COUPLED ELECTROKINETICS-ADSORPTION TECHNIQUE FOR SIMULTANEOUS REMOVAL OF HEAVY METALS AND ORGANICS FROM SALINE-SODIC SOIL

S. LUKMAN¹, *, M.H. ESSA¹, NUHU. D. MU’AZU² and A. BUKHARI¹

¹King Fahd University of Petroleum and Minerals, Department of Civil and Environmental Engineering, Dhahran 31261, Saudi Arabia
²University of Dammam, Department of Environmental Engineering, Dammam, Saudi Arabia

*Corresponding Author: S. Lukman, King Fahd University of Petroleum and Minerals, Box # 8632, Dhahran 31261, Saudi Arabia; E-mail: salihulukman@yahoo.com

EXTENDED ABSTRACT

In situ remediation technologies for contaminated soils are faced with significant technical challenges when the contaminated soil has low permeability. Popular traditional technologies are rendered ineffective due to the difficulty encountered in accessing the contaminants as well as when employed in settings where the soil contains mixed contaminants such as petroleum hydrocarbons, heavy metals and polar organics. This mixed contaminants scenario could produce synergistic or antagonistic effects on removal of the respective contaminants. Though electrokinetic methods have proven to be more effective than most traditional techniques used in remediating low permeability soils contaminated with mixed contaminants, there are still challenges - the application of optimal voltage gradient and the effective remediation of sodic soil (high acid buffering and alkaline). In this study, an integrated in situ remediation technique which couples electrokinetics with adsorption, using locally produced granular activated carbon from date palm pits in the treatment zones that are installed directly to bracket the contaminated soils at bench-scale is investigated. Natural sodic clay soil sampled from a coastal area, spiked with contaminant mixture (kerosene, phenol, Cr, Cd, Cu, Zn, Pb and Hg) was used in this study to investigate the efficiency of contaminant removal. The heavy metals digested from the samples were analyzed using flame atomic absorption spectrometry, whereas the organics were extracted using accelerated solvent extractor and injected into gas chromatography – mass spectrometry for analytical quantification. From the results obtained, the overall adsorption selectivity sequences for the single and multi-component scenarios are Cr > Pb > Cu > Cd > Zn and Cr > Cu > Pb > Cd > Zn respectively. For the 21-day period of continuous electrokinetics-adsorption experimental run, efficiency for the removal of Zn, Pb, Cu, Cd, Cr, Hg, phenol and kerosene were found to reach 26.8, 55.8, 41.0, 34.4, 75.9, 87.1, 100.0 and 49.8 % respectively. The results obtained suggest that integrating adsorption into electrokinetic technology is a promising solution for removal of contaminant mixture from sodic soils.

Keywords: Electrokinetics, adsorption, sodic soil, process fluids, Lasagna process

1. INTRODUCTION

Rapid proliferating industrialization has been recorded in recent decades. One of the major environmental consequences of these progressive achievements is the improper release of elevated amounts of variety of organic and inorganic pollutants into the environment. These pollutants could enter the environment directly as a result of accidents, spills during transportation, and leakage from waste disposal sites, storage sites and industrial facilities...
etc, thereby contaminating the environment. Co-occurrence of complex chemical mixtures such as total petroleum hydrocarbons (TPH), phenols, heavy metals (such as Cr, Cd, Cu, Zn, Pb and Hg), radionuclides and pesticides at remediation sites pose potential dangers to human health and the environment, and further complicate the remediation process. Some of the pollutants encountered in contaminated soils may be treated using processes like biodegradation, vapor extraction, chemical oxidation, thermal desorption, and incineration. Satisfactory results may not be obtained when these treatment processes are applied to low-permeability soils or those sites contaminated by mixed contaminants (inorganic and organic wastes) because of the difficulty in accessing the contaminants to uniformly deliver treatment reagents. Therefore, innovative remediation technologies must be developed to study the in situ removal of contaminant mixture from soil to ensure a sustainable environment. This has given birth to an important area of current research in in situ soil remediation technology (Chang and Lin, 2006; Ho et al., 1995; Reddy, 2011; Reddy et al., 2010). In situ treatment technologies for contaminated soils and groundwater have been the subject of a great deal of research in the last three decades owing to their attendant advantages; potential lower cost, less environmental disruption and reduction in worker exposure to hazardous materials (Ho et al., 1995). Sodic soils (usually found in arid and semiarid regions) possess high electrical conductivity (4 dS/m) which prevents the application of appropriate voltage gradient in an electrokinetic study owing to current limitations. In addition, these soils are associated with high pH > 8.2, dominated by 2:1 type clay minerals and exchangeable sodium at high levels (Abrol et al., 1988; Evangelou, 1998). These properties make sodic soils to be high acid buffering, alkaline and very difficult to remediate if they are contaminated with heavy metals due to precipitation concerns in alkaline environment. These extreme soil characteristics pose great difficulty in having such soils remediated from mixed contaminants using electrokinetic-based technique. Despite these challenges posed by the soil characteristics, there is the need to investigate possible remediation of such soils using the integrated electrokinetics-adsorption technique given its promise in remediating low permeability soils (Athmer and Ho, 2009). The usual voltage gradient of 1 V/cm for bench-scale studies when applied to such soils could lead to high electric current flow. This in turn could lead to excessive soil heating, reduction in the soil moisture content, high energy and process fluid consumption, and in some cases, higher percentage removal of contaminants. It has been observed that contaminated soils do not contain single contaminants. Several pollutants appear in the soil as mixed components. In reality, soil polluted with organic contaminants often contains other contaminants such as heavy metals. The implication of the presence of the different nature of the two contaminant groups is that there may be synergistic or antagonistic effects on their respective removal using electrokinetic remediation technique (Elektorowicz, 2009; Maturi and Reddy, 2006). Reddy (Reddy, 2007) posited that the presence of mixed contaminants will retard individual contaminant migration and removal. Also, as organic pollutants are removed by electroosmotic flow and heavy metals by electromigration, the solubility as well as hydrophobicity disparities between the organic pollutants and heavy metals indicates the complexity of electrokinetic remediation of soils polluted with mixed contaminants. To date, several studies have been conducted using electrokinetics (EK) for mixed contamination (Maturi and Reddy, 2008; Reddy et al., 2009; Reddy et al., 2006; Reddy and Karri, 2008). Of the several electrokinetic remediation techniques, Lasagna process has been found to yield the best removal efficiency of organic contaminants from soils (Hu et al., 2012). The general concept of the Lasagna process is the transportation of contaminants from contaminated soil section into treatment zones using major electrokinetic transport mechanisms (i.e. electroosmosis or electromigration). Once at the treatment zones, the contaminants may be removed from the pore water by sorption,
degradation or immobilization depending on treatment zone design (Ho et al., 1999b; Ho et al., 1997; Ho et al., 1999c; Ho et al., 1995). Detailed studies of all previous works on the Lasagna process which span from bench scale investigations to full field-scale remediation of contaminated soils have been reported elsewhere (Athmer and Ho, 2009; Ho et al., 1999a; Ho et al., 1999b; Ho et al., 1997; Ho et al., 1999c; Ho et al., 1995; Ma et al., 2010; Ma et al., 2007a; Ma et al., 2007b; Swift and Tarantino, 2003). Lasagna process usually uses activated carbon as the sorbent material to improve the removal of contaminants from contaminated soil (Ho et al., 1995; Ma et al., 2007a; Ma et al., 2007b).

The main aim of this study is to investigate the possible application of the coupled electrokinetics-adsorption innovative technique that combines electrokinetics and adsorption using locally produced granular activated carbon (GAC) from date palm pits for remediation of local sodic soil contaminated with mixture of toxic pollutants comprising of petroleum byproduct (kerosene), recalcitrant organic compound (phenol) and heavy metals (Cr, Cu, Cd, Zn, Pb and Hg).

2. MATERIALS AND METHODS

2.1. Characterization
Clay used in this study is a local Saudi Arabian clay from Al-Hassa oasis. The clay pH, moisture content, soil organic matter (SOM), electrical conductivity, surface area, elemental analysis using scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods were determined according to the protocol outlined in the American Society of Testing and Materials (ASTM) standards and reported elsewhere (Lukman et al., 2013). The GAC used in the present study was produced locally from date palm pits as described elsewhere (Essa and Al-Zahrani, 2009; Vohra et al., 2010).

2.2. Adsorption testing
Single and competitive adsorption of five heavy metals (Cr, Cd, Cu, Zn, Pb) were performed to determine the selectivity sequence and to understand the adsorption behavior of these metals under different pH conditions. This is particularly important to this study, because, soil mineralogy affects heavy metal adsorption behavior and selectivity sequence under different pH conditions. Lukman et al. (2013) reported the detailed procedures carried out for the competitive adsorption testing.

2.3. Coupled electrokinetics-adsorption study
A total of three bench-scale experiments were performed to investigate the treatability of the contaminant mixture using the coupled electrokinetics-adsorption technique and to understand the operating peculiarities of the sodic soil. Two of the experiments had GAC chambers bracketing the contaminated soil chamber and were operated at voltage gradients of 0.6 V/cm and 1 V/cm. The third one utilized only electrokinetics at voltage gradient of 0.6 V/cm.

2.3.1. Reactor Design and Experimental Procedures
The Plexiglass reactor total volume was about 2268 cm³, made of seven chambers. The overall reactor dimensions are: 24 cm (long) x 10 cm (width) x 12 cm (depth). Approximately 1 kg of local KSA soil was artificially spiked with kerosene, heavy metals (Cu, Cr, Cd, Pb, Zn and Hg) and phenol at predetermined concentrations. Thorough mixing was done using mechanical mixer (Gilson Company Inc.) so as to achieve a homogeneous distribution of the contaminants around the soil matrix. The mixed spiked soil was placed in a fume-hood for drying over a period of time necessary to evaporate the solvents (hexane and distilled water). Distilled water was added to adjust the final moisture content of the soil to about 33 %. The
initial conditions of the soil pH, moisture content, organic matter and electrical conductivity were measured as well as the actual initial concentrations of the contaminants. Then, the uniformly mixed contaminated soil was placed into the cell layer by layer. Each layer was compacted with stainless steel spatula so that the amount of void space was minimized. The Lasagna cell used for the experiments consists of the cell, two graphite electrodes serving as anode and cathode, DC power supply (LG, GP - 505), process fluid reservoirs, heavy duty recirculation pump (BVP Instratec®), portable data logger (TDS - 303, Tokyo Sokki Kenkyujo Co., ltd) for real-time monitoring of temperature, electric current and voltage across the system (Figure 1). The two electrode compartments with 240 mL working volume, placed at each end of the cell, was isolated from the soil zone by a porous Perspex plate and filter paper. The conditioning of the electrolyte was controlled by circulation of the anolyte (2 N NaOH) and catholyte (1 N HNO₃) using pump that is directly attached to the electrode compartments. Two planar-shaped electrodes, 10 cm × 10 cm × 0.5 cm, were used to generate a uniform electric field. Within the described cell, two treatment zones that cut across the cell vertically bracketing the spiked soil compartment were filled with the GAC. The data monitoring system was recording electric current variation, applied voltage and temperature of the soil compartments on-line following a 30 min preset time step and automatically stores them for subsequent retrieval using floppy disc which can be read using personal computer for easy data and energy consumption analysis. Treatment without GAC i.e. using only electrokinetics was conducted so as to ascertain the contribution of the GAC in contaminant removal. The power supply provides a constant DC electric voltage for the electrokinetic test. Every week, fractions of the soil specimens were taken to determine the residual concentrations of the contaminants, soil pH, water content, organic matter and electrical conductivity. Upon the completion of each test, the electrode assemblies were disconnected and the soil specimen was extruded from the cell, sectioned into parts, weighed and preserved in glass vials for organic extraction, heavy metal digestion and subsequent analyses using the analytical procedures outlined below.

Figure 1: Coupled electrokinetics-adsorption experimental setup

2.3.2 Analytical Procedures for Contaminant Extraction and Analysis

Heavy Metals: Extraction of heavy metals from soil samples was performed according to guidelines spelt out in EPA Method 3050B for acid digestion of soils, sediments and sludges (EPA, 1996a) and analyzed using flame atomic absorption spectrometry (AAnalyst 700, Perkin Elmer). All soil samples were extracted in duplicates. EPA Method 7000B (EPA,
was employed for heavy metal analysis using flame atomic absorption spectrometry except for mercury which was analyzed using mercury analyzer (Solid Mercury Analyzer SMS 100, Perkin Elmer) according to EPA Method 7473 (EPA, 2007b).

**Kerosene and Phenol:** A mixture of methylene chloride and hexane (1:1) (v/v) was used as the extraction solvent. Soil samples were extracted using pressurized fluid extraction according to EPA Method 3545 procedures (EPA, 1996b) using accelerated solvent extractor (ASE 200, Dionex). No separate extraction procedure is required for phenol, because, it will also be extracted along with kerosene from the soil sample. Volume of extract generated was then injected into the GC-MS (Clarus 580, Perkin Elmer) equipped with autosampler for analysis. TPH quantification was done by using the total chromatographic area counts using retention time range for the elution of hydrocarbon within the kerosene range C₈ - C₁₆. Guidelines spelt out in EPA Method 8270D (EPA, 2007c) for the quantification of semi-volatile organics by GC-MS were adhered to.

### 3. RESULTS AND DISCUSSION

#### 3.1. Clay and GAC characteristics

The physico-chemical properties and morphological characteristics of the clay and GAC are detailed elsewhere (Essa and Al-Zahrani, 2009; Lukman *et al.*, 2013).

#### 3.2. Single and competitive adsorption results

Lukman *et al.* (2013) have found out that the adsorptive capacities of Cu and Zn ions are higher in the multi-component adsorption scenario than in the single component scenario. The adsorption selectivity sequences for the single and multi-component scenarios are Cr > Pb > Cu > Cd > Zn and Cr > Cu > Pb > Cd > Zn respectively.

#### 3.3. Coupled electrokinetics-adsorption results

Overall, three experiments were conducted using an initial intended concentration of 100 mg/kg for each contaminant. Three designations used are EK-GAC-1, EK-GAC-2 and EK for coupled EK and adsorption 1 and 2 and EK respectively. EK-GAC-1 utilized 1 V/cm and served to produce some preliminary information such as the feasibility of attaining reasonable percentage removal and process fluid conditioning requirements. EK-GAC-2 and EK were then run simultaneously at 0.6 V/cm to ascertain the preference of using the integrated approach over EK alone. A discussion of the test results in terms of soil pH, current, electroosmotic flow and contaminant removal efficiency is presented below.

##### 3.3.1. Soil pH distribution

The pH value of the investigated clay is naturally alkaline (pH = 9), which promotes heavy metals precipitation and adsorption onto the clay surface depending on the metal speciation. At the end of the 21-day period, the pH distribution within the soil was found to be approximately 12 (Figure 2) for all the three runs despite dissimilar application of voltage gradients which might be expected to increase the rate of production of $H^+$ and $OH^-$ radicals and their subsequent migration to the opposite electrodes for higher voltage gradient. This high pH environment might be explained by the presence of calcite in the soil minerals which increases the acid buffering capacity of the soil. It is expected that the carbonates will neutralize the $H^+$ ions generated at the anode which suppresses the development and migration of acidic pH front near the anode. Results obtained for electrokinetic remediation of glacial till by Reddy and his co-workers (Reddy *et al.*, 1997) have corroborated this finding. Bipolar effect was also investigated for EK-GAC-2, but pH gradient is not observed, hence bipolar effect is not present.

CEST2013_0340
3.3.2. Soil moisture content, organic matter and electrical conductivity

Soil moisture content enhances dissolved contaminant transport by ionic migration and electroosmosis and hence affects removal efficiency. In the present study, the GAC chamber was initially saturated with water while the spiked soil specimen was kept at an initial moisture content of 33 % in each case. This value increased to 52.6, 38.46 and 35.11 % for EK-GAC-1, EK-GAC-2 and EK respectively at the end of the 21-day period. Absence of GAC chambers in the EK run may be responsible for its lowest moisture content at the end of the run. Soil organic matter plays an important role in the adsorption of heavy metal ions even in soils where its value is very low (Sparks, 2003). This is because, SOM possesses very high specific surface area and cation exchange capacity (CEC) which may range between 150 and 300 cmol/kg (Stevenson, 1982).

The majority of a surface soil’s CEC is in fact attributable to its soil organic matter. The initial SOM for the spiked chambers of EK-GAC-1, EK-GAC-2 and EK were 8.22, 6.38 and 6.38 % respectively. At the end of the experiments, these initial values decreased for EK-GAC-1 and EK-GAC-2 and increased slightly for EK.

Soil electrical conductivity (EC) varies with the amount of moisture held by soil particles. Electrical conductivity of clay typically lies between 0.01 and 1 dS/m. Abrol et al. (1998) classified sodic soils to have EC often less than 4 dS/m 25 °C. The EC of the pristine clay
sample is 2.76 dS/m which indicates that it has an excess of dissolved salts which makes it to be classified as sodic soil with exchangeable sodium percentage (ESP) of more than 15. Upon spiking the soil, the EC jumped to 4.73 dS/m due to increase in the dissolved ions and decreased at the end of the runs to 3.17 and 4.32 dS/m for EK-GAC-2 and EK respectively (Figure 3). Higher reduction in EC of EK-GAC-2 may be explained by the higher contaminant removal efficiency.

3.3.3. Variations of current, temperature and cumulative electroosmotic flow
The average electric current recorded for EK-GAC-1, EK-GAC-2 and EK are 0.88, 0.61 and 0.71 A respectively. Maximum current of 2.8 A was recorded by EK-GAC-1 test and may be attributed to its higher voltage gradient which facilitates faster ionic movement in pore fluid. Dynamic changes in the solution chemistry may be responsible for the observed fluctuating current trend observed in all the tests. Maturi and Reddy (2008) observed somewhat similar current fluctuation. The current values recorded in the tests are 2 – 3 orders of magnitude higher than those obtained in similar studies employing the Lasagna process and electrokinetics only. This unique and important observation may be explained by the sodicity of the investigated soil which provides large amount of dissolved ions in the pore fluid for effective current conduction. High current flow through the soil may have significant impact on the soil temperature, electroosmotic flow rate, electrode and process fluid deterioration, removal efficiency and energy consumption. The average temperature recorded for EK-GAC-2 and EK are 28.5 and 30 °C respectively. For the same tests, the maximum temperature is 34.6 and 40.5 °C respectively. High temperature will reduce the soil moisture content due to pore fluid evaporation and subsequent reduction in current and electroosmotic flow. Though thermal effects due to temperature rise have not been reported to be significant in bench-scale studies (Ho et al., 1997), our finding from this study reveals that increasing the voltage gradient more than 1 V/cm leads to considerable rise in the soil temperature which may not be neglected for practical purposes and modeling studies. As such, the general notion of using 1 V/cm for most bench-scale studies needs to be investigated if the soil possesses some properties that were not studied before. Electroosmotic flow is maintained throughout the duration of the tests, EK-GAC-2 and EK tests maintain an average pore volume of 0.75 and 0.66 respectively. Total electroosmotic volumes are 1388 and 1214 mL which translated into total pore volumes flushed to be 17.35 and 15.17 for EK-GAC-2 and EK tests respectively. Expectedly, the maximum temperature and electroosmotic flow recorded coincided with the period in which maximum current was recorded. Electroosmotic flow is not influenced by hydraulic gradient in this study as it occurs even under negative hydraulic gradient. Higher electroosmotic flow is expected to occur in the test with higher voltage gradient. It is obvious that the soil zeta potential is not reversed in this study which could reverse the electroosmotic flow. This is because it remains unidirectional throughout the test period.

3.3.4. Contaminant removal efficiency
After the operational period of 21 days, significant removal is observed for most of the contaminants in all the tests as presented in Figure 4. Highest and lowest percent removal is observed in phenol and Zn ions respectively. Only phenol achieved 100 % removal possible because it is miscible with water and behaves in the same way as other cationic species (Acar et al., 1995). Acar and his co-workers (Acar et al., 1992) achieved similar percent removal after two pore volumes were flushed. Lukman et al. (2013) observed that Zn is the least selective by this soil in competitive aqueous medium, most especially in the alkaline region. From Zn speciation using its Pourbaix diagram (Beverskog and Puigdomenech, 1997), it may be said that Zn precipitates as zinc hydroxide at the initial soil pH despite its
existence in the form of hydroxo-complexes at pH > 11. Calcareous soils, similar to the one studied here, have been found to perform relatively poorly for Zinc removal (Ottosen et al., 2009).

![Figure 4. Comparison of the contaminant removal efficiencies for all the tests](image)

Among the trace elements studied in EK-GAC-1 and EK-GAC-2 tests, Hg removal was highest. This may be attributed to the presence of excess $\text{Cl}^-$ under aerobic conditions and subsequent formation and migration of the mercury complex $\text{HgCl}_2^{2-}$ according to the following reaction (Hansen et al., 1997).

$$O_2 + 2\text{Hg} + 8\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow 2\text{HgCl}_4^{2-} + 4\text{OH}^-$$

Figure 5 depicts how precipitated metal hydroxides can redissolve at high pH values. This occurs due to the formation of complexes with OH- anions. These complexes are negatively charged and have increased pore fluid solubility. Consequently the removal efficiency of these heavy metals is enhanced even under high alkaline condition prevailing in the present study.

Higher electroosmotic flow observed in EK-GAC-1 and EK-GAC-2 tests may be responsible for higher removal of kerosene in these tests than EK test (Figure 4). Generally, introducing GAC chambers in EK-GAC-2 test lead to higher percent removal of all contaminants than the case without the GAC chambers (EK test). In addition, higher voltage gradient produced higher percent removal (EK-GAC-1 and EK-GAC-2 tests).

### 3.3.5. Conditioning and energy consumption

Due to the rapid electrochemical decomposition of water at the electrodes and subsequent generation of $H^+$ and $OH^-$ ions at the anode and cathode respectively, there was need to condition the anode and cathode chambers with $H^+$ and $OH^-$ neutralizing chemicals. 2 N $\text{NaOH}$ and 1 N $\text{HNO}_3$ were used as the anolyte and catholyte respectively. Automatic process fluid recycling was intended, but due to the soil sodicity which lead to the passage of high current in the soil, periodic monitoring of the process fluids pH was necessary. For the EK-GAC-1 test, the catholyte becomes completely basic ($pH \approx 13$) after 6 hr, while the anolyte lasted up to 12 – 18 hr before becoming completely acidic ($pH \approx 0.5$). For the EK-GAC-2 and EK tests, the catholyte may last up to 12 hr before it needed replacement.
Figure 5. Variation of theoretical solubilities of some heavy metal hydroxides with pH (Weiner, 2008)

Higher current flow in EK test led to higher rate of process fluids deterioration and higher energy consumption. The total energy consumed per m$^3$ of soil treated during the 21-day period is estimated at 8.2, 3.4 and 4 kWhr / m$^3$ for EK-GAC-1, EK-GAC-2 and EK tests respectively.

4. CONCLUSIONS
The potential of coupling electrokinetics and adsorption using locally produced granular activated carbon from date palm pits for the remediation of natural sodic soil was investigated. The soil was spiked with kerosene, phenol, Cr, Cd, Cu, Zn, Pb and Hg at given concentrations and three tests (EK-GAC-1, EK-GAC-2 and EK) were run for a period of 21 days. Application of voltage gradient of 1 V/cm to the spiked soil led to high current generation, high electroosmotic flow, high rate of deterioration of process fluids and anode electrodes, high percent removal and high energy consumption. Phenol and Zn were found to have the highest and lowest removal efficiency. It is suggested that different types of electrodes should be investigated (for this type of soil) together with the operating parameters (such as polarity reversal rate, pulse and continuous current application) affecting percent removal for simultaneous optimization of the Lasagna process.

5. ACKNOWLEDGEMENT
The authors would like to acknowledge the support provided by King Abdul-Aziz City for Science and Technology (KACST) through the Science & Technology Unit at King Fahd University of Petroleum & Minerals (KFUPM) for funding this work through Project No. 11-Env1669-04, as part of the National Science, Technology and Innovation Plan.

REFERENCES