Reduction of heavy metal from soil in Bakri Landfill, Muar, Johor by using Electrokinetic method

ATS Azhar1*, E Muhammad1, E Zaidi2, AM Ezree1, M Aziman1, ZAM Hazreek1, ZM Nizam1 and MS Norshuhaila3

1Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat Johor, MALAYSIA
2Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat Johor, MALAYSIA
3Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat Johor, MALAYSIA

Corresponding author: saifulazhar870@gmail.com

Abstract. The present study focuses on the contamination levels and distribution of heavy metals in soil samples located at Bakri Landfill area, Muar, Johor, Malaysia. The aim of this study is to determine the type of heavy metal elements that contribute towards soil contamination and to reduce them based on the comparison of elemental analysis between pre and post Electrokinetic (EK) processes. The ppm level concentration of elements in this landfill soil is measured by using X-ray Fluorescence analysis. ICP-MS testing was carried out for liquid samples analysis. There were two set of EK experiments conducted. In first phase, voltage was maintained at 3 Vcm⁻¹ and prolonged for 3 hours, while second phase was operated at 1 Vcm⁻¹ for 48 hours. In this work, distilled water was used as an electrolyte for the process and two identical copper foil were used as electrodes due to high electrical conductivity. The application of EK remediation revealed that successful removal of Rb and Ba elements in the soil were observed by 2-3%, however other heavy metals have not changed.

1. Introduction
The excessive deposition of heavy metals such as Pb, As, Cd and etc in the soil enhances toxicity which has harmful impact on the environment as well as eco-system. In recent years, due to increase of population and industrial development, human activities had caused the soil being contaminated by heavy metals which has been gradually intensified over the years. Accumulation of these harmful heavy metals in the soil is a result of emissions from the growing industrial areas, sewage sludge, wastewater irrigation, pesticides, electronic components and organic wastes. Su et al. [1] reported that heavy metals such as Lead (Pb), Copper (Cu), Chromium (Cr), Zinc (Zn), Nickel (Ni) and Cadmium (Cd) are the main constituents of contaminated soil. Lead is one of the elements toxic to brain, kidneys and reproductive system [2-5]. Furthermore, 20-50 μgL⁻¹ of Pb is contained in exhausts of a four wheeled vehicles which is potentially toxic to human body, 95% of which accumulates in bones, damages several organs such as liver, kidney, nervous system and specially the digestive and respiratory tract.
Electrokinetic (EK) method is an innovative technique manipulated for remediation of contaminated water and soil consisting organic/inorganic substances and heavy metals [6-9]. EK process can be divided into three major processes; electroosmosis, electromigration and electrophoresis. The operational procedure is based on external direct current, applied to cathode and anode by means of a power supply. An electrolytic solution, for instance water is required to initiate the process. However, several chemicals, such as EDTA, acetic acid, and other oxidizing/reducing agents had also been justified by researchers for higher efficiency of mobilization of contaminants and stabilizing pH [10-13]. The application of direct electric current through electrodes submerged in water induces electrolysis. Oxidation reaction occurs at anode resulting in release of oxygen and hydrogen ions creating acidic front, while reduction of water at the cathode results in the formation of hydrogen and hydroxide ions which turns the solution into basic. Following reactions indicate the mechanism of electrolysis:

At Anode: \[ 2H_2O - 4e^- \rightarrow O_2 + 4H^+ \] (1)
At Cathode: \[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \] (2)

The use of electrochemistry in remediation of contaminated soil has gained significance over the years. Electrode material and voltage applied across them plays an important role during the reaction. Using graphite electrodes at variable voltages revealed 0.167 mVs⁻¹ osmotic permeability by Pamukcu & Wittie, also mentioned that removal of heavy metals largely depends on high water content and degree of saturation [14]. An about 37% removal rate was achieved. Similar electrode material was used by Acay et al. [15], however, the voltage was kept constant at the rate of 1 Vcm⁻¹. The removal efficiency obtained was 50% or less. Lead (Pb) was removed 7% by Rutigliano et al. [16] in an experiment for 600 hours at a constant voltage of 100 V by using silver electrodes. Another researcher, Utchimuthu et al. [10] used graphite electrodes at 12 V for 5 days revealing 12-20% contaminant removal efficiency. Although after several attempts there was a need to optimise EK system on the basis of electrode material.

Current research focuses on EK remediation technique applied to landfill soil to influence the mobilization of heavy metals in the presence of distilled water as the electrolytes and two identical copper electrode sheets. To quantify surface and chemical composition of soil, X-ray Fluorescence Analysis (XRF analysis) is conducted. Whereas, ICP-MS testing is performed for the liquid samples obtained from the electrolytic chambers to observe the mobilization of elements out of the soil.

2. Materials and Methods

2.1. Sample Collection and Preparation

Soil samples were collected from at least one leachate point in the landfill and were tested in the laboratory. On the site, field density test was conducted by using core cutter method. Radioactive exposure rate and pH were determined by using Gamma survey meter and In-situ pH meter, respectively. Table 1 provides the physical properties of landfill soil. The sample was first dried in an oven at 105°C and sieved through 63μm mesh. Then, 9 g soil was mixed with 3 g of licowax (CH₂) in order to bind soil grains into pellets using PE-MAN hydraulic press at a pressure of 15 tons. These samples were prepared for elemental composition by XRF analysis. This process was repeated after EK process to observe the migration rate of elements.
Table 1. Properties of Soil Sample Obtained From Landfill Site

| Atterberg’s Limits | Moisture Content | Specific Gravity (Gs) | Dry density (δ_dry) | Bulk density (δ_bulk) | Exposure rate |
|-------------------|------------------|-----------------------|---------------------|----------------------|--------------|
| LL | PL | PI | 34 % | 23.2% | 10.8% | 28.57% | 2.5 g/cm³ | 1.25 g/cm³ | 1.614 cm³ | 60 µR hr⁻¹ |

2.2. Experimental Setup

The schematic test setup is shown in Figure 1 consisting of a rectangular container with three chambers. Soil sample was retained in the middle chamber with dimensions of 17 x 28 cm and a depth of 20 cm, the side chambers were aided with distilled water used as an electrolyte. Two rectangular copper electrodes were mantled for cathode and anode. The selection of electrodes is dependent on the high conductivity of the material. A filter paper was inserted as permeable membrane between soil and electrode chambers to maintain osmosis. A DC power supply was used to regulate direct current in the soil cell system.

![Figure 1. Electrokinetic setup](image)

Overall, two experiments were performed. Initially, 90 V direct electric current was maintained through 3 hour duration and XRF analysis was performed. The second experiment was carried out at rate of 1 V cm⁻¹ that made 28 V for 48 hours [10]. XRF and ICP-MS testing were performed for soil and water samples obtained from EK cell. Prior to EK process, soil was sieved under 425 µm particle size and was mixed with proportional ratio to develop slurry condition [12]. It was then compacted by applying pressure homogeneously to get specific density [12]. Table 2 specifies the loadings applied on the soil sample.

Table 2. Sequence of stress application to consolidate the samples [17].

| Loading (kPa) | Jack Pressure (psi) |
|--------------|---------------------|
| 10.1         | 82.9                |
| 26.4         | 179.5               |
| 42.8         | 276.7               |
| 67.9         | 425.5               |
3. Results and Discussions

In this section, the elemental distributions of heavy metals before and after EK remediation of landfill contaminated soil are discussed in detail. The first process, EK1, was operated by adding tap water in the electrode chambers. A potential difference of 3 Vcm\(^{-1}\) was applied by using a power supply for 3 hours. It has revealed that Rb and Ba were slightly reduced while the rest of elements were accumulated thoroughly. The concentrations of elements in the soil sample before and after first EK process are shown in Figure 2. The second process, EK2, was maintained at 1 Vcm\(^{-1}\) for 48 hours. Ba and Zn concentrations were reduced as shown in Figure 3. Here, it is perceived that high voltage at less time duration reduced Rb and Ba by ±2% and ±3%. While, in EK2, low voltage for long duration reduced ±1% Ba and ±3% Zn as shown in Table 3.

![Comparison of Pre and post EK](image)

*Figure 2. Mobilization of heavy metals across the soil sample before and after first EK process.*

The extraction of heavy metals from soil is observed based on the difference in pH levels in anolyte and catholyte. This EK remediation was aided with distilled water as anolyte and catholyte. After 48 hours of treatment, anolyte formed acidic front and pH was recorded at 4.4. Whereas, pH of catholyte was 11 which predicted the deposition of several elements. The results from ICP-MS analysis of acidified and basified water presented a range of dissolved heavy metals shown in Figure 4. From all the elements, Ba and Rb were abundant in the soil samples. Due to the radical difference of pH in catholyte and anolyte, less concentration of elements was attained in water samples. Additional oxidation and reduction agents might be useful to increase the efficiency of removal. This statement is contradicted with the justification of pH control by [18–20].
Comparison of Pre and post EK

| Elements | Pre EK | Cathode | Middle | Anode |
|----------|-------|---------|--------|-------|
| Cr       | 11    | 10      | 11     | 10    |
| Co       | 10    | 12      | 12     | 11    |
| Ni       | 89    | 89      | 88     | 85    |
| Zn       | 10    | 11      | 11     | 8      |
| As       | 212   | 218     | 217    | 220   |
| Rb       | 33    | 30      | 33     | 35    |
| Cs       | 349   | 350     | 346    | 352   |
| Ba       | 228   | 233     | 232    | 226   |
| Ce       | 140   | 141     | 143    | 142   |
| Pb       | 102   | 100     | 103    | 101   |

Figure 3. Mobilization of heavy metals across the soil sample before and after second EK process

Metal extraction from Electrodes

| Elements | Cathode | Anode |
|----------|---------|-------|
| Cr       | 0.005   | 0.005 |
| Co       | 0.01    | 0.01  |
| Ni       | 0.015   | 0.015 |
| Zn       | 0.02    | 0.02  |
| As       | 0.025   | 0.025 |
| Rb       | 0.03    | 0.03  |
| Cs       | 0.025   | 0.025 |
| Ba       | 0.03    | 0.03  |
| Pb       | 0.03    | 0.03  |

Figure 4. Results by ICP testing of water sample obtained from electrode chambers
Table 3. Percentage removal of Heavy metals

|        | Rb\textsubscript{37} | Ba\textsubscript{56} | Pb\textsubscript{82} | Zn\textsubscript{30} |
|--------|----------------------|----------------------|----------------------|----------------------|
| Pre EK | 100%                 | 100%                 | 100%                 | 100%                 |
| Post EK1 | 97.99%               | 97.03%               | -                    | -                    |
| Post EK2 | -                    | 99.15% (at mid)     | -                    | 97.19%               |

The comparison of pre and post EK revealed less mobilization of heavy metals due to the use of water as the electrolytes. From ICP-MS results, traces of heavy metals observed might have altered the pH as shown in Figure 4. Comparing these results with Figure 2, Zn was slightly reduced while other heavy metals were deposited near cathode and anode. However in previous case, Zn was gathered at electrodes as well as in the mid soil mainly due to influence of voltage gradient.

It is anticipated that this reverse reaction is due to the deoxidization of metals as it is valid in case of Cr(VI) in [18]. Besides that there was a change in pH of distilled water which also influence further solubility of heavy metals. For this reason additional surfactants, chelating agents, and other complex agents are necessary to control pH and increase removal efficiency [20-22]. Furthermore, in comparison of both EK, voltage plays an important role in removal efficiency. Increased voltage leads to high removal efficiency as in [23-24].

4. Conclusions
The mobilization of heavy metals in a soil medium depends upon several factors, electric potential, time duration of voltage, and solubility of metals in water. Solubility of heavy metals is dependent on pH value, it increases with increase in pH. Removal of heavy metals from soil subjected to high concentrations of contaminants is limited while distilled water is introduced as anolyte and catholyte. Therefore, the acids and alkaline solutions possessing high metal removal efficiency are suitable for remediation. Furthermore, additional experiments are required to perform optimization for different proportions of various chemicals.

References
[1] Su C, Jiang L, Zhang W, 2014 A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. Environ Skept Critics. 3(2):24–38.
[2] Duker A A, Carranza E J M and Hale M, 2005. Arsenic geochemistry and health. Environ Int. 31(5):631–41.
[3] Hashemi S E, Rezace A, Mousavi S M and Nikodel M R, 2014 Optimization of pyrene removal from contaminated soil by electrokinetic remediation process. 1(1):16–22.
[4] Tajudin S A A, Azmi M A M, Shahidan S, Abidin M H Z & Madun A, 2016 Relationship of physical parameters in Pb-contaminated by stabilization/solidification method, MATEC Web of Conferences 47 03015.
[5] Tajudin S A A, Azmi M A M & Nabila A T A, 2016 Stabilization/Solidification Remediation Method for Contaminated Soil: A Review, IOP Conference Series: Materials Science and Engineering 136 1-6.
[6] Z A M Hazreek, M Aziman, A T S Azhar, W D Chitral, A Fauziah and S Rosli (2015) The Behaviour of Laboratory Soil Electrical Resistivity Value under Basic Soil Properties Influences, IOP Conference Series: Earth and Environmental Science, Vol 23, pp. 1-7.
[7] Yusof M F, Setapa A S, Tajudin S A A, Madun A, Abidin M H Z and Marto A (2015) The Soil-Water Characteristic Curve of Unsaturated Tropical Residual Soil, IOP Conference Series: Materials Science and Engineering Vol 136.
[8] Ling J H, Sabarudin M, Saiful A A T, Syazie N A M, Ismail B, Mohd I M M, Adnan Z & Ali A W M, 2016 Construction of Infrastructure on Peat: Case Studies and Lessons Learned, MATEC Web of Conferences, 47 03014

[9] Ali A W M, Sabarudin M, Mohd I M M, Saiful A A T, Ismail B, Adnan Z, Azrul Z K & Ling J H, 2016 Construction of Buildings on Peat: Case Studies and Lessons Learned, MATEC Web of Conferences 47 03013

[10] Uthtimuthu N, Saravanakumar K & Amarnath J, 2012 Removal or reducing Heavy Metal (Lead) from soil by Electrokinetic Process. (IJERA) I journal of ER and A. 2(3):2367–73.

[11] Elicker C, Filho P J S & Castagno K R L, 2014 Electroremediation of heavy metals in sewage sludge. Brazilian J Chem Eng 31(2):365–71.

[12] Tajudin S A A, Marto A, Azmi M A M, Madun A & Abidin M H Z, 2015 Utilization of sugarcane Bagasse ash for stabilization/solidification of lead-contaminated soils, Jurnal Teknologi 77(11) 119–125

[13] Adams G O, Fufeyin P T, Igelenyah E & Odukoya E, 2014 Assessment of Heavy Metals Bioremediation Potential of Microbial Consortia from Poultry Litter and Spent Oil Contaminated Site. Int J Environ Bioremediation Biodegrad 2(2):84–92.

[14] Pamukcu S & Wittle J K, 1992 Electrokinetic removal of selected heavy metals from soil. Environ Prog 11(3):241–50.

[15] Acar Y B, Galeb R J, Alshawabkeh A N, Marks R E, Puppala W, Bricka M & Parker R, 1995 Electrokinetic remediation : Basics and technology status 40.

[16] Rutigliano L, Fino D, Saracco G, Specchia V, Spinelli P. Electrokinetic remediation of soils contaminated with heavy metals. J Appl Electrochem. 2008;38(7):1035–41.

[17] Tajudin S A A, 2012 Electrokinetic Stabilization of Soft Clay 1–316.

[18] Fansheng M, Lingli L, Juling W & Yeyao W, 2013 Effect of pH control at the cathode for the electrokinetic remediation efficiency. Proc 3rd Int Conf Intell Syst Des Eng Appl ISDEA 646–50.

[19] Cameselle C, 2015. Enhancement Of Electro-Osmotic Flow During The Electrokinetic Treatment Of A Contaminated Soil. Electrochim Acta 181:31–8.

[20] Jamshidi-Zanjani A, Khodadadi A, 2017 A review on enhancement techniques of electrokinetic soil remediation. J Appl Electrochem. 2008;38(7):1035–41.

[21] Liu Y, Chen J, Cai Z, Chen R, Sun Q & Sun M, 2017 Removal of copper and nickel from municipal sludge using an improved electrokinetic process. Chem Eng J 307:1008–16.

[22] Zhang P, Jin C, Sun Z, Huang G & She Z, 2016 Assessment of Acid Enhancement Schemes for Electrokinetic Remediation of Cd/Pb Contaminated Soil. Water, Air, Soil Pollut 227(6):217.

[23] Zhu S, Zhang J & Dong T, 2009 Removal of fluorine from contaminated field soil by anolyte enhanced electrokinetic remediation. Environ Earth Sci 59(2):379–84.

[24] N N Nik Daud & K C Hong, 2014 Influence of moisture content in electrokinetic remediation process of contaminated soil JAGA.