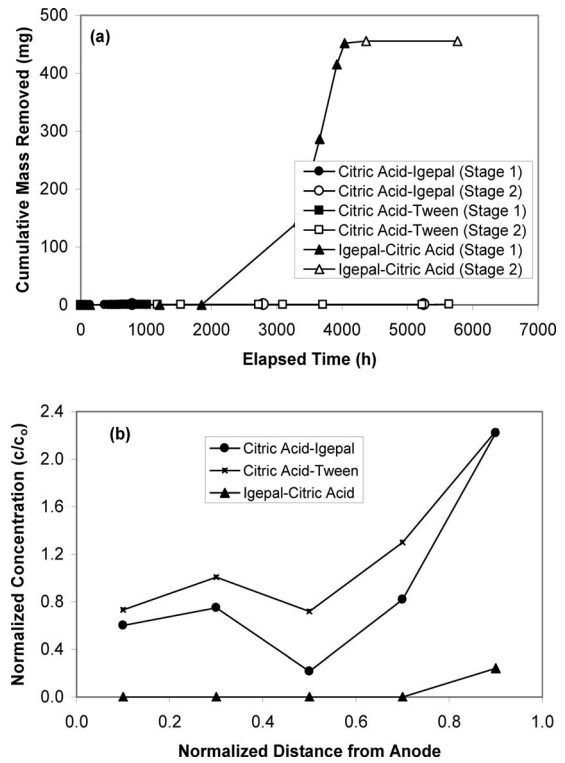


Fig. 5. (a) Cumulative phenanthrene mass removal; (b) normalized phenanthrene concentration profiles in the soil sections

tests in which citric acid was used first. The conductivity values increased gradually in the Igepal CA-720-citric acid test in which Igepal CA-720 was used first. These results correspond to the conditions of the soil at the end of the experiment. These results mean that the concentration of ions in the interstitial fluid at the end of the test Igepal CA-720-citric acid is higher than the two others, due to the presence of citrate ions, among others. In the test with citric acid-Igepal CA-720 and citric acid-Tween 80, the flushing with the surfactant solution favors the elimination of citrate ions (used in the Stage 1) from the interstitial fluid decreasing the total ionic concentration. Furthermore, the lower dielectric constants of surfactants compared to an aqueous solution of citric acid explain the differences in conductivity among the three experiments.

Phenanthrene is a polyaromatic hydrocarbon with a very low solubility in water which results in a negligible elimination from polluted soil with a simple water flushing process. Moreover, the compacted kaolinite specimen used in these tests shows a very low hydraulic conductivity (about 10^{-8} cm/s) and the hydraulic flow, even under high hydraulic gradient conditions, is extremely low, which clearly demonstrated that the hydraulic injection alone is ineffective. In contrast, significant electroosmotic flow can be generated under electric potential which allows flushing of the selected solutions through the soil from the anode. The chemical conditioning of the flushing solution is necessary for the removal of heavy metals or hydrophobic organics. In this case, the simultaneous removal of both sort of contaminants require the specific sequence in the flushing solutions to achieve high removal of both phenanthrene and nickel, as it is explained below.

Fig. 5(a) shows the cumulative mass of phenanthrene removed in the three tests: citric acid-Igepal CA-720, citric acid-Tween 80, and Igepal CA-720-citric acid tests. The Igepal CA-720-citric acid test had about 456 mg of phenanthrene removed into the

solution, which is equal to the initial mass of phenanthrene that was present in the soil. The phenanthrene removed during the first stage 5% Igepal CA-720 flushing in this test is similar to the test in which 5% Igepal CA-720 was used alone in previous investigations (Maturi et al. 2009). In both the tests, 5% Igepal CA-720 completely removed phenanthrene out of the soil. The 5% Igepal CA-720 concentration was found to be sufficient for the removal of phenanthrene because of the availability of more number of micelles at that concentration. However, the sequence of the flushing solutions is very important in the final results in phenanthrene elimination. When the surfactant was flushed after the citric acid was flushed, the phenanthrene removal into the solution was negligible. This may be due to the low pH of the soil that may have existed after the flushing with the acid. It is known that the oxyethylene (polar) group binds to the protonated soil particle surface at lower pH (Ko et al. 1998a,b). Therefore, at a low pH, less amount of surfactant will be available for the solubilization of phenanthrene. No phenanthrene was detected in the solution in the test with citric acid-Tween 80. It can be explained by the low pH values after citric acid flushing as in Igepal CA-720 test, but also by the lower ability of Tween 80 removing phenanthrene determined in previous investigation (Khodadoust et al. 2004, 2005). At the end of the each experiment, phenanthrene mass balance was checked for each experiment based on the initial total mass in the kaolinite sample, the mass removed in the effluent, and the mass remaining in the soil (Maturi 2004). The discrepancy in mass balance was found to be $\pm 5\%$, which often is acceptable in electrokinetic testing. Based on mass balance, it is demonstrated that loss by possible evaporation or biological degradation are insignificant in all of the experiments reported in the paper.

Fig. 5(b) shows that the normalized phenanthrene concentration with respect to the initial phenanthrene concentration in the soil in all the three tests. In Igepal CA-720-citric acid test, phenanthrene was not found in all the soil sections except in the section that was near the cathode, which has a small phenanthrene concentration of about 116 mg/kg. The high phenanthrene removal in this test was due to the solubilization of phenanthrene in the micelles formed at that surfactant concentration. In the citric acid-Igepal CA-720 and citric acid-Tween 80 tests, the low pH values that existed due to the flushing with citric acid first did not favor the phenanthrene solubilization. At low pH conditions, surfactant sorbs to the soil making it less available for phenanthrene solubilization. However, there was some mobilization of phenanthrene from anode to cathode due to the available residual surfactant, but not enough to transport phenanthrene out of the soil. During the citric acid stage, significant migration of phenanthrene may not have occurred because of their different nature, which may not have favored phenanthrene solubilization in citric acid.

Fig. 6(a) shows the cumulative mass of nickel removed in the three tests, citric acid-Igepal CA-720, citric acid-Tween 80, and Igepal CA-720-citric acid tests. In citric acid-Igepal CA-720 test, about 96% of initial mass of nickel that was present in the soil was removed into the solution. In citric acid-Tween 80 test, about 89% of initial mass of nickel was removed into the solution. The maximum removal of nickel in both the cases was during the citric acid flushing stage. A small amount of nickel was removed during the surfactant flushing stage, which was due to the residual acid that was in the soil. Citric acid may have dissolved the nickel precipitates and hence the higher removal. In Igepal CA-720-citric acid test, the removal of nickel into the solution was negligible. Though Igepal CA-720 flushing was followed by citric acid

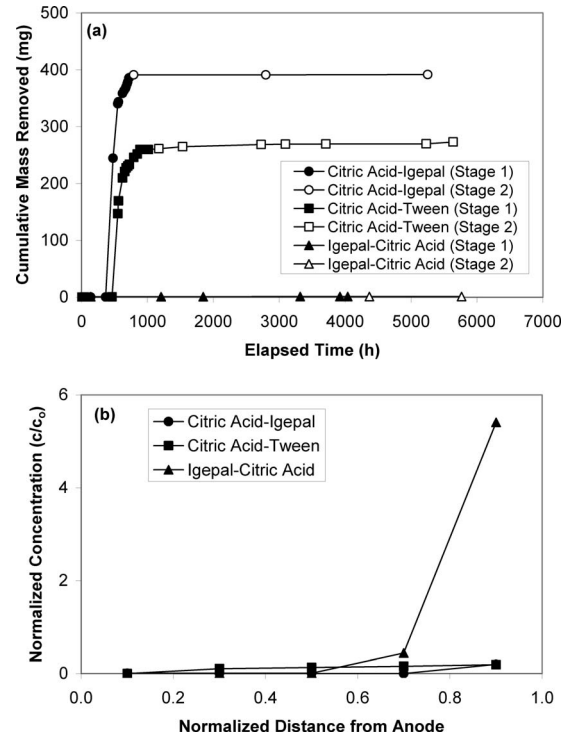


Fig. 6. (a) Cumulative nickel mass removal; (b) normalized nickel concentration profiles in the soil sections

flushing, the sorption of Igepal CA-720 to the soil may have made citric acid unavailable for the solubilization of nickel.

Fig. 6(b) shows the nickel concentration in the soil sections after they were extruded from the cells after the completion of the electrokinetic tests, citric acid-Igepal CA-720, citric acid-Tween 80, and Igepal CA-720-citric acid tests. In the citric acid-Igepal CA-720 and citric acid-Tween 80 tests, the mobilization of nickel was significant and was from anode to cathode. The normalized nickel concentration was less than 0.2 in all the soil sections. Moreover, citric acid-Tween 80 test had slightly higher concentrations of nickel in all the soil sections than in citric acid-Igepal CA-720 test [Fig. 5(a)]. This shows an excellent agreement with the mass removal in solution, which shows that 96 and 89% of the initial nickel present in the soil was transported into the solution in the citric acid-Igepal CA-720 and citric acid-Tween 80 tests, respectively. The Ni mass balance was checked at the end of each experiment in a similar way to the phenanthrene mass balance. The results confirm that the maximum discrepancy is about 5%, which is often considered acceptable in electrokinetic testing.

The mobilization of nickel was mainly due to the low pH conditions that existed during the flushing with citric acid, which may have favored the solubilization of nickel without any precipitation, and then it was transported by electromigration and electroosmosis. During the flushing with the surfactant, nickel may have migrated slightly due to the electroosmotic flow, but the high pH conditions that existed near the cathode region may have retarded further migration. In the Igepal CA-720-citric acid test, there was migration of nickel from anode to cathode, but most of the nickel accumulated near the cathode region. In this test, flushing with surfactant followed by citric acid did not result in the complete removal of nickel. Citric acid, which favored the solubilization of nickel in citric acid-Igepal CA-720 and citric acid-Tween 80 tests, did not result in complete removal of nickel in Igepal CA-720-citric acid test. As the Igepal CA-720 was

flushed in the first stage, it may have sorbed to the soil affecting the soil-solution-contaminant interaction during the citric acid flushing stage. As expected, surfactant could not remove nickel because of its different nature. However, the electroosmotic flow during the surfactant flushing caused a flushing action that aided in the slight mobilization of nickel in the soil. Nevertheless, the Ni profile in the soil suggest that a longer treatment time of the Stage 2 with citric acid could result in the total removal of Ni from the soil into the cathode solution.

Conclusions

The objective of this study was to develop a sequentially enhanced electrokinetic remediation process that could remove both PAHs and heavy metals from soils including the low permeability soils. Based on the results of the experiments, the following conclusions can be drawn:

1. The presence of surfactants tended to reduce the electric conductivity of the soil and the electroosmotic flow compared with the stages where citric acid was used as flushing solution.
2. In general, flushing with Igepal CA-720 resulted in higher electroosmotic flow and current intensities due to the lower viscosity compared to Tween 80.
3. The flushing with an alkaline solution (0.01 M NaOH) at the anode was not sufficient to neutralize the acid front generated by water electrolysis, and the kaolinite specimen was acidified. Furthermore, the use of citric acid as flushing solution in the first stage favored the acidification of the sample. Therefore the removal of Ni was favored in these tests, but the removal of phenanthrene was negligible.
4. A complete phenanthrene mass removal was achieved in Igepal CA-720-citric acid test in which 5% Igepal CA-720 followed by 1 M citric acid were flushed. The total removal of phenanthrene was achieved during the Igepal CA-720 flushing stage. Unfortunately, the second stage with citric acid was not sufficient to acidify the kaolinite specimen and the presence of Igepal CA-720 affected the interaction soil-solution-contaminant. Ni migrated to the cathode but was accumulated into the kaolinite specimen in the region close to the cathode due to the high pH conditions. Probably, a longer treatment time or a pH control on the cathode will result in the total removal of Ni.

Overall, it can be concluded that sequential electrokinetic flushing of 5% Igepal CA-720 followed by citric acid may be effective for the removal of both PAHs and heavy metals in low permeability soils.

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