

## REMOVAL OF HEAVY METALS FROM CONTAMINATED CLAY SOILS USING PULSED ELECTROKINETIC PROCESS

**MU'AZU N.D.<sup>1</sup>, USMAN A.<sup>2</sup>, BUKHARI A.<sup>2</sup>, ESSA M.H.<sup>2</sup> and LUKMAN S.<sup>3</sup>**

<sup>1</sup>Environmental Engineering Dept, University of Dammam, Saudi Arabia, <sup>2</sup>Civil Engineering Dept King Fahd University of Petroleum & Minerals Saudi Arabia, <sup>3</sup>Civil Department, University of Hafr Al-Batin, Saudi Arabia  
E-mail: nmdalhat@gmail.com

### ABSTRACT

Electrokinetic technique was employed for the removal of Cr, Cu, Hg and Pb from contaminated clay and bentonite soils under pulsed current supply mode. The effects of voltage gradient, pulse duty cycle and bentonite/clay ratio on the simultaneous removal efficiencies of the heavy metals were investigated. A total of thirteen (13) experiments were designed and conducted according to factorial design with each experiment allowed to continuously ran for 3 weeks. Sample drawn at specified interval showed that increase in bentonite ratio significantly decreased the removal efficiency of the heavy metals, while, increase in both voltage gradient and pulse duty cycle increased the heavy metals removal efficiencies with increased in energy consumption. Additionally, increase in voltage gradient increased the electrical conductivity and the soil pH due to due to continuous refill and replacement of process fluids as they decomposed under the induced voltage gradient. Under different operating conditions, the maximum removal efficiencies obtained for Cr, Cu, Hg, and Pb were 21.87, 83.2, 62.4 and 78.06 % respectively. Significance reduction is the energy consumption was achieved as results of the pulsing of the power supply which replaces the traditional continuous mode.

**Keywords:** Clay, bentonite, soil remediation, heavy metals, pulsed electrokinetic

### 1. Introduction

Prevalent global pollution problems related to environmental release of heavy metals necessitate devising effective remediation of polluted soils and groundwater. As consequence, a number of physico-chemical remediation technologies have been proposed for treatment of soils and groundwater contaminated with heavy metals. Among the existing technologies, electrokinetics remediation (EKR) techniques have attracted increased interests due to number of advantages they offer over other techniques like remediation of low permeability soils [1]. However, EKR are usually complex process that requires high technicality and also take long period of time thereby consuming huge amount of electricity to ensure remediation effectiveness and success. Consequently a number researchers dissipated significant efforts in attempting to understand strategies for improving and enhancing the effectiveness of EKR while energy consumption in order to make EKR cost-effectiveness. These strategies include addition of chelating reagents and surfactant, pH conditioning of electrolytes, using ion selective membrane, polarity reversal, pulsed voltage and integrating EKR with other remediation techniques (hybrid techniques)[1-2]. The main objective of this study is to investigate the effect of voltage gradient, bentonite and clay ratio and pulse duty cycle (on/total current flow) on the energy consumption and simultaneous removal of mixed-heavy metals (Cr, Cu, Hg and Pb) contaminated soil with electrokinetic technique.

### 2. Materials and methods

#### 2.1. Clay and Bentonite Characterization

Clay and bentonite used throughout in the study were obtained from Al-hassa oasis in Saudi Arabia and were earlier fully characterized by Lukman *et al* [1].

## 2.2. Pulsed Electrokinetic Reactor

The reactors used for the PEKR experiments were three compartments cell made up of Plexiglas, each having capacity of treating up to 2400cm<sup>3</sup> of contaminated soil. The middle chamber was for the contaminated soil while the two (2) sides chambers were for the electrode and electrolytes. The experimental set-up is depicted in Figure 1 which consists of two graphite electrodes (12cm × 10cm × 0.5cm each) serving as anode and cathode, a DC power supply (Sorensen SGI series), a pump (Thermo Scientific FH100) for refilling and replacing process fluids and data logger . 1N HNO<sub>3</sub> and 2N NaOH were used as the anolyte and catholyte, respectively.



Figure 1: Pulsed Electrokinetic Set-up

## 2.3. Experimental Procedure and Heavy Metals Extraction and Analysis

Soil sample of about 3 kg was spiked artificially with Cr, Cu, Pb and Hg each at an initial concentration 100 mg/l to attain moisture content of 45-50%. Thorough mixing followed to ensure homogeneity of the heavy metal distribution in the soil. The spiked soil was then carefully placed in the reactor and compacted. Experiment was started each time with the appropriate experimental conditions (bentonite and clay ratio, voltage gradient and pulse duty cycle) according to the experimental design presented in Table 1.

Table 1: Experimental Design

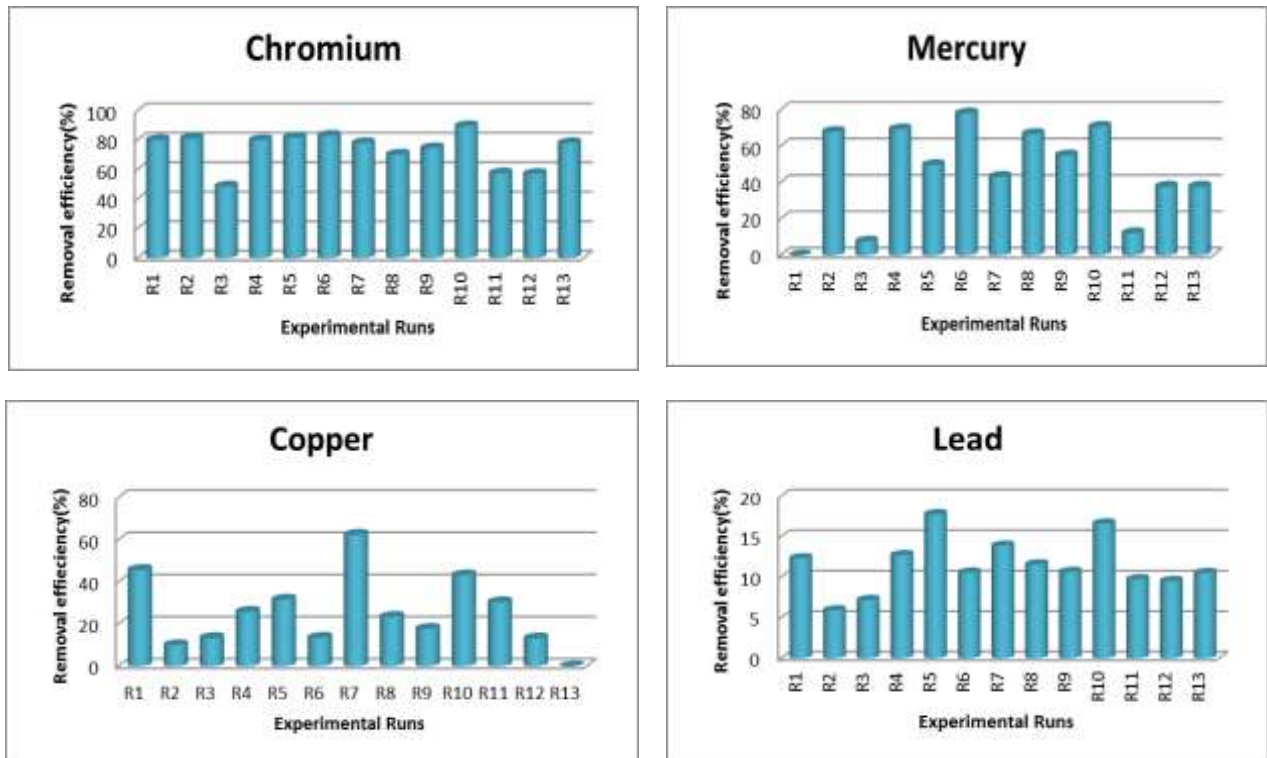
| Expt Run | Bentonite Clay ratio | Voltage Gradient | Pulse Duty Cycle |
|----------|----------------------|------------------|------------------|
| R1       | 0.3                  | 0.2              | 0.9              |
| R2       | 0.3                  | 0.6              | 0.5              |
| R3       | 0.3                  | 0.2              | 0.5              |
| R4       | 0.3                  | 0.6              | 0.9              |
| R5       | 0.5                  | 0.4              | 0.9              |
| R6       | 0.1                  | 0.6              | 0.7              |
| R7       | 0.1                  | 0.2              | 0.7              |
| R8       | 0.1                  | 0.4              | 0.5              |
| R9       | 0.3                  | 0.4              | 0.7              |
| R10      | 0.1                  | 0.4              | 0.9              |
| R11      | 0.5                  | 0.2              | 0.7              |
| R12      | 0.5                  | 0.4              | 0.5              |
| R13      | 0.5                  | 0.6              | 0.7              |

Each experiment lasts for three weeks and performed under room temperature. The electric current and electro-osmotic depth and electrolyte pH were monitored on 12 hourly bases. At the end of each week, soil sample were drawn to measure soil pH, moisture content, electrical conductivity and contaminants concentrations remaining. The heavy metal extraction from soil sample and analysed as per procedure detailed by Lukman *et al* [1].

### 3. Results and discussions

#### 3.1. Heavy Metals Removal Efficiencies

The results depicted in Figure 2 shows the overall removal efficiencies of the heavy metals at the end of the three weeks according to the experimental design. There exist variability of the heavy metals removal based on the experimental conditions as well as the ratio of the clay o the bentonite. It can be observed from Figure 2 that the metals with highest and lowest range of removal efficiencies are Cr and Pb ions respectively.



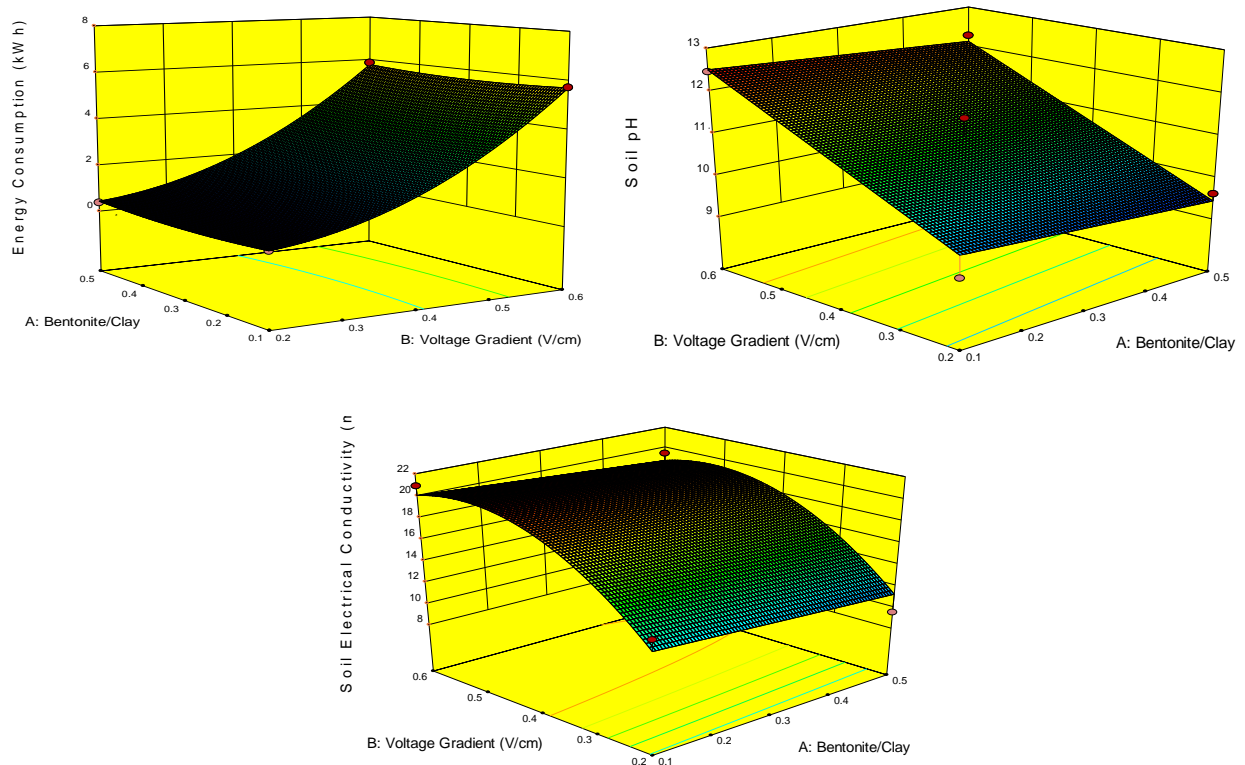
**Figure 2:** Heavy metals removal efficiencies for the different experimental conditions

The lowest range of Pb removal may attributed to formation of  $Pb(OH)_2$  at pH values beyond 10 leading more removal by adsorption than electrokinetic. The high range of removal efficiency noticed with Cr in this study is because the Cr is in the form of Cr(VI) which is highly mobile and exist as anions and easily migrate towards anode during process. These could be attributed to the fact that chromium removal is favored under alkaline condition in soils as its adsorption onto soil substantially decrease with pH increase [3]. The monitored soil pH as depicted in Figure 3, shows that the pH value ranges between 8.1 to 12.5. The overall removal efficiencies of heavy metals can be observed to be decreased with increase in bentonite ratio which may be due to the high surface of the bentonite (higher surface area of  $42.13m^2/g$ ) favoring. The increase in pulse duty cycle in all the experimental runs has been observed to increase the removal efficiencies. This could be attributed to the overall increase in the amount of the electric current supplied. The voltage gradient as one of the major factor considered in the success of electrokinetic remediation which usually favor the removal efficiencies. However, the removal efficiencies of some of the heavy metals; Cd and Cu were found to decrease with increase in the voltage gradient. This may be attributed the metals ion existing in anionic form and high current generated at due to increase in voltage may lead to high electroosmotic flow towards the cathode which opposes the anionic species migrating towards the anode [4].

#### 3.2. Soil pH variation and control

Soil pH variation: Table 5.1 and 5.2 shows that pH of the bentonite and clay respectively as 9.0 and 8.3. This portrays the soil pH as alkaline in both cases implying that both contains

appreciable soluble salts that easily hydrolyze in alkaline condition as the case with sodium carbonate [5]. This may enhance the adsorption and precipitation of heavy metals depending on the surface area and metals speciation. The soil pH variation over the three weeks of treatment time ranges from about 8.1 to 12.5 as depicted in Figure 3 for the thirteen experimental runs. The rise in the soil pH amongst the experimental runs may be attributed to the variation in voltage gradient as higher voltage gradient leads to increase in electrochemical decomposition of electrolyte producing more OH<sup>-</sup> ions which migrate into the soil and hence raise the soil pH [6].



**Figure 3:** Effects of bentonite/clay, voltage gradient and pulse duty cycle on Energy consumption, soil pH and soil Electrical Conductivity

### 3.3. Soil electrical conductivity and Moisture Content

For all the 13 experimental runs carried out, an increase in the electrical conductivity predominates throughout the 3 weeks run. The 3D response surface plot in Figure 3 indicated that the electrical conductivity increase with increases in voltage gradient (and also increase in pulse duty cycle). Water is electrochemically dissociated at the anode and cathode leading to rapid production of H<sup>+</sup> and OH<sup>-</sup> ions respectively, in order to neutralize these ions, a need for the use of processing fluids arises where 1 N HNO<sub>3</sub> and 2 N NaOH were used on 12 hourly bases for refill and replacement as they degrade. Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> continuously move into the soil and migrates to the cathode and anode electrodes respectively hence leading to continuous increase in the electrical conductivity as treatment progresses [7]. The moisture content of the soil affects electrokinetic in such a way that increase the dissolution rate of contaminants, thereby enhancing their transport by both electro-migration and electroosmosis [8-9]. The soil moisture content was monitored throughout this study and it was found to vary less, the initial moisture content was kept at a range of 47 to 53% and a maximum difference of 3% was recorded over the entire monitoring period as depicted in figure 5.8. This maintained moisture content may be attributed to the continuous refill and replacement of the degraded process fluids.

### 3.4. Energy Consumption

Energy consumption variation was mainly due to the increase in voltage gradient (0.2 - 06 V/cm) and the pulsed duty cycle. The higher the pulse duty cycle the higher the energy consumption due to the overall increase in amount of the supplied current. The amount of bentonite has little or no effect on the energy consumption. The increase in soil electrical conductivity increases the current flow which ultimately increases the energy consumption. In the next section gives a clear variation of these factors with energy consumption.

### 4. Conclusions

The effects of voltage gradient, pulse duty cycle and bentonite/clay ratio on simultaneous removal Cr, Cu, Hg and Pb from contaminated clay and bentonite soils using pulsed electrokinetic remediation technique was investigated. Results obtained show that increase in pulse duty cycle and voltage gradient increases energy consumption as well as removal efficiency. Conversely, increase in the bentonite ratio decreased the removal efficiency of the heavy metals with no significant effect on the energy consumption. Under different operating conditions, the highest removal efficiencies obtained efficiency for Cr, Cu, Hg, and Pb were 21.87, 83.2, 62.4 and 78.06 % respectively. Increase in voltage gradient was found to increase the soil electrical conductivity, this is due to increase in rate of anolyte and catholyte decomposition leading to production of more mobile Na<sup>+</sup> and OH<sup>-</sup> ions that increases the electrical conductivity. Electrical conductivity was found to increase continuously with treatment time due to continuous refill and replacement of process fluids as they degrade. Significance reduction in the energy consumption was achieved as results of the pulsing of the power supply which replaces the traditional continuous mode.

### ACKNOWLEDGEMENTS

The authors would like to acknowledge the support provided by King Abdul-Aziz City for Science and Technology (KACST) under NSTIP through Project No. 11-Env1669-04 at King Fahd University of Petroleum & Minerals (KFUPM)

### REFERENCES

1. Lukman, S., *et al.*, Coupled Electrokinetics-Adsorption Technique for Simultaneous Removal of Heavy Metals and Organics from Saline-Sodic Soil. *The Scientific World Journal*, 2013. **Article ID 346910**: p. 1-9.
2. Virkutyte, J., M. Sillanpää, and P. Latostenmaa, Electrokinetic soil remediation -- critical overview. *The Science of The Total Environment*, 2002. **289**(1-3): p. 97-121.
3. Virkutyte, J., M. Sillanpää, and P. Latostenmaa, Electrokinetic soil remediation — critical overview. *Science of The Total Environment*, 2002. **289**(1–3): p. 97-121.
4. Lukman, S., Study on integrated electrokinetics-adsorption remediation technique for simultaneous removal of heavy metals and organics from saline-sodic soil: effects of operating parameters, in *Civil Engineering*. 2013, King Fahd University of Petroleum and Minerals, Saudi Arabia.
5. Abrol, I., J.S.P. Yadav, and F. Massoud, *Salt-affected soils and their management*. 1988: Food & Agriculture Org.
6. Lukman, S., *et al.*, Geochemical Modeling of Trivalent Chromium Migration in Saline-Sodic Soil during Lasagna Process: Impact on Soil Physicochemical Properties. *The Scientific World Journal*, 2014. **2014**.
7. Reddy, K.R., Special issue on contaminant mixtures: fate, transport, and remediation. *Journal of Hazardous, Toxic, and Radioactive Waste*, 2011. **15**(3): p. 128-129.
8. Lukman, S., *et al.*, Coupled electrokinetics-adsorption technique for simultaneous removal of heavy metals and organics from saline-sodic soil. *The Scientific World Journal*, 2013. **2013**.
9. Saichek, R.E. and K.R. Reddy, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil. *Chemosphere*, 2003. **51**(4): p. 273-287.