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Enhanced electrokinetic remediation of mixed heavy metal and organic contaminants in low permeability soils

Amélioration du traitement électrocinétique d'assainissement des sols à faible perméabilité contenant un mélange de métaux lourds et contaminants organiques

Krishna R. Reddy & Kranti Maturi

*University of Illinois, Department of Civil and Materials Engineering
842 West Taylor Street, Chicago, Illinois 60607, USA
e-mail: kreddy@uic.edu*

ABSTRACT

In the present study, the feasibility of using electrokinetic remediation for the removal of mixed contaminants, specifically mixtures of heavy metals and PAHs, from low permeability soils is investigated. Laboratory bench-scale electrokinetic experiments were conducted using kaolin soil spiked with both phenanthrene and nickel to simulate typical field contamination. Different types of flushing solutions were evaluated by performing a series of batch experiments and the most effective solutions were selected for the electrokinetic experiments. Based on the results, it was concluded that solubilization of the contaminants as well as the sustained electroosmotic flow are the critical factors that contribute to the removal of both heavy metals and PAHs from low permeability soils.

RESUME

L'étude présente la possibilité d'utilisation du traitement électrocinétique pour l'assainissement des sols à faible perméabilité, contaminés par des mélanges de contaminants, particulièrement par des mélanges de métaux lourds et d'hydrocarbures aromatiques polycycliques (HAP). Des expériences de traitements électrocinétiques en laboratoire ont été menées sur des sols kaolins enrichis à la fois en phénanthrène et en nickel pour simuler une contamination typique de terrain. Différentes solutions de lavement ont été évaluées par une série d'expériences, et celles produisant les meilleurs résultats ont été sélectionnées pour des expériences de traitements électrocinétiques. L'étude a démontré que la solubilisation des contaminants ainsi que le flux électroosmotique prolongé sont des facteurs critiques contribuant à l'extraction et au recouvrement à la fois des métaux lourds et des hydrocarbures aromatiques polycycliques (HAP), présents dans des sols à faible perméabilité.

1 INTRODUCTION

The co-existence of toxic heavy metals and polycyclic aromatic hydrocarbons (PAHs) at many of the contaminated sites all over the United States and worldwide poses a severe threat to the environment. Very few technologies, such as soil washing and bioremediation, are available to treat these mixed wastes (Sharma and Reddy, 2004). However, these technologies may be ineffective due to several reasons such as inability to treat contaminants in low permeability soils, high cost, and longer treatment time.

Previous research has shown that electrokinetic remediation has the potential to remove either heavy metals (Reddy and Chinthamreddy, 2003; 2004; Reddy et al., 2003) or PAHs (Reddy and Saichek, 2004) from soils. However, the efficiency of electrokinetic remediation was not tested when these contaminant groups co-exist. Because of the different nature of the two contaminant groups, suitable extracting solutions should be selected which could solubilize or form complexes with both the contaminant groups.

The present study was conducted to evaluate different flushing solutions for the simultaneous removal of heavy metals and PAHs from low permeability soils using electrokinetics. Bench-scale electrokinetic experiments were conducted using low permeable kaolin soil spiked with nickel and phenanthrene. The experiments helped to assess relative remedial performance of each flushing solution.

2 MATERIALS AND METHODS

The electrokinetic test setup used in this study was similar to that used in previous electrokinetic research (Reddy and Chinthamreddy, 2003; 2004; Reddy et al., 2003). The

electrokinetic cell is made of Plexiglas with 6.2 cm inside diameter and 19.1 cm length. 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 reported by Reddy et al. (2003). In the present study, phenanthrene (500 mg/kg) was selected as a representative PAH, and nickel (500 mg/kg) was selected as a representative heavy metal. The following specific flushing solutions were selected based on a series of batch experiments: a cyclodextrin (10% hydroxypropyl- β -cyclodextrin), a surfactant (5% Igepal CA-720), and a cosolvent (20% n-butylamine). A baseline experiment with deionized water was also conducted. The flushing solutions were used at the anode and were buffered with 0.01 M NaOH to maintain neutral pH conditions in each of the experiments (Saichek and Reddy, 2004). A periodic voltage gradient of 2 VDC/cm was applied in all the tests (Reddy and Saichek, 2004).

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 till 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 moisture content, nickel and phenanthrene concentrations, pH, and electrical conductivity. The pH and electrical conductivity of the aqueous solutions collected near the cathode were also measured.

The phenanthrene concentration in the soil was determined using Soxhlet extraction procedure in accordance with the USEPA test method 3540C and gas chromatography, GC (USEPA, 1986). The liquid samples collected near the cathode from the electrokinetic tests were analyzed for phenanthrene after performing liquid-liquid extraction using a GC. The nickel concentration in the soil was determined by acid digestion in accordance with USEPA 3050 procedure (USEPA, 1986) and using an atomic absorption spectrophotometer (AAS) in accordance with the USEPA method 7520 (USEPA, 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 USEPA method 7520.

3 RESULTS AND ANALYSIS

Figure 1 shows the current and the cumulative electroosmotic flow during the experiments at various elapsed times for the baseline (deionized water), 10% HPCD, 5% Igepal, and 20% n-butylamine tests. Initially, all the tests had high electric currents, which later reduced and became relatively stable after 500 hours except in the test with 10% HPCD for which current decreased more with time (Figure 1(a)). 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, but over time these ions are depleted as they electromigrate and move into the electrode chambers. At the same time, ions that are constantly being generated at the anode, possess a high mobility and they move into the soil due to the electrokinetic transport mechanisms of electromigration and electroosmosis. The initial higher current in the tests may also 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.

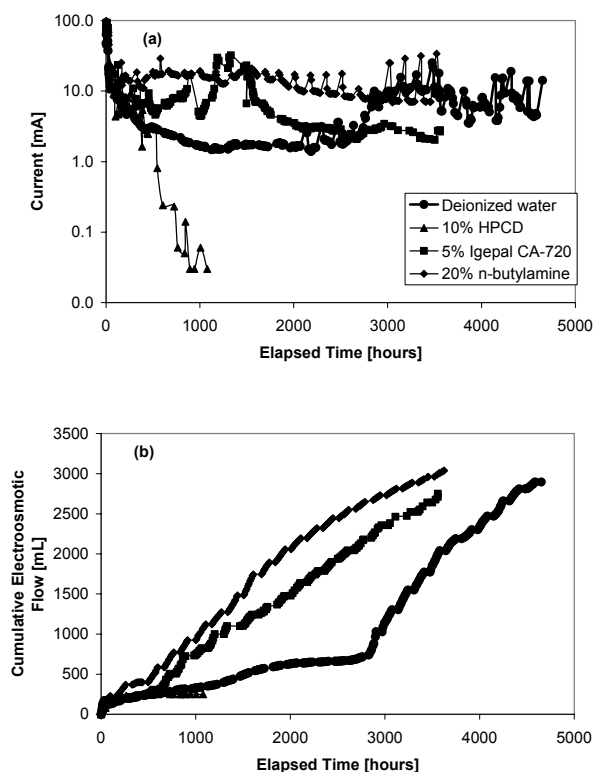


Figure 1. Measured (a) electric current and (b) electroosmotic flow during electrokinetic testing

The rate of electroosmotic flow was consistent with the measured current in each test. The flow was high in the test with 20% n-butylamine test, whereas the flow rate was low in the test with 10% HPCD (Figure 1(b)). The low flow in HPCD test may be due to low dielectric constant of the HPCD solution. The electroosmotic flow is directly proportional to the dielectric constant according to the Helmholtz-Smoluchowski theory (H-S theory). Initially, in all the three tests, the electroosmotic flow was more as the current was high. Gradually, there was a reduction in the flow as the current decreased. In the test with 10% HPCD, due to the rapid depletion of the mobile ions, the current almost reduced to zero and hence it resulted in low electroosmotic flow.

Figure 2 shows the pH and electrical conductivity distribution profiles in the soil for the four tests. When voltage potential is applied to the electrokinetic cell, electrolysis reaction takes place at the electrodes, and H^+ and OH^- ions are generated at anode and cathode, respectively. This results in a low pH near the anode and a high pH near the cathode. During the course of testing, the acidic solution generated at the anode gradually moves through the soil towards the cathode by electromigration and electroosmotic flow, and this lowers the pH of the soil.

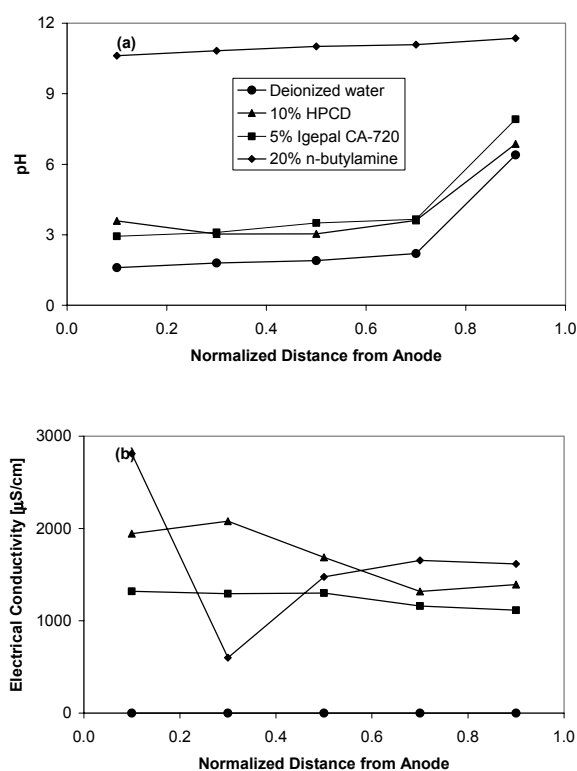


Figure 2. Measured (a) soil pH and (b) soil electrical conductivity after the electrokinetic treatment

For the test with deionized water, the pH value was 1.6 near the anode and it gradually increased to 6.4 towards the cathode. The pH was in the range of 3 and 4 near the anode and in the range of 7 and 8 near the cathode for the tests with 10% HPCD and 5% Igepal. The high alkalinity of 20% n-butylamine increased the soil pH to 10-11 throughout the soil. The low pH in the region near the anode indicates a greater H^+ concentration and a more positively charged mineral surface. When the mineral surface becomes positively charged, the zeta potential becomes positively charged, and by H-S theory, the electroosmotic flow towards the cathode is reduced. 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. For the most part, the pH values for the baseline test were lower than the other tests. Figure 2(b) shows the electrical conductivity distribution profiles of all the tests. The results show that the tests in which flushing solutions were used had very high conductivity values when compared to those in the baseline (deionized water) test.

Figure 3(a) shows the cumulative mass of phenanthrene in solution removed in each test. As shown in the figure, the test with 5% Igepal resulted in high amount of phenanthrene removal, while all the other three tests resulted in very low removal of phenanthrene. For significant mass removal, desorption, solubilization as well as soil-solution-contaminant interaction are essential. In the case of the test with 5% Igepal, the high removal may be due to sufficient solubilization of phenanthrene.

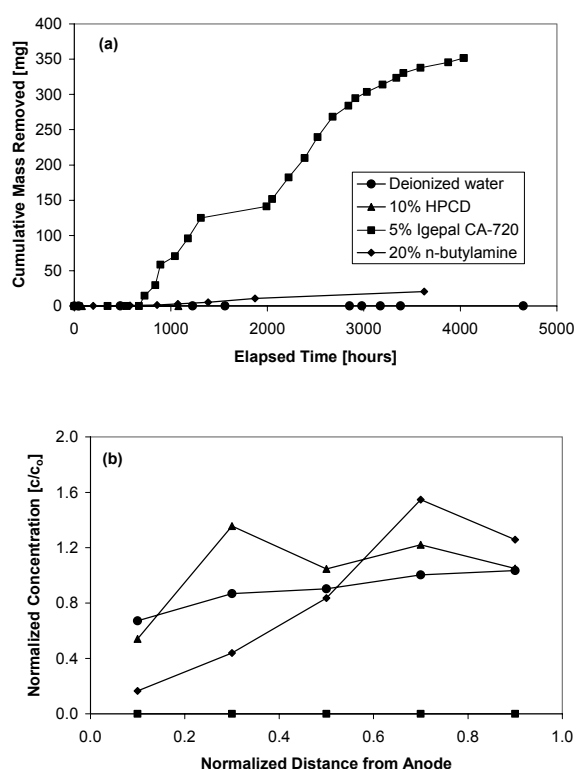


Figure 3. (a) Phenanthrene removal during electrokinetic treatment and (b) residual phenanthrene concentration in soil after electrokinetic treatment

Figure 3(b) shows the normalized phenanthrene concentration in the soil at the end of the electrokinetic tests. These results show that the phenanthrene concentration was negligible throughout the soil indicating that all of the phenanthrene present in the soil was removed. The phenanthrene concentrations decreased significantly near the anode and increased near the cathode for the test with 20% n-butylamine. This shows that n-butylamine was effective for solubilization of phenanthrene and caused migration towards the anode as a result of electroosmosis. The test with 10%HPCD showed low migration trend towards the cathode. In baseline test with deionized water, the phenanthrene mobilization was not significant, which may be due to the poor solubility of phenanthrene in water. The high mobility with

Igepal may be due to the solubilization of phenanthrene and also due to the increased soil-solution-contaminant interaction that resulted because of the increased electroosmotic flow. Moreover, the pH values were low in the entire soil specimen which could have caused the clay particles to have an open structure and hence there was a high interaction between the solution and phenanthrene. The high removal of phenanthrene with Igepal was also found in previous studies (Reddy and Saichek, 2004).

Figure 4(a) shows the cumulative mass of nickel removed in all the tests. It can be observed from these results that there was no significant removal of nickel in all the four tests. Figure 4(b) shows the nickel concentration in the soil sections after the termination of the electrokinetic tests. The mobilization of nickel was significant in all the tests. The baseline test, 10% HPCD test and 5% Igepal test results are approximately the same, indicating that these flushing solutions did not have any impact on nickel migration. However, the n-butylamine test results showed retarded migration of nickel. Initially, the soil pH was low and nickel existed as cation and migrated towards the cathode. As the n-butylamine solution was flushed, the soil pH increased due to high alkalinity of this solvent solution. Due to increased pH, nickel adsorbed and/or precipitated in the soil, leading to low migration. Clearly, the use of n-butylamine will not be beneficial for the removal of nickel.

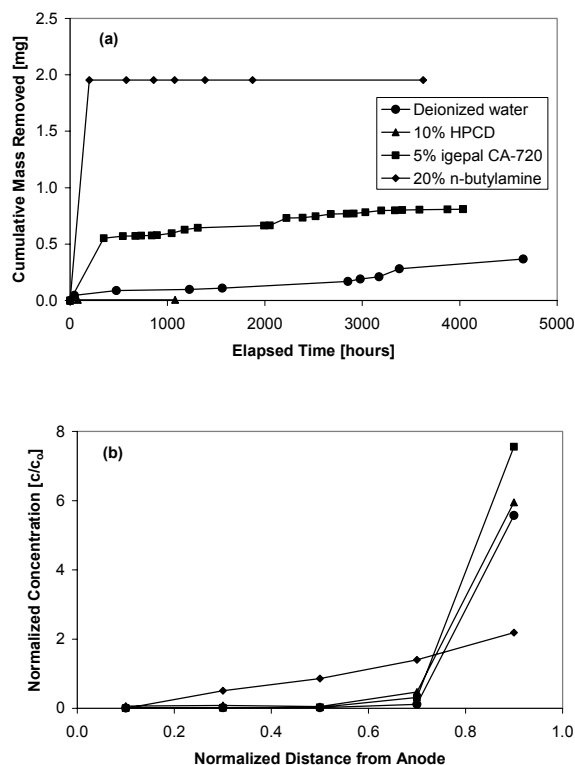


Figure 4. (a) Nickel removal during electrokinetic treatment and (b) residual nickel concentration in soil after electrokinetic treatment

4 CONCLUSIONS

The objective of this study was to evaluate the potential flushing solutions for the simultaneous removal of co-existing heavy metals and PAHs from soils having low permeability using electrokinetics. Nickel was found to migrate towards the

cathode and most of it accumulated within the soil close to the cathode due to the high pH conditions generated by electrolysis reaction in all the tests except in the test with the cosolvent. In the test with cosolvent, nickel precipitated throughout the soil because of the high pH of the cosolvent solution. The experiment with surfactant as a flushing solution resulted in a complete removal of phenanthrene. In the experiment with cyclodextrin, approximately one pore volume of flushing resulted in approximately 50% phenanthrene removal from the soil near anode. However, further migration was retarded because of the reduced electroosmotic flow. In the case of the experiment with cosolvent as a flushing solution, though the electroosmotic flow was high, lower solubility of phenanthrene in the cosolvent due to the insufficient concentration of the cosolvent caused the low removal of phenanthrene. It was concluded that solubilization of the contaminants as well as the sustained electroosmotic flow are the critical factors that contribute to the removal of both heavy metals and PAHs from low permeability soils.

ACKNOWLEDGEMENTS

This study was a part of a comprehensive study on electrokinetic remediation of soils, partly funded by the U.S. National Science Foundation through grant number CMS 0100073. The support of this agency is gratefully acknowledged.

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