APPLICATION OF ELECTROKINETIC IN CONTROLLING HEAVY METALS MIGRATION IN SAND: A FEASIBILITY STUDY

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DEDICATION

To my supervisor, for his guidance and encouragements.

To my beloved parent, for their love and supports.
ACKNOWLEDGEMENT

Sincere appreciation goes to my supervisor Dr. Leonard Lim from whom I received the necessary guidance and encouragements throughout my project work.

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ABSTRACT

Uncontrolled migration of heavy metals from human activities in the subsurface can lead to the degradation of environmental quality and potential use of soil and groundwater. This paper studies the feasibility of using electrokinetics in controlling the migration of heavy metals in sand. Copper and iron (initial concentration of 100 mgL$^{-1}$) are the target heavy metals in this study as they are the most commonly found heavy metals from human activities such as mining and land filling. The performance of electrokinetic in controlling the migration of these heavy metals is tested in a sand tank at combination of water velocity and electrical gradient of 1.3 cm h$^{-1}$, 0.5 V cm$^{-1}$ and 0.88 cm h$^{-1}$, 1 V cm$^{-1}$, respectively. The formation of gas at electrodes, scouring on carbon anode and corrosion of crocodile clips during experiment (0.88 cm h$^{-1}$, 1 V cm$^{-1}$) showed the occurrence of electrokinetics. Further studies need to be conducted to optimize the operating conditions for effective application of electrokinetic in controlling heavy metals migration in sand.
ABSTRAK

Pencemaran logam berat yang tidak terkawal daripada aktiviti manusia dalam tanah boleh menjejaskan kualiti alam sekitar dan potensi penggunaan tanah. Kajian ini meninjau kesesuaian penggunaan elektrokinetik dalam mengawal pergerakan logam berat dalam pasir. Kuprum dan besi (kepekatan awal: 100 mg L\(^{-1}\)) adalah logam berat yang disasarkan dalam kajian ini kerana ia adalah logam berat yang paling biasa didapati hasil dari aktiviti manusia seperti perlombongan dan pengisian tanah. Prestasi penggunaan electrokinetik dalam mengawal pergerakan logam berat ditinjau dalam tangki pasir digabungkan dengan halaju air dan kecerunan electrik masing-masing sebanyak 1.3 cm h\(^{-1}\), 0.5 V cm\(^{-1}\) dan 0.88 cm h\(^{-1}\), 1 V cm\(^{-1}\). Pembentukan gas pada electrod-electrod, pengerukan pada anod karbon dan kikisan klip buaya semasa eksperimen (0.88 cm h\(^{-1}\), 1 V cm\(^{-1}\)) menunjukkan berlakunya electrokinetik dalam pasir. Kajian lanjutan perlu dijalani bagi mengoptimumkan keadaan operasi untuk memaksimumkan penggunaan electrokinetic dalam mengawal pergerakan logam berat di dalam pasir.
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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Some natural geochemical processes and human activities can contribute to contamination of heavy metal in groundwater which can affect the quality of water resources for drinking and irrigation. Low concentration of heavy metal in groundwater can affect human health if consumed. For example, concentration of arsenic as low as 50 μg L⁻¹ can cause fatality if consumed. An instance of groundwater contamination by natural geochemical processes is the well known groundwater contamination by arsenic, due to the oxidation of arsenic core compound by air led arsenic release from its core and reaching the underground aquifers, which affected about 77 million people in Bangladesh (Das et al., 2004). The concentration of arsenic in groundwater ranged from 50 to 3200 μg L⁻¹, which exceeded the permissible limit of 10 μg L⁻¹ by WHO (World Health Organization) (Mukherjee et al., 2006). Geochemical alterations of sulfide minerals and anthropogenic activities have caused the presence of lead (Pb) occur in a site in Miri, Sarawak (Prasanna et al., 2012). However, more after than not, groundwater contaminated by heavy metal are due to human activities such as mining. Arsenic was found in the vegetables and paddy harvested from agricultural land in Chenzhou City as the groundwater was contaminated by arsenic from mining and smelting of various metals in the nearby industrial districts (Liao et al., 2005). Serious arsenic poisoning cases have been reported in the diet of local people as all vegetables and rice plants produced in the industrial districts had contaminated by arsenic that endanger human health. When mining is below the water table, mining water can directly and indirectly through seepage pollute
groundwater. Arsenic was found in drinking water intake point due to the nearby disused tin-mining site contribute to arsenic release into groundwater from tin-ore near Johor (Yusof et al., 2001). Improper disposal of mine waste at a open pit copper mine at the Mamut Basin, Sabah had caused copper mine discharge into ground resources and affect the quality of useable water which contaminated by high level of several metals, especially copper (Ali et al., 2004). There is a need for appropriate groundwater remediation technique and preventive measures to control the groundwater pollution particularly at mining sites (Zhang et al., 2005). As high concentration of heavy metal contaminated in groundwater is environmental and health concern.

Various techniques for recovery of heavy metals from groundwater have been developed to remove heavy metal in-situ, among them are bioremediation and phytoremediation. Bioremediation and phytoremediation are low cost in-situ site remediation techniques which depend on the natural capability of organisms to take up the heavy metal in the soil and groundwater (Juwarkar et al., 2010; Krishnani and Ayyappan, 2006). However, these techniques are limited by the slow process and sometimes produce toxic by-products. It is still necessary to develop advanced and innovative methods to control the contamination of heavy metals in groundwater. Even though current technologies consist of several methods of groundwater recovery, electrokinetic process may be considered as one of the techniques that has more advantages than bioremediation and phytoremediation (Ghosh et al., 2012).

Electrokinetic is a faster groundwater recovery process than bioremediation. Electrokinetic is an in-situ treatment of soil and groundwater typically using direct current. This technique involves electrodes embedded in the site usually for remediate and recovery of heavy metal contaminant that present in soil and groundwater. Direct current (DC) power supply connects to the electrodes provides a constant electric potential gradient to encourage the movement of
ions within the soil and groundwater medium. The ions and charged substances in the groundwater will react in the direction towards the opposite charge electrode when electric field is apply. This technique enables the recovery of pollutant such as heavy metals for example nickel, cadmium, chromium, copper, and lead (Paramkusam et al., 2008; Sah and Lin, 2000; Al-Hamdan and Reddy, 2011). Further discussion on the electrokinetic mechanism will be discussed in the Chapter 2. There are several processes involved in electrokinetic: electrolysis, electroosmosis, electrophoresis, and electromigration (Hodges et al., 2013; Shang, 2011; Sah and Lin, 2000).

Electrokinetic can be installed by boring a hole for inserting the electrode. Electrokinetic is effective in treating various soil type contaminated by a wide range of heavy metals (Page and Page, 2002; Virkutyte et al., 2002). Electrokinetic can be applied in both saturated and partially saturated soil conditions. Hence, it is important to carry out study in electrokinetics method to control the removal efficiency of heavy metal in groundwater in order to increase the quality groundwater supply. This technique has been applied in some countries and efficient in treat a wide range of contaminants in groundwater (Sah and Lin, 2000).

However, the direction and quantity of contaminant movement during electrokinetic process is influenced by the contaminant concentration, soil type and structure, current apply, solubility and mobility (Yeung, 2011). Most of the electrokinetic researches are done in low hydraulic permeability soil and limited studies had done in other soil type (Page and Page, 2002). This study focuses in the laboratory electrokinetic technique in sand and study the removal efficiency of heavy metals in the groundwater flow in order to control the contamination level in groundwater. Figure 1.1 shows the electrokinetic remediation of metals-contaminated sediments.
1.2 Aim

The aim of this study is to observe the feasibility of electrokinetics in controlling heavy metal migration in sand.

1.3 Statement of Need

In Malaysia, groundwater polluted by heavy metal mostly occurs in mining sites. If contaminated groundwater is not treated, these problems are likely to worsen with time. Some communities in Malaysia still rely on groundwater as drinking water sources. In instances which groundwater is not treated, the contaminants will migrate through the aquifer and eventually flow into rivers. Rivers is the main water intake point for water supply system. Consequently the river water quality will deteriorate and the existing water treatment system in Malaysia might no longer be suitable for treating the water. There is need to monitor and recovery the groundwater quality to prevent and minimize further problem related to groundwater pollution occur in the future.
1.4 Scope of Work

Due to time constraint, this study is limited to test for two types of heavy metals in laboratory: copper and iron. This study only focuses on feasibility of the electrokinetic in sand.

1.5 Structure of Report

This report consists of five chapters namely: introduction, literature review, methodology, results and discussion, and conclusion.

Chapter 1: Introduction highlights the issue of groundwater pollution by heavy metal, introduces the concept of electrokinetic is introduced and proposes the use of electrokinetic to reduce the pollution level had been discussed. Aim and objectives of this study are mentioned.

Chapter 2: Literature review discusses the mechanisms of electrokinetic and the factors and parameters which affecting the electrokinetic technique done by researchers. The strengths and weakness of related researches are reviewed.

Chapter 3: Methodology highlights and explains in detail the methods and material use in this study. Experiment setup of the sand tank mentioned in this chapter.

Chapter 4: Results and discussion include the observation during experiments and the result get explain in detail. Observation and findings is discussed.

Chapter 5: Conclusion concludes the result, effectiveness and limitation from experiment and some recommendation for further studies.
2.1 Electrokinetic Mechanism

Electrokinetic is the application of direct current to the subsurface through electrodes. When direct current applied, dissolved, charges ions and non-ionic species will migrate towards to the opposite charge electrodes (Paramkusam et al., 2008; Gu and Yeung, 2012; Virkutyte et al., 2002). Electrokinetic mechanism can be described in four stages: electrolysis at the electrodes, electroosmosis of water, electrophoresis of charged particles, and electromigration of heavy metal ions.

Stage 1: Electrolysis at the electrodes

The electrokinetic process is initiated by applying direct current into saturated or partially saturated soil, through the positive (anode) and negative (cathode) terminal. This promotes the electron transfer of ionic species towards the electrodes of opposite charge, through the electrolysis of water. Oxidation occurs at anode where oxygen gas and hydrogen ion are released (Eq. 2.1). The generation of hydrogen ion decreases the pH, forming an acidic medium around the anode. Reduction occurs at cathode where hydrogen gas and hydroxide ion are released (Eq. 2.2). In contrast, the cathode generates hydroxides ions, forming an alkaline medium (Athmer et al., 2013; Gu and Yeung, 2012; Hodges et al., 2013). The electrolysis of water is as shown in Eq. 2.1 and Eq. 2.2.

\[
\text{Oxidation at the anode: } \quad 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (2.1)
\]
Stage 2: Electroosmosis of water

The hydrogen (H\(^+\)) and hydroxide (OH\(^-\)) ions generated at anode and cathode, respectively, will move across the soil to the electrode of opposite charge, a phenomena known as electroosmosis (Virkutyte et al., 2002; Acar and Alshawabkeh, 1996). The H\(^+\) ions move from anode to concentrate at cathode, and vice versa for OH\(^-\) ions. This phenomena lead to the reduction and increment of pH at cathode and anode, respectively. Simultaneously, air bubbles are produced at both electrodes: cathode (hydrogen gas, H\(_2\)) and anode (oxygen gas, O\(_2\)). The mobility of H\(^+\) ions is 1.8 times faster than of OH\(^-\) ions (Hodges et al., 2013; Ghosh et al., 2012). H\(^+\) ions will concentrate promote the acidic environment toward the cathode, thus dissolve the heavy metals in ionic form across the soil medium.
Stage 3: Electropherosis of charged particles

Charged particles, dispersed particles and colloids which bound to mobile particulate matter attract to the opposite charge electrodes. As the water ions move during electrokinetic, the charged particle will follow the electroosmotic flow to reach to the opposite charged electrodes. Positively charged particle will attract to the negatively charged soil surface and hence displace the heavy metal that attach to the soil particles surface at alkaline condition. Thus, heavy metal ions will be in the soluble phase in soil medium.

Stage 4: Electromigration of heavy metal ions

Heavy metals ions are likely to be adsorbed onto the negatively charged soil particles surface. Acidic environment will hinder heavy metal contaminants from absorbed to the soil particle surface and dissolved them in ionic form in the subsurface. Hydrogen ions in acidic environment will displace the heavy metal ions from adsorbing to the soil particles surface (Acar and Alshawabkeh, 1996) and allows heavy metals migrate in groundwater.

These mobile heavy metal ions transports through electromigration concentrated at cathode (Ghosh et al., 2012; Xiao et al., 2009). Further contaminants removal work may be done at cathode such as electroplating, pumping near the electrode, complexing with ion exchange resins, or electrodeposition near cathode (Virkutyte et al., 2002).

2.2 Parameters Affecting the Performance of Electrokinetic

The parameters affecting the performance of electrokinetic can be categorized into soil and operating conditions.

8
2.2.1 Soil Condition

2.2.1.1 Soil Buffering Capacity

Different type of soils gave different rate of the heavy metal migration during laboratory experiments. Al-Hamdan and Reddy (2008) had done laboratory electrokinetic experiments to examine the migration of heavy metals chromium (Cr(VI)), nickel (Ni(II)), and cadmium (Cd(II)) by using two different clayey soils, kaolin and glacial till. It was found that the positively ions of $\text{H}^+$ and heavy metal ions move faster towards the cathode than the negatively charge substance towards the anode in kaolin and an acidic condition developed through the medium. High buffering capacity in glacial till produces an alkaline condition throughout the electrokinetic process medium and the migration of heavy metal is slower than in kaolin (Al-Hamdan and Reddy, 2008). As the applied voltage increased, Al-Hamdan and Reddy (2008) found the migration rate of chromium (VI) towards the cathode increased in kaolin but not in glacial till due to the high acid buffering capacity in glacial till. The high buffering capacity in glacial till ables to maintain a constant pH level in the soil. Increased voltage during electrokinetic still maintain the pH of the high buffering capacity soil and did not affect the electromigration of heavy metal ions, thus did not affect in the migration rate. Georgia kaolinite was selected to use in electrokinetic by Acar and Alshawabkeh (1996) due to its high electroosmotic water transport efficiency and overall increase in the removal process of heavy metals.

All kinds of soil exists an excess negative surface charge which the surface charge density increase in the order from sand, silt, kaolinite, illite, to montmorillonite (Acar et al., 1995). Heavy metal contaminants in aqueous form are attracted by the static electrical force of
negatively charge soil surface. The soil electronegativity and the dissociation energy of ions will affect the attraction of metal ions to the soil particles. Enhancement solution may be added to the soil medium to increase the solubility of the heavy metals contaminants, and thus improve the electromigration rate.

2.2.1.2 Groundwater pH

During electrokinetic, electrolysis of water produced H\(^+\) and OH\(^-\) ions both at anode and cathode. This process will lower the pH at the anode and increase it at the cathode. Heavy metals are likely to be adsorbed onto the negatively charged soil particles in natural environment (Virkutyte et al., 2002). Acidic environment must be introduced in the electrokinetic to allow heavy metals to desorb from soil particles surface into soluble phase and migrate in the groundwater. Hydrogen ions will then displace the heavy metal ions from adsorbing to the soil particle in acidic condition (Xiao et al., 2009). The pH of soil should be maintained in the condition which enables maximum mobility of the selected metals.

The pH is an important parameter that helps to keep all contaminants in dissolved phase during electrokinetic. Glacial till resist pH change in the soil medium and always creating an alkaline condition. In electrokinetic, glacial till medium tends to inhibit the release of heavy metals from soil particle surface into groundwater and encourages the precipitation of heavy metals in their hydroxide form (Ghosh et al., 2012).

The magnitude of the pH gradient is dependent on the initial pH of soil and the formation of H\(^+\) ions at the anode and OH\(^-\) ions at the cathode. Premature precipitation may occur near to cathode due to the metal ions react with the hydroxide ions produced from the electrolysis at cathode (Sah and Lin, 2000). Premature precipitation of metal hydroxides or depositions of
metal oxides are undesired condition particularly in electrokinetic remediation recovery works at cathode. The increase of OH\(^{-}\) ion concentration in soil can lead to the precipitation of metallic contaminants near to the cathode due to the basic condition, thus inhibiting transport of metal contaminants towards cathode. Elsayed-Ali et al. (2009) conducted an electrokinetic experiment to test the effect of the initial pH of soil to the amount of copper that can be extracted from different regions of the cell. As a result, by lowering pH in soil condition, more OH\(^{-}\) can be neutralized, and less metallic contaminant precipitate in the medium. There is an optimum pH of 2.6 and above which OH\(^{-}\) ions causes the precipitation of copper in the soil and hydrogen ions decreases the electroosmosis rate (Elsayed-Ali et al., 2009). Soil pH is a factor that decreases the effective transport of heavy metal ions to the cathode.

Acidic condition allowed metal ions remain mobile in the solution and prevent the metal ions from absorbed to the soil particles in subsurface (Sah and Lin, 2000; Xiao et al., 2009). Consequently, acidic pH in the groundwater and soil has to be achieving to increase the effectiveness of electrokinetic. The metals ions can migrate to the cathode effectively and further recovery of heavy metal at cathode may be done.

2.2.1.3 Hydraulic Conductivity of Soil

Electrokinetic remediation will only work in slow flow, either slow groundwater flow or low hydraulic conductivity soil such as clay. This is aligned with the typical removal efficiency of heavy metals reported in the literature approximately 55 to 95% for sand and clay (Virkutyte et al., 2002), respectively. In soil with high hydraulic conductivity such as sand, faster advection of groundwater flow will suppress the slower electroosmosis and electromigration of heavy metals.
Low hydraulic conductivity (for example 5 to $8 \times 10^{-8}$ cm$^{-1}$ for Georgia kaolinite compacted at the wet of optimum water content) tends to develop a negative hydraulic gradient and reduce the electroosmosis rate during the electrokinetic. Conductivity of the soil pore significantly affects the electroosmotic flow rate. Decrease in the amount of groundwater flow due to decrease in electroosmotic flow rate, develop the consolidation in soil medium (Acar and Alshawabkeh, 1996). This can be described when there is a decrease in groundwater flow, the heavy metal ions in soluble phase tend to move within the electric field toward the cathode compartment which against the groundwater flow. Concentration and mobility of the ionic species present in the soil will affect the conductivity of the soil pore water. When there is reduction in contaminant concentration, it was found that the removal efficiencies of the heavy metals also decrease (Virkutyte et al., 2002). This is due to the reduction in the contaminant ions content in the groundwater and thus reduce the repealing force between the cation and anion.

2.2.2 Operation Condition

2.2.2.1 Current Density

Increased applied voltage directly increases the current density in an electrical circuit. In electrokinetic, the increase in current density will increase the electrolysis and electromigration. The migration rate of heavy metals and the production rate of H$^+$ and OH$^-$ ions increases with the voltage applied (Acar and Alshawabkeh, 1996; Ghosh et al., 2012). The concentration of nickel was found to decrease at anode and increase at cathode with time when an applied voltage of 5 to 25 V during electrokinetics (Ghosh et al., 2012).
In laboratory experiment, constant voltage which generates constant current was usually applied in experiments based electrokinetic process with the purpose of maintaining the potential difference both at anode and cathode (Acar and Alshawabkeh, 1996). Greater current density generated will produce more amounts of H\(^+\) and OH\(^-\) ions both at anode and cathode. The constant current apply is to maintain the recharge of groundwater in anode site that depend on the groundwater recharge rate of the site. At the initial stage of electrokinetic, the higher current is generated with higher electrical gradient to help the electrolysis process at electrode. The current is then reducing to a constant value through the entire remediation process (Al-Hamdan and Reddy, 2008).

2.2.2.2 Electrode Arrangement

Multiple anode system was recommended for enhance the electrokinetic remediation process (Figure 2.2) (Virkutyte et al., 2002). Multiple anode arrangement had been used to investigate the effects of electrode geometry on the removal efficiency of metals. Cathode and anode cylinder well was constructing, cathode well in the central cylinder and the anode well at the outer cylinder. Eight identical anode electrodes were placed in octagonal with respect to the cathode electrode. Removal efficiencies of lead, zinc and copper were found to be 29%, 18% and 18% in this electrode arrangement in removal of metals with the combination of three metals (lead, zinc and copper). These result showed a much lower removal efficiency value than the values that were obtained when the usual two-plate electrode arrangement used in the electroremediation experiments (32%, 37% and 31%) (Turer and Genc, 2005). Proper arrangement of electrode is need to achieve better removal efficiency. Proper arrangements of electric field direction by arrange the electrodes to increase the intensity of electric field and will influence the migration of H\(^+\) and OH\(^-\) by direction and distance. Figure 2.2 shows the
multiple anodes system which used for electrokinetic remediation of soil and groundwater in United States (US).

Figure 2.2: Multiple anodes system US EPA, 1998 (Source: Virkutyte et al., 2002)

2.2.2.3 Type of Electrode

During electrokinetic, inert electrodes such as carbon, graphite, platinum, gold, and silver are used and produce $\text{H}^+$ and oxygen gas at the anode and $\text{OH}^-$ ions and hydrogen gas at the cathode (Virkutyte et al., 2002; Shang, 2011). Inert electrodes such as carbon, graphite, platinum, gold, silver, titanium, stainless steel, and plastic electrodes contribute to the electroosmotic flow from anode to the cathode. Metallic electrodes such as steel, aluminum and copper are usually used electrodes in electrokinetic remediation for recovery of heavy metal in groundwater. Corrosion at the electrodes usually occurs during the electrokinetic, which can lead to other environmental problem (Shang, 2011). Inert electrodes are used in electrokinetic to avoid the corrosion at electrodes (Acar and Alshawabkeh, 1996).