INTERNATIONAL SOCIETY FOR SOIL MECHANICS AND GEOTECHNICAL ENGINEERING

Remediation of Contaminated Soil of Thi-Qar Oil Refinery Plant

Réhabilitation des sols contaminés de l'usine de raffinage de pétrole de Thi-Qar

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ABSTRACT: This research aims to study the geotechnical properties of contaminated soil samples obtained from Thi-Qar Oil Refinery plant and apply an adequate remediation technique. The soil samples are contaminated with petroleum products discharged from Thi-Qar oil refinery plant as byproducts. The contaminant will be considered as total petroleum hydrocarbons (TPH) in this study to avoid the complications arising from dealing with the effects of each individual constituent of contaminant on the geotechnical properties of the soil. The soil samples, which were found contaminated with different percentages of TPH, are classified as CL-ML, according to the USCS. Furthermore, the contaminated soil samples are remediated by applying the enhanced electrokinetic method, which is regarded as an efficient method for treating low-permeability soils contaminated with petroleum products. The efficiency of this method is due to the ease of conducting it, economic advantage, time saving benefit and applicability in the field. The electrokinetic method is enhanced by using three types of co-solvents (70DW30ETH, 30DW70ETH, and ETH) applied with an adequate hydraulic gradient to determine the effects of each co-solvent on the efficiency of the electrokinetic technique. The remediation technique proposed herein produced favorable results to improve the geotechnical properties of the TPH-contaminated soil samples. The removal efficiency of TPH from the contaminated soil samples are 17, 53 and 31% for soil sample NA10 treated with (70DW30ETH), (30DW70ETH) and (100ETH) respectively.

RÉSUMÉ: Le but de cette recherche était d'étudier les propriétés géotechniques des échantillons de sol provenant de raffinerie de pétrole de Thi-Qar. Les échantillons de sol étaient contaminés par des produits pétroliers rejetés par les sous-produits de l'usine de la raffinerie de pétrole Thi-Qar. Les contaminants des sous-produits seront traités comme les hydrocarbures pétroliers totaux (TPH) dans cette étude pour éviter les complications découlant de faire face aux effets de chaque constituant individuel de contamination sur les caractéristiques géotechniques du sol.

KEYWORDS: Contamination, electrokinetic, remédiation, clayey soil, hydrocarbons, flushing

1 INTRODUCTION

Petroleum products are regarded as general environmental contaminants and most of the soils were found to be contaminated with the petroleum products that had been tipped over in the course of their production and transportation. When contaminants in the soil are present above an acceptable degree, they cause the soil to deteriorate or undergo certain alterations in their geotechnical properties (Cameselle and Reddy 2012). One of the most conventional remediation practices is the electrokinetic (EK) technique. This technique is widely applied for remediation of those soils contaminated with heavy metals, chloro-organic and oil products. The EK method is based on the principle of application of a low intensity electrical current between two electrodes, which are inserted at the outer edges of the contaminated soil. The contaminants possessing an electrical charge will be moved towards the electrode of the opposite charge by electromigration. Also, the electro-osmotic flow is another component of electrokinetic, which acts as the driving force in moving the soluble contaminants towards the electrodes (Saichek and Reddy 2005).

Reddy et al. (2011) conducted three bench-scale electrokinetic experiments to investigate the remediation of clayey soil contaminated with pentachlorophenol (PCP), lindane (LND), and dinitrotoluene (DNT) without employing any solubilizing or reducing agents in the purging solution. The results indicated that a direct electrochemical reductive process at the electrodes degraded the PCP, DNT, and LND. In their work, Cameselle and Reddy (2012) examined the influence of electro-osmosis on the removal of phenanthrene from soils by using the electrokinetic treatment enhanced with the use of solubilizing agents (deionized water, Tween 80 and ethanol). From the results, it was evident that deionized water provided the highest electro-osmotic flow (EOF) and the use of surfactants like Tween 80 reduced the EOF due to the increase in the viscosity of the solution.

Karkush et al. (2013) studied the effects of four types of contaminants on the geotechnical properties of clayey soil. Each contaminant exerted different effects on the geotechnical properties of the tested soil samples. The effects of industrial wastewater discharged from the thermal electricity plant on the geotechnical properties of the clayey and sandy soil samples were studied by Karkush and Abdul Kareem (2016) and Karkush and Resol (2017). Karkush and Altaher (2016) estimated the risk of soil contamination resulting from the industrial wastewater discharged from Thi-Qar oil refinery plant. This paper assesses the effects of remediation on the clayey soil samples contaminated with total petroleum hydrocarbons by employing the enhanced EK technique. The enhancement was accomplished by using a flushing solution composed of different ratios of deionized water (DW) and ethanol (ETH). ETH is selected because of its ability to dissolve organic compounds, and because of its non-toxicity, so it is considered an environment friendly surfactant.

2 EXPERIMENTAL WORK

2.1 *Study area and soil sampling*

The soil samples are obtained from the site adjacent to Thi-Qar oil refinery plant in Al-Nasiriyah city, located in the south of Iraq. The byproducts resulted from the industrial process of Thi-Qar oil refinery plant are disposed directly to the soil in this site. The groundwater table ranges from 2 to 2.5 m from the existing ground level. The soil samples were obtained from three locations and from three different depths (0.0, 1.0 and 2.0) m for each location. The three locations were specifically selected to represent a highly contaminated area, a slightly contaminated part and an intact area. This classification was based on the color and visual classification of soil samples. The global positioning system (GPS) coordinates of the three sampling locations and description of soil samples are given in Table 1.

Table 1. Coordinates, description and designation of the soil samples.

Spot GPS Coordinate	Depth m	Zone	Soil Description	Symbol
N 305923 E 0461325	0.0	Highly contaminated soil	Soft to very soft black to grayish clayey silt with sand, oil and roots	NA10
	1.0			NA11
	2.0			NA12
N 305916 E 0461333	0.0	Slightly contaminated soil	Medium to stiff brown to gray clayey silt with salts, red and black spots	NA20
	1.0			NA21
	2.0			NA22
N 305930 E 0461354	0.0	Intact soil	Medium brown clayey silt with sand and salts	NA30
	1.0			NA31
	2.0			NA32

The disturbed soil samples are studied to identify the effects of the contamination on its geotechnical properties; these soil samples are also used in the bench-scale experiments of the enhanced EK tests. Three trial pits were excavated in the site to obtain the soil samples. Then, the soil samples are placed in airtight plastic bags, labeled and transported to the laboratory. The geotechnical properties of the soil samples are listed in Table 2 (Karkush and Altaher, 2017). The initial TPH concentrations are (3624, 3554, 3417.3) ppm in the soil samples labeled NA10, NA11 and NA12, respectively.

Table 2. Physical properties of the tested soil samples.

Property	NA10	NA11	NA12
γ_f, kN/m³	18.25	18.15	18.25
ω, %	26	28	31
Gs	2.71	2.72	2.62
Sand, %	5	6	4
Silt, %	51	79	62
Clay, %	44	15	34
LL, %	46	47	49
PL, %	28	28	30
$\gamma_{d,max}$, kN/m³	19.5	18.9	18.7
ω_{opt}, %	12	15	14
k, cm/s	4.5×10^{-7}	2.5×10^{-7}	1.4×10^{-7}
USCS	CL-ML	ML	ML

2.2 *Set-up of the electrokinetic test and test procedure*

The bench-scale experimental model is designed to determine the practicability of removing the TPH contaminant from the soil samples using the EK technique as shown in Fig. 1.
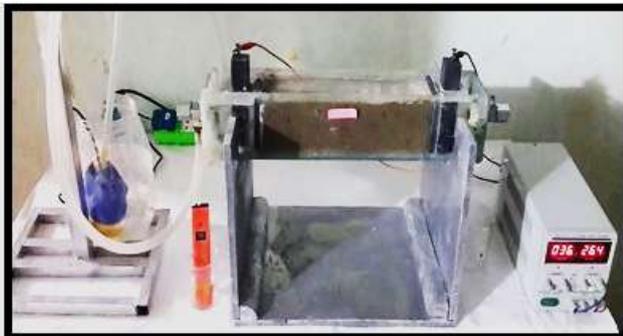

Figure 1. Set-up of the EK experiment.

The principal actions of contaminant transport in the EK technique are electromigration and the electro-osmosis. The EK technique is augmented with a flushing solution applied with adequate hydraulic gradient, which involved mixing DW and ETH in different ratios. The flushing solutions used are:
1) 70 % of DW and 30% of ETH (70DW30ETH)
2) 30 % of DW and 70% of ETH (30DW70ETH)
3) 100 % of ETH (100ETH).

Fig. 2 shows the schematic diagram of the enhanced EK test set-up used in this study. The test setup chiefly consists of the EK cell, which contains two electrode compartments, two electrode reservoirs, power supply, and a multimeter. The electrode compartments are provided with valves to control the inflow and outflow of the cell, a pump, perforated graphite electrodes, porous stone and filter papers. The EK cell is a box made of glass, 50 cm length, 8.5 cm width and 10 cm height. The soil sample dimensions are 30 cm in length with square cross-sectional area of edge 8.5 cm. The porous stone and filter paper are used to prevent the fine soil particles from being transported into the reservoirs of the anode and cathode. A gas ventilation tube provided in the electrode compartments enabled the gases produced during the electrolysis processes to escape. In addition, the pH of the solute collected in the cathode reservoir is measured with a pH meter (Coring 350 probe). The EOF is determined by monitoring the outflow through the cathode compartment.
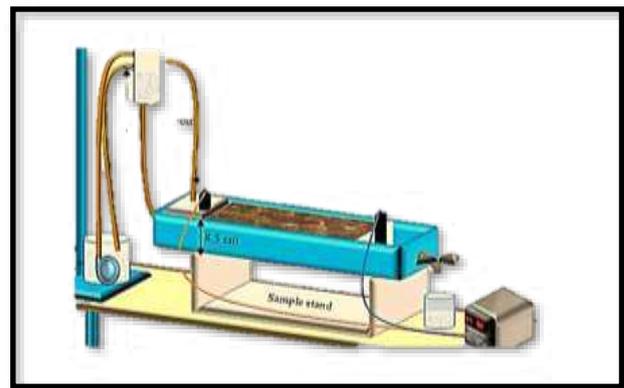

Figure 2. Schematic diagram of the EK experiment.

The steps of testing procedure are:
1. Preparing the EK cell components, electrodes, flushing surfactants and hydraulic gradient system.
2. The contaminated soil sample was first dried at 30-35 ºC to prevent the TPH content from evaporating. Then, the soil sample is mixed with natural moisture content and placed in the EK cell, based on the field unit weight. A filter paper is inserted between the soil and the porous stone and both are put in front of the electrodes.
3. A purging solution is poured into the anode compartment. The anode reservoir is filled with only DW for five days and then continued with a purging solution for the next five days. The cathode reservoir is filled with DW alone for the entire duration of the experiment.
4. The purging solution at anode is applied with a hydraulic gradient of 2 to enhance the removal efficiency of EK technique.
5. The electrodes are then connected to the power supply, and an efficient potential gradient of 1 VDC/cm is maintained between the electrodes.
6. The electrical current moving through the soil sample, the water flow in the cathode compartment and pH in the cathode reservoir are measured at several time intervals during the experiment.
7. The test is completed when the current became constant or no change is registered in the EOF.
8. At the end of each experiment, samples of the solutions in the reservoirs and the electrode compartments are collected and sent for analysis. The electrodes, the tubing and the reservoirs are changed for each new test. The soil sample is then extruded from the cell by hand and divided into four portions. The pH and residual TPH concentration are measured with the pH meter and UV device, respectively.

3 RESULTS AND DISCUSSIONS

3.1 *Electrical current*

The trend of variation of electrical current with time is shown in Fig. 3. Some fluctuations observed in the soil sample remediated with EK enhanced with (70DW30ETH). The electrical current increased rapidly within the first few hours, and then showed a steady rise within the next 100 hours to reach its maximum value after about 125 hours. The current then quickly decreased and remained constant after around 200 hours. The 10-day remediation period is divided equally into two-time periods. During the first period, DW is used as a purging solution; the electrical current raised rapidly during the first hours of the experiment and then steadied until it became stable. Whereas, in the period, when the flushing solution (70DW30ETH) is used, the electrical current has begun to decrease rapidly with time as shown in Fig. 3. A similar behavior of the electrical current with time has been reported in other studies by Reddy and Chinthamreddy (2004); Reddy et al. (2004); Yuan et al. (2006) and Colacicco et al. (2010). The effects of the different co-solvents as flushing solutions have been examined, and the variations in the electrical current with time for soil sample NA10 remediated with three types of co-solvents are shown in Fig. 4.
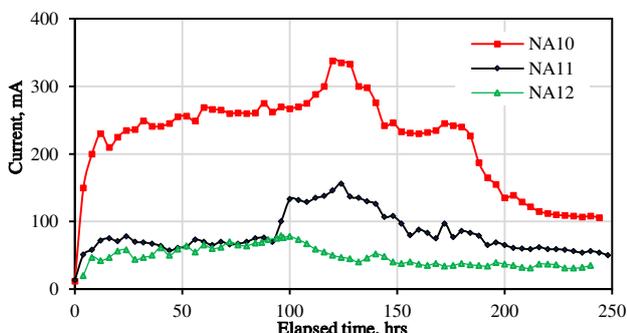

Figure 3. Current variation with time for soil samples NA10, NA11 and NA12 remediated with (70DW30ETH).
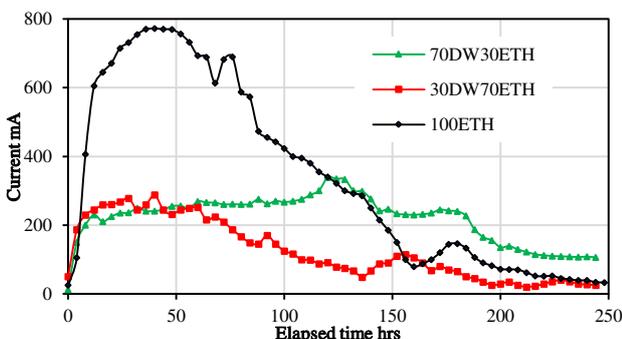

Figure 4. Electrical current variation with time for soil sample NA10 remediated with different cosolvents.

3.2 *The pH of the effluents*

The pH of the effluent at the cathode compartment is measured over time during the EK experiments as shown in Fig. 5. The pH value raises rapidly to reach its maximum value within the first 16 hours of the experiments. This action may be attributed to the production of OH^- at the cathode compartment near the outflow end, while Bruell et al. (1992) had observed increasing the pH value at the cathode in the EK remediation of soil contaminated with organic materials. The high EOF towards the cathode causes a drop the pH value near the cathode in response to opposite migration of the OH^- ions towards the anode (Reddy et al. 2002). However, in this research, when DW is used as the purging solution, the EOF is low, which caused the

pH value to rise near the cathode. The pH of the co-solvent solution affects the pH of the soil samples remediated by the EK technique. During the EK experiments, the acidic solution generated at the anode was observed to move through the soil towards the cathode, thus decreasing the pH of the soil (Acar et al. 1995). The pH of the effluent at the cathode is measured at specific time intervals during the EK experiments enhanced with three concentrations of co-solvents applied with adequate hydraulic gradient for soil sample NA10, as shown in Fig. 6.
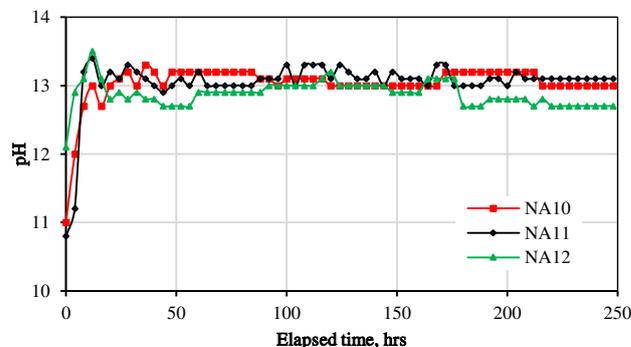

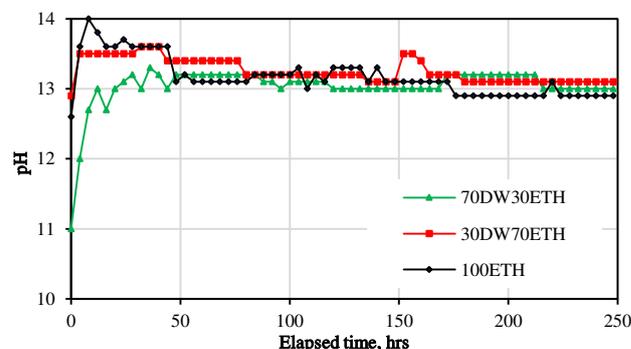Figure 5. Variation of pH with time of samples NA10, NA11 and NA12.

Figure 6. Variation of pH value with time of sample NA10 remediated with different cosolvents.

3.3 *Electro-osmosis flow (EOF)*

The highest electro-osmotic flow is observed when the EK experiment is enhanced with DW with adequate hydraulic gradient, as shown in Fig. 7. When ETH is used as the co-solvent, it induced the EOF to drop due to the decreasing the electrical conductivity of the soil. The combined effects of the electro-osmotic flow and the ability of the co-solvent to dissolve the contaminants may have removed the organic compounds from soil. The results of experiments indicated that the use of DW alone induces a high EOF; however, neither the transport nor removal of the petroleum hydrocarbon was observed. On the contrary, the use of ETH stimulated the drop in EOF, although the removal efficiency is high (Cameselle and Reddy 2012). The low EOF depends upon the dielectric constant and viscosity of the co-solvent. From the results of the EK experiments, it is evident that the ETH is efficient as a flushing solution for remediation of the contaminated soil with TPH; however, contaminant migration is limited due to the change in the solution chemistry that is produced over time and/or distance from the anode (Saichek and Reddy 2005). The accumulative electro-osmotic effluent flow was assessed over time during the EK experiments enhanced with three types of co-solvents for soil sample NA10, as shown in Fig. 8. The effluent collected from the EK tests after a few hours from the beginning of the test is very low. However, soon after that, a big jump in the EOF volume is observed irrespective of the type of flushing solution. The value of the collected effluent steadied and remained constant until the

completion of the test, with DW as the flushing solution. However, when ETH is used as flushing solution, the accumulative electro-osmotic flow began to jump again to the highest value of the collected effluent and remained constant until the end of the test. This occurred because the EOF is directly proportional to the electrical current and dissolved contaminants in the pore fluid (Faisal et al. 2014).
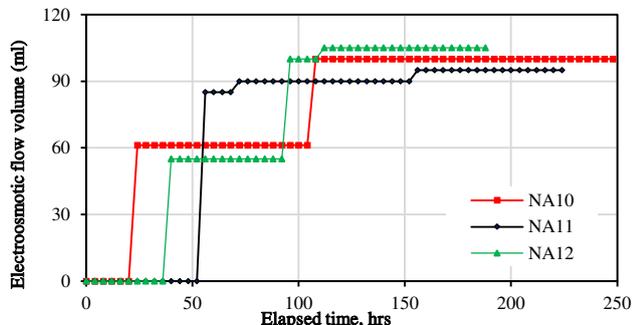

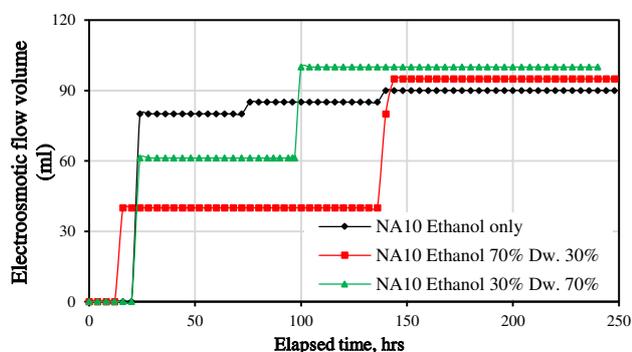Figure 7. Accumulative EOF versus time at cathode.

Figure 8. Accumulative EOF versus time at the cathode of sample NA10.

3.4 *TPH removal*

To evaluate the efficiency of the enhanced EK technique, the concentration of TPH in the remediated soil samples is compared with the initial concentration of TPH. The variation observed in the concentrations of TPH with the distance across the soil samples remediated with flushing solution 70DW30ETH are shown in Fig. 9. The remaining TPH is redistributed from the anode to the cathode along the sample axis. Thus, the hydrocarbon concentration is observed to decrease, except near the cathode. The removal efficiency is 17, 7 and 2 % in the soil samples NA10, NA11 and NA12, respectively.
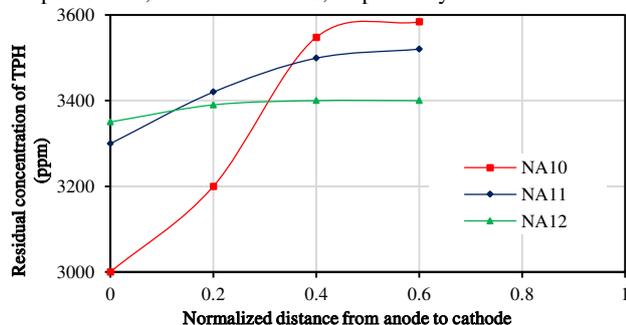

Figure 9. Variation of residual TPH concentration with distance in samples (NA10, NA11 and NA12) after EK remediation.

4   CONCLUSION

The main conclusions drawn from the results of the EK remediation technique conducted on three soil samples NA10,

NA11 and NA12 confirmed the efficiency of this method for remediation of low-permeability soil contaminated with TPH. The efficiency of this method is seen in terms of the ease of conducting it, economic advantage, time saving benefit and applicability in the field. The removal efficiencies of TPH from contaminated soil samples remediated by the EK technique are 17, 7 and 2 % in the soil samples NA10, NA11 and NA12, respectively, when the co-solvent composed of 70% of DW with 30% of ETH is used. The removal efficiencies of TPH are 17, 53 and 31% from the soil sample NA10 treated with the three co-solvents (70DW30ETH), (30DW70ETH) and (100ETH), respectively. The efficiency of EK technique increases when the co-solvent used to enhance it is changed and applied with adequate hydraulic gradient. The results confirmed that the presence of salts in clayey soil produces a remarkable increase in the buffering capacity of the soil. This increase may be the reason for the delayed formation and development of the acid front phenomena. Therefore, this is the reason for the relatively low degree of contaminant removal ($\leq 50\%$) from this soil.

5   REFERENCES

Acar, Y. B., Gale, R. J., Alshawabkeh, A. N., Marks, R. E., Puppala, S., Bricka, M., and Parker, R. 1995. Electrokinetic remediation: basics and technology status. Journal of Hazardous Materials, 40(2), pp. 117-137.

Bruell, C. J., Segall, B. A., and Walsh, M. T. 1992. Electroosmotic removal of gasoline hydrocarbons and TCE from clay. Journal of Environmental Engineering, ASCE, 118(1), pp. 68-83.

Cameselle, C., and Reddy, K. R. 2012. Development and enhancement of electro-osmotic flow for the removal of contaminants from soils. Electrochimica Acta, 86, pp. 10-22.

Colacicco, A., Gioannis, G. D., Muntoni, A., Pettinao, E., Polettini, A., and Pomi, R. 2010. Enhanced electrokinetic treatment of marine sediments contaminated by heavy metals and PAHs, Chemosphere, 81, pp. 46-56.

Faisal, A. A. H., Abbas, T. R., and Khalil, A. 2014. Contaminated soil by an upward electro-kinetic process. Global Journal on Advances in Pure and Applied Sciences, 2(2014), pp. 66-73.

Karkush, M. O., and Abdul Kareem, M. S. 2016. Behavior of pile group subjected to lateral cyclic loading in contaminated soils. International Journal of GEOMATE, 10(21), pp. 1943-1949.

Karkush, M. O., and Altaher, T. A. 2016. Risk assessment of AL-Nassyriah oil refinery soil. Journal of Civil Engineering Research, 6(1), pp. 16-21.

Karkush, M. O., and Altaher, T. A. 2017. Geotechnical evaluation of clayey soil contaminated with industrial wastewater. Archives of Civil Engineering, 63(1), pp.47-62.

Karkush, M. O., Zaboon, A. T. and Hussien, H. M. 2013. Studying the effects of contamination on the geotechnical properties of clayey soil. Coupled Phenomena in Environmental Geotechnics, Taylor & Francis Group, London, pp. 599-607.

Reddy, K. R., and Chinthamreddy, S. 2004. Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions. Journal of Environmental Engineering, 130 (4), pp. 442-455.

Reddy, K. R., Danda, S., and Saichek, R. E., Maturi, K. 2004. Complicating factors of using ethylenediamine tetraacetic acid to enhance electrokinetic remediation of multiple heavy metals in clayey soils. Journal of Environmental Engineering, 130 (11), pp. 1357-1366.

Reddy, K. R., Saichek, R. E., Maturi, K., and Ala, P. 2002. Effects of soil moisture and heavy metal concentrations on electrokinetic remediation. Indian Geotechnical Journal, 32 (2), pp. 258-289.

Saichek, R. E. and Reddy, K. R. 2005. Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: A Review, Critical Reviews in Environmental Science and Technology, 35, pp.115–192.

Yuan, S., Tian, M., and Lu, X. 2006. Electrokinetic movement of Hexachlorobenzene in clayed soils enhanced by Tween 80 and beta cyclodextrin. Journal of Hazardous Materials, 137(2), pp.1218-1225.