Remediation of Contaminated Soil with Petroleum Industrial Wastewater

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ABSTRACT

The contamination of soil with the wastes of oil industry products that are complex mixtures of hydrocarbons increased recently due to the large development of oil industries in Iraq. This study deals with the remediation of low permeability contaminated clayey soil by using the enhanced electrokinetic technique (EK). The contaminated soil samples obtained from Thi-Qar oil refinery plant in Al-Nassyriah city, where the byproducts of refinery plant are disposed into that site. The byproduct contaminant treated as total petroleum hydrocarbons (TPH) to avoid dealing and complexity of treating the individual minerals and compounds consisting the contaminant. The initial concentrations of TPH were (702.7, 1168, 1235) ppm in the contaminated soil samples NA_{10}, NA_{11}, and NA_{12} respectively. The remediation technique includes a bench-scale experimental study by applying the enhanced electrokinetic test on the soil sample NA_{12} that contains the higher concentration of TPH in compared with other soil samples. A constant DC voltage gradient of 1.0 VDC/cm was applied for a period of 10 days. This technology was enhanced by using flushing solution of ethanol and deionized water, which was mixed in ratios of 30% and 70% respectively. The results of this study showed that the removal of TPH at the anode was about 15% and the concentration of TPH decreased at anode, which reflect the migration of TPH towards the cathode.

Keywords: electrokinetics technique, remediation, total petroleum hydrocarbon, enhanced electrokinetic, clayey soil.

معالجة التربة الملوثة بالمخلفات النفطية

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الخلاصـــــــــة

ان تلوث التربة بالمخلفات الناتجة من الصناعات النفطية والتي هي عبارة عن مزيج معقد من الهايدروكربونات قد ازدادت في الآونة الأخيرة بسبب التطور الكبير في الصناعات النفطية. هذه الدراسة تتناول معالجة التربة الطينية الملوثة ذات النفاذية المنخفضة بتقنية الكهروحركية، هذه العينات تم الحصول عليها من موقع مصفى ذي قار الواقع في مدينة الناصرية حيث تطرح الملوثات النفطية. أن الملوث المطروح الى الموقع تم تمثيله في هذه الدراسة بمحتوى الهيدروكربونات الكلي لتجنب دراسة العناصر والمركبات المكونة لهذا الملوث بشكل منفصل. وكانت التراكيز الابتدائية للهيدروكربونات النفطية (702.7، 1168، 2235)ppm لعينات التربة الملوثة NA_{10} و NA_{11} و NA_{12} على التوالي. تم إجراء تجارب المعالجة باستخدام تقنية الكهروحركية المحسنة على عينة NA_{12} لأنها تمثل اعلى تركيز من الهايدروكربونات وتعتبر اكثر تلوثا. تم تسليط انحدار جهد كهربائي مقداره 1.0 فولت /سنتيميتر على طول نموذج التربة لفترة معالجة 10`أيام. هذه التقنية عززت باستخدام محاليل الغسل المكونة من الإيثانول والماء الأيوني التي تخلط بنسب 30٪ و 70٪ على التوالي. وأظهرت نتائج هذه الدراسة ان كفاءة الازالة للملوث في الأنود كانت 15٪ وكذلك انخفاض تركيز محتوى الهايدروكربونات الكلي في قطب الأنود بسبب هجرة الملوث بأتجاه الكاثود.

الكلمات الرئيسية: تقنية الكهروحركية، المعالجة ، محتوى الهايدروكربونات النفطية، الكهروحركية المحسنة، التربة الطينية.

1. INTRODUCTION

The soil and groundwater contamination grow rapidly in the world and cause serious environmental problems. The different human activities and urbanization such as agriculture, mining, and industrial lead to contamination of soils. Contamination may be in the form of organic compounds, inorganic compounds and heavy metals. The common types of soil contaminants are heavy metals and petroleum-based hydrocarbon compounds, **Cameslle et al., 2013**. Many of the soils are contaminated with petroleum products because of oil spills during oil production and transportation. The electrokinetic technique (EK) uses low-level of constant voltage DC power supply, potential gradients in the range of 20–200 V/m or alternatively a constant current density in the range of 0.025–5 A/m^2 between the electrodes. When an electric field is applied to a wet soil, the cation will move toward the anode and anions are moved toward the cathode as shown in **Fig.1**, **Karim, 2015.** Several studies have demonstrated to use water, as an electrolyte solution does not improve the removal of mixed contaminants from soils. Therefore, different strategies were used to enhance the removing of contaminants from soil or water. These strategies involve: (1) increasing duration of remediation, (2) increasing the electric potential gradient between electrodes, (3) using cation/anion exchange membranes in the electrodes, and (4) using enhancement solutions such as (solvents or surfactants) with different hydraulic gradients. Using of enhancement co-solvents has been approved to be the most efficient strategy to get high removal efficiency, **Reddy, 2013.**

Karkush et al., 2013 studied the effects of four types of contaminants on the geotechnical properties of clayey soil. The different types of contaminants have different effects on the geotechnical properties of tested soil samples. The effects of industrial wastewater disposed from thermal electricity plant on the geotechnical properties of clayey and sandy soil samples were studied by **Karkush and Abdul Kareem, 2015** and **Karkush and Resol, 2015**. **Karkush and Altaher, 2016** measured the risk of contamination resulting from contamination of clayey soil contaminated by industrial wastewater disposed from Thi-Qar oil refinery plant. This paper deals with remediation of clayey soil contaminated with industrial wastewater disposed from Thi-Qar oil refinery plant by using enhanced EK technique. The enhancement achieved by using flushing solution (deionized water and ethanol). The selection of ethanol surfactant ($C_2H_2O_5$) was based on its proven ability to solubilize organic contaminants in previous studies, environmental compatibility, and non-toxicity, thus reducing the risk of future environmental problems after the remediation process, making it an environmentally friendly surfactant.

2. EXPERIMENTAL WORK

2.1 Site Review and Soil Sampling

The contaminated soil samples used in this work were obtained from Thi-Qar oil refinery plant in Al-Nassyriah city, which is located in the south part of Iraq with georeferencing coordinates (GPS coordinate: N 305916.2, E 0461332.8). A part of this site is considered the disposal area for the by-products from the oil refinery. A pit was excavated using a shovel to obtain the soil samples from three different depths (0.0, 1.0 and 2.0) m below the existing ground level (E.G.L). The groundwater table was about 2.25 m below E.G.L. The site soil can be classified according to the unified soil classification system (USCS) as a medium to stiff clayey silt (ML) but because of the presence of contaminants in the soil, the consistency of soil samples changed to soft and very soft soil. The location of the study area where the soil samples obtained is explained in **Fig. 2.** The physical properties of tested soil are given in **Table 1**.

2.2 Electrokinetic Test Set-up and Testing Procedure

The bench-scale experimental set-up was designed to examine the feasibility of TPH contaminants removal from soil sample with EK technique, which mainly depends on the electromigration and the electroosmotic actions. The EK was enhanced by using flushing solution, which consisted of two components (70 % of deionized water and 30% of ethanol). The schematic diagram of the electro-kinetic test setup used in this study to combined hydraulic flushing-electrokinetic experiments is shown in **Fig. 3.** The test setup includes of an electrokinetic cell, two electrode compartments, two electrode reservoirs, power supply, and multimeter. The electrode compartment consists of valve to control the flow into the cell, pump, perforated graphite electrode, porous stone and filter paper. The porous stone and filter paper were used to prevent soil particles from migration to the anode and/or the cathode reservoirs. Gas vents were provided in the electrode compartments to allow escaping the gases resulting from the electrolysis reactions. A tube was attached to gas vent ports to collect any liquid that may be removed with the ventilated gases. In addition, pH meter (Coring 350 probe) was used to measure the pH of the soil collected in cathode reservoir. The outflow through the electrode compartment was also monitored to determine the electro-osmotic flow.

The testing procedure can be summarized by the following points:

1) Preparation the electro-kinetic cell with all components described previously (electrodes, flushing surfactants and device used to control hydraulic gradient);
2) The contaminated soil sample was dried at a temperature of (30-35) ^{o}C. Then, mixed with the natural moisture content and placed in the electro-kinetic cell depending on the field unit weight. The filter paper was placed between the porous stone and soil and both were placed in front of the electrodes;
3) The electrode compartments were filled with a purging solution (PS).The anode reservoir was filled with deionized water alone for five days and then continued with 70% of DW. and 30% of Ethanol for other five days, while the cathode reservoir was filled with deionized water during 10 days from starting experiment;
4) Then, connecting the electrodes to the power supply with an appropriate potential gradient of 1 VDC/cm to be applied to the soil sample.
5) The water flowed in the cathode compartment, the electric current across the soil sample, and pH in the cathode were measured with time during the experiment period.
6) The test was finished when the electrical currents become constant or no significant change in EO flow was observed.
7) At the end of each experiment, the aqueous solution from the reservoirs and the electrode compartments were collected and analyzed. The electrodes, the tube, and the reservoirs were exchanged for the new test. Thereafter, the soil sample was extruded from the cell and divided into four sections. Each section was tested for pH and residual TPH concentration by using UV device.

To ensure the accuracy and control of the test results, the following points were taken into consideration:

a) Soaking the electrokinetic cell and reservoirs in a dilute acid solution for 24 hrs and then rinsing with potable water firstly and with distilled water secondly;
b) Boiling the porous stones in distilled water for several hours;
c) Using new electrodes and filter papers for each experiment; and
d) Checking the UV device before and after each experiment.

3. RESULTS AND DISCUSSION

3.1 Electric Current

The variation of electrical current with time follows the trend shown in **Fig. 4** with some fluctuations for the soil sample NA_{12} remediated with deionized water and ethanol. The electric current increased rapidly in the first few hours, then increased steadily within next 100 hours to reach its maximum value at the time of 125 hours, after that, the current decreased quickly to become constant after 200 hours approximately. The remediation period (10 days) was divided into two equal parts, in the first part of remediation period; the deionized water was used as a flushing solution, where the electrical current increased quickly during the first hours of the test and then become steady. While, in the second part of remediation period, 30 % of ethanol was mixed with 70 % of deionized water to form the flushing solution, the electrical current began to decrease quickly with time as shown in **Fig. 4**.

The high initial electrical current occurs due to the dissolution of salts in the soil, which causes increasing the mobility of ions, **Mitchell, 1993; Reddy** and **Karri, 2006;** and **Reddy et al., 2011**. During the EK remediation process, OH^- and H^+ ions are generated at the cathode and anode due to electrolysis, respectively. Increasing the ions in soil will increase the mobility and constant production of H^+ ions at the anode will help to increase the electrical current, but over time, these ions are depleted as they electromigrated and move into the electrode chambers due to the processes of electromigration and electroosmosis. The migrations of ions will cause lowering of the electrical current due to depletion in the amount of mobile ions in the soil, **Saichek** and **Reddy 2005.**

3.2 pH of Effluent

The pH of the effluent at the cathode was measured over time during EK experiment of contaminated soil sample NA_{12} and the variation of pH with time is shown in **Fig. 5**. The value of pH increased rapidly to reach its maximum value in the first 16 hours of experiments. This may be due to the production of OH^- at the cathode near the outflow end. The same behavior was observed by **Bruell et al., 1992** in remediation of soil contaminated with organic compounds by electrokinetic technique. Increasing the electroosmotic flow action towards the cathode leads to decreasing the value of pH near the cathode due to the opposite migration of negative hydroxide (OH^-) ions towards the anode **Reddy et al., 2011.** In this research, in case of using deionized water as flushing solution, the electroosmotic was low; therefore, the value of pH was higher near the cathode. The pH value of co-solvent solution has a small influence on the pH value of soil sample remediated by EK technique. During the experiment of EK, the generated acidic solution at the anode will move gradually by electromigration and electroosmotic flow through the soil towards the cathode. This action will lead to lowering the pH value of soil, **Acar et al., 1995.** The pH of the effluent at the cathode was measured over time during EK experiments enhanced with three concentrations of co-solvents for soil sample NA_{12} are shown in **Fig. 5.**

3.3 Electroosmosis Flow (EOF)

The highest electroosmotic flow was observed during the EK experiment enhanced with deionized water as shown in **Fig. 6.** The use of co-solvent such as ethanol decreases the electroosmotic flow due to increasing the electric current resistivity. Removing of organic materials from soil may be resulting from the combined effects of the electroosmotic flow and the ability of the co-solvent to dissolve the contaminants. Based on observation of results during the experiments, the deionized water alone developed a high electroosmotic flow, but no transport or removal of petroleum hydrocarbon was observed. On the contrary, using of ethanol as co-solvent causes decreasing in electroosmotic flow but the removal efficiency was high which confirms the findings of **Cameselle** and **Reddy, 2012.** The flushing solution properties such as dielectric constant and the viscosity may be responsible for low electroosmotic flow. The results of the EK experiments indicated that using the ethanol as flushing solution was advantageous for treating the soil near the anode region, but contaminant migration was limited by changing the soil and/or solution chemistry that occurred with time and/or distance from the anode, **Saichek** and **Reddy, 2005.**

3.4 Total Petroleum Hydrocarbon Removal

To evaluate the efficiency of enhanced EK technique, the concentration of TPH in the remediated soil samples were compared with the initial concentrations of TPH. The initial concentrations of TPH were (702.7, 1168, 2235) ppm in the soil samples NA_{10}, NA_{11} and NA_{12} respectively. The variation of TPH concentrations with distance for the soil sample NA_{12} remediated with 70% of DW and 30% of ethanol are shown in **Fig. 7**. The results of tests proved the redistribution of total hydrocarbons remained in the treated soil sample, as a result the concentration of the hydrocarbons decreased everywhere in the soil sample except near the cathode. The removal efficiency ratio was about 15% for soil sample NA_{12}. This ratio was very small, so it is very important to use an effective co-solvent as an enhancement for EK technique.

4. CONCLUSIONS

The main conclusions drawn from the results of this study, through applying the electrokinetic remediation technique on soil sample NA_{12}, is the efficient and economical applicability of such technique in remediation of low permeability and heterogeneous soils that have been contaminated by organics material such as total petroleum hydrocarbons (TPH). The removal efficiency of TPH from contaminated soil sample NA_{12} remediated by enhanced EK technique was 15%. The removal efficiency decreased in advance towards the cathode, which means moving of TPH particles towards the cathode. The results proved that the presence of salts in the clayey soil causes a noticeable increase in the buffering capacity of soil. This increase may be the basis for a delay in the formation and development of acid front phenomena. Therefore, a relatively low removal of contaminant ($\leq 50\%$) in this soil occurred. The type of co-solvent and hydraulic gradient used to apply such solvent plays an important role in the enhancement of EK technique.

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Table 1. Physical properties of tested soil samples.

Property	**NA_{10}**	**NA_{11}**	**NA_{12}**
Field unit weight, kN/m^3	18.25	18.15	18.25
Water content, %	26	28	31
Specific gravity, 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
PI, %	18	19	19
Maximum dry density, gm/cm^3	19.5	18.9	18.7
Optimum moisture content, %	12	15	14
k, cm/s	4.5×10^{-7}	2.5×10^{-7}	1.4×10^{-7}
USCS	CL-ML	ML	ML

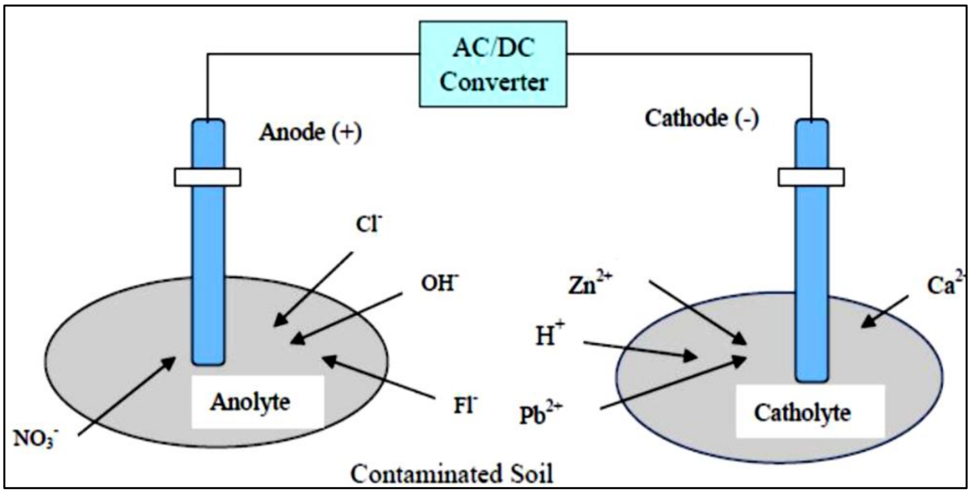

Figure 1. The concept of electrokinetic extraction of contaminants (After Karim, 2015).

Figure 2. Satellite image of Thi-Qar oil refinery.

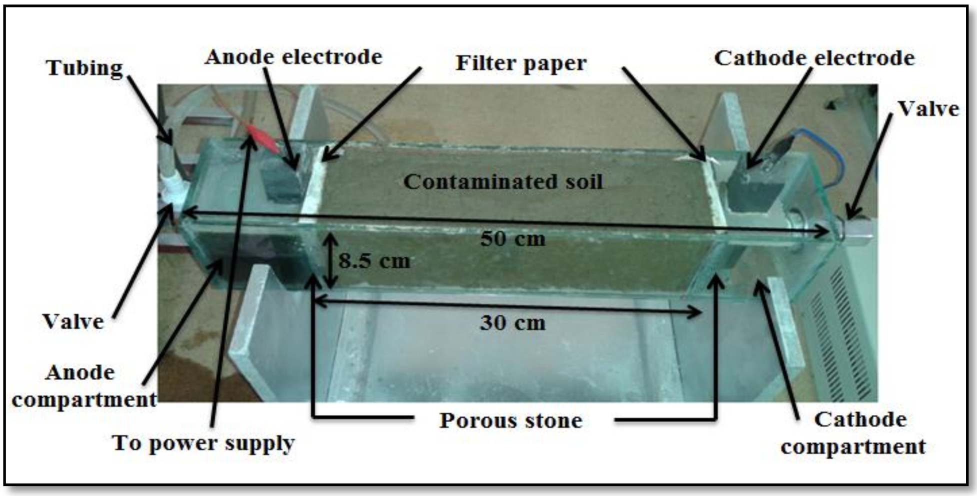

Figure 3. Schematic diagram of the used electrokinetic cell.

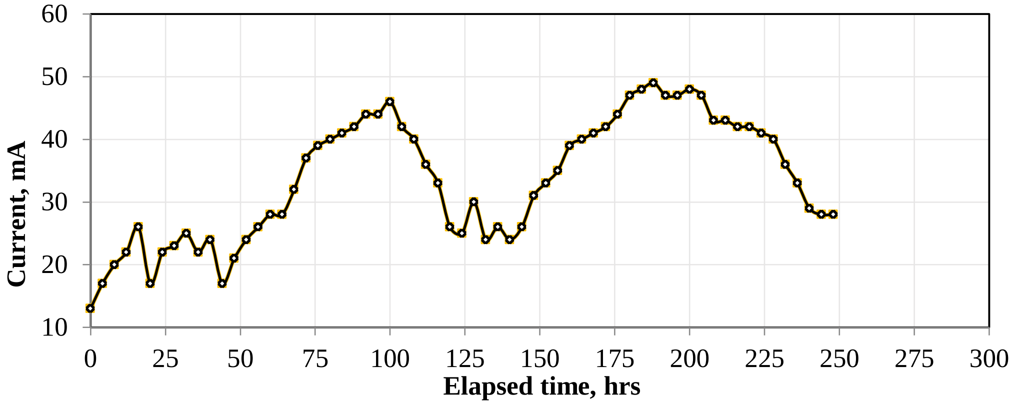

Figure 4. Electrical current variation with time of soil sample NA_{12}.

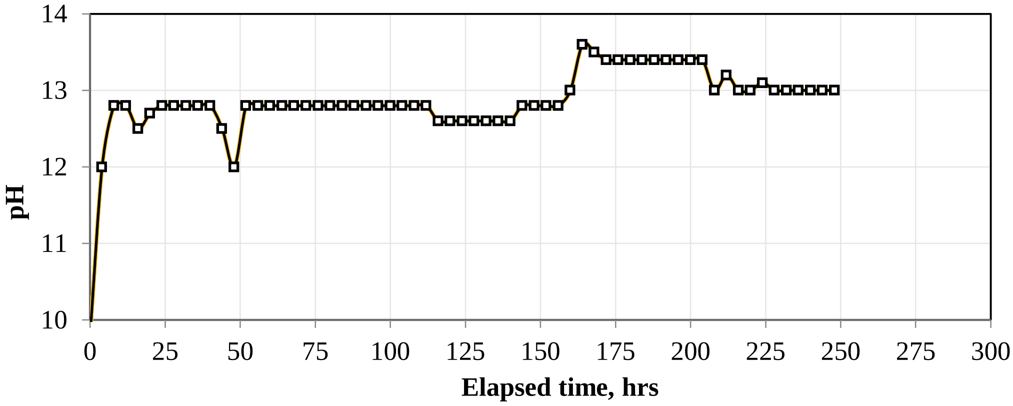

Figure 5. Variation of pH with time of soil samples NA_{12}.

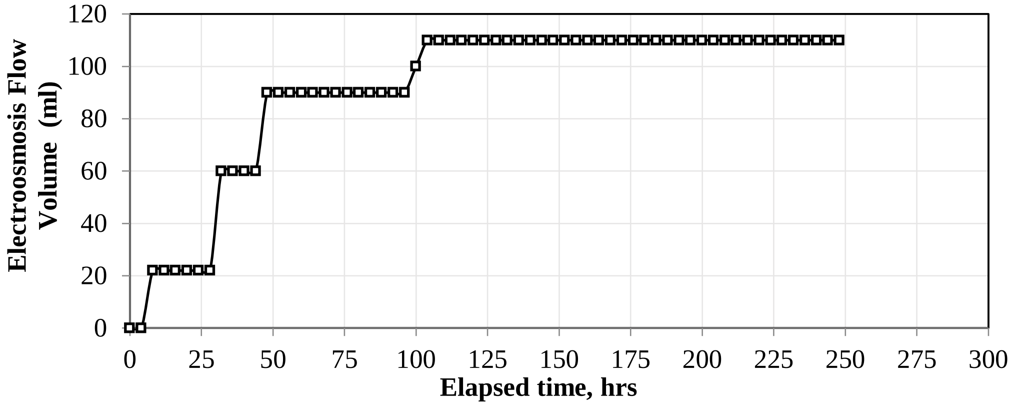

Figure 6. Accumulative electroosmosis flow versus time at cathode of soil sample NA_{12}.

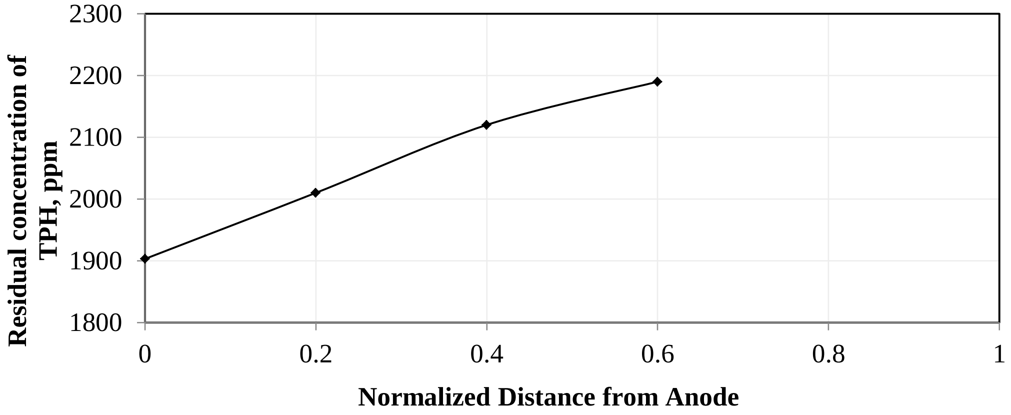

Figure 7. Variation of residual TPH concentration with distance for soil samples NA_{12}.