ELECTROKINETIC PROCESS IN SOIL REMEDIATION FOR LEAD REMOVAL

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THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2016

UNIVERSITI MALAYA

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Matric No: **KHA120057**

Name of Degree: **KHA-DOCTOR OF PHILOSOPHY**

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ABSTRACT

Soil washing is one of the popular soil remediation methods which is widely studied for treating heavy metal contaminated land. However, this method suffers from high wash solution consumption, which eventually increases treatment cost. In order to solve this problem, a study on the incorporation of electrokinetic process into soil washing as soil remediation method was carried out, as electrokinetic process can transport metal ions using electricity in the absence of hydraulic gradient. In this study, two-stage electrokinetic washing was introduced as a novel soil remediation method in treating lead (Pb) contaminated soil at low wash solution consumption. This process consists of: i) initial soil washing to provide desorption condition in the soil, and ii) electrokinetic process to transport desorbed Pb from the soil. The study revealed that two-stage electrokinetic washing could enhance Pb removal efficiency by 4.98-20.45% in comparison to normal soil washing. Among the wash solutions, 0.1M citric acid emerged as the best wash solution as it not only yielded high removal efficiency at low power consumption compared to 0.01M $NaNO_3$, 0.1M HNO_3 and 0.01M EDTA but also maintained a stable system, low solution: soil ratio and low effluent generation.

A further study on the effect of operating parameters using citric acid as the wash solution revealed that the increase in electric potential difference and wash solution concentration enhanced the removal efficiency and the interaction between these two parameters was significantly positive whereby low pH and high current density were the most important criteria in the removal process. However, unfavourable high effluent generation and power consumption were also observed under these conditions. An optimisation study on these parameters showed that an optimum removal efficiency of 84.14% with negligible extra effluent generation and low power consumption of 2.27kWh/kg Pb removed could be achieved under 7.58V and 0.057M citric acid concentration. The study proved that two-stage electrokinetic washing

process could enhance the soil remediation efficiency by ≈16% than normal soil washing under similar low consumption of wash solution at <0.8mL:1g soil and operating conditions.

Other than incorporating into soil washing, the ability of electrokinetic process as soil pretreatment method in contaminated soil volume reduction was also investigated for single Pb contaminated soil and Pb/Cr co-contaminated soil. The results showed that electrokinetic process could provide soil volume reduction by concentrating Pb and Cr into smaller soil volume in both types of soils via electromigration without hydraulic flow. The study also suggested that the performance of electrokinetic process was strongly dependent on the types of wetting agents, types of contaminants and soil conditions, whereby 0.1M citric acid was suitable for single Pb contaminated soil while 0.1M EDTA showed better performance in treating Pb/Cr co-contaminated soil. Further study on the application of approaching electrode technique in electrokinetic process revealed that this technique did not enhance the electromigration significantly in the present study. Nevertheless, approaching electrode was found to reduce the power consumption by 18% to 42% for single Pb contaminated soil and 22.5% for co-contaminated soil.

ABSTRAK

Pencucian tanah merupakan salah satu teknik rawatan tanah popular di mana ia telah dikaji secara meluas dalam rawatan tanah yang dicemari oleh logam berat. Akan tetapi, kaedah ini mengalami penggunaan larutan pencucian yang tinggi dan ini menyebabkan peningkatan kos rawatan. Untuk menyelesaikan masalah ini, satu kajian dalam penggabungan proses elektrokinetik dalam pencucian tanah telah dijalankan atas sebab keupayaannya dalam pengangkutan ion logam dengan menggunakan daya elektrik tanpa kewujudan cerun hidraulik. Dalam kajian ini, pencucian elektrokinetik dua peringkat telah digunakan sebagai teknik novel dalam rawatan tanah yang dicemari oleh plumbum (Pb) dengan menggunakan larutan pencucian yang rendah. Proses ini terdiri daripada: i) pencucian tanah awal untuk memberi keadaan *desorption* dalam tanah, dan ii) proses elektrokinetik untuk mengangkut Pb dari tanah. Kajian menunjukkan bahawa pencucian elektrokinetik dua peringkat dapat meningkatkan kecekapan penyingkiran Pb sebanyak 4.98-20.45% berbanding dengan proses pencucian tanah biasa. 0.1M Asid sitrik muncul sebagai larutan pencucian terbaik kerana ia tidak sahaja menunjukkan kecekapan penyingkiran yang tinggi dan penggunakan kuasa yang rendah berbanding dengan 0.01M $NaNO_3$, 0.1M HNO_3, dan 0.01M EDTA, malah dapat mengekalkan kestabilan sistem, nisbah larutan: tanah yang kecil dan penghasilan efluen yang kecil.

Kajian selanjutnya pada kesan parameter-parameter operasi dengan menggunakan asid sitrik sebagai larutan pencucian menunjukkan bahawa peningkatan perbezaan potensi elektrik dan konsentrasi larutan pencucian dapat meningkatkan kecekapan penyingkiran dan interaksi parameter-parameter tersebut adalah positif dan ketara di mana pH yang rendah dan arus yang tinggi adalah kriteria-kriteria penting dalam proses penyingkiran. Tetapi, ini juga meningkatan penjanaan efluen dan pengunaan kuasa. Pengoptimuman parameter-parameter tersebut menunjukkan bahawa kecekapan penyingkiran optimum pada 84.14% dengan ketiadaan efluen ekstra dan

penggunaan kuasa yang kecil pada 2.27kWh/kg Pb disingkir dapat dicapai pada 7.58V dan 0.057M konsentrasi acid sitrik. Kajian membuktikan bahawa proses pencucian elektrokinetik dua peringkat dapat meningkatkan kecekapan penyingkiran sebanyak ≈16% berbanding dengan pencucian tanah biasa dalam keadaan optimum sistem dan penggunaan jumlah larutan pencucian yang sama pada nisbah <0.8mL:1g soil.

Selain pengabungan dalam proses pencucian tanah, keupayaan proses elektrokinetik sebagai kaedah pra-rawatan tanah dalam pengurangan isipadu tanah tercemar juga dikaji untuk tanah yang dicemar oleh Pb dan Pb/Cr. Kajian menunjukkan proses elektrokinetik dapat mengurangkan isipadu tanah tercemar dengan memadatkan kepekatan Pb dan Cr dalam isipadu tanah yang lebih kecil dengan proses elektromigrasi tanpa aliran hidraulik. Kajian juga mencadangkan prestasi proses elektrokinetik banyak bergantung kepada jenis larutan pencucian, bahan cemar serta keadaan tanah, di mana 0.1M asid sitrik lebih sesuai untuk tanah tercemar oleh Pb tunggal manakala 0.1M EDTA memberi prestasi yang lebih bagus dalam tanah yang dicemar oleh Pb dan Cr. Kajian selanjutnya dalam aplikasi teknik penghampiran elektrod dalam proses elektrokinetik menunjukkan teknik ini tidak meningkatkan elektromigrasi secara ketara dalam kajian ini. Akan tetapi, teknik penghampiran elektrod dapat mengurangkan penggunaan kuasa sebanyak 18% ke 42% untuk tanah tercemar oleh Pb tunggal dan 22.5% untuk tanah tercemar oleh Pb dan Cr.

ACKNOWLEDGMENTS

Firstly, I would like to express my deepest gratitude to both of my supervisors, Prof. Ir. Dr. Mohd Ali Hashim and Prof. Dr. Bhaskar Sen Gupta for their helps and supervisions during my candidature period. Their patient guidance in this study is much appreciated.

Besides that, I would like to thank University of Malaya for their financial supports of PPP research grant during my study. My grateful thank is also dedicated to my colleague, Dr. Soumyadeep Mukhopadhyay for his help especially in soil characterisation study.

Lastly, I would like to thank my family and my beloved wife for their courage and support during my study.

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A	Cross sectional area of the column, m^2
AA	Approaching anode
AC	Approaching cathode
Al	Aluminium
ANOVA	Analysis of Variance
As	Arsenic
BBD	Box-Behnken Design
β	Dubinin-Radushkevich isotherm constant (mol^2kJ^{-2})
$CaCl_2$	Calcium chloride
Cd	Cadmium
CH_3COOH	Acetic acid
Cit	Citrate ion
Cl^-	Chloride ion
Cl_2	Chlorine
Co	Cobalt
C	Metal concentration in the soil (mg/kg)
C_0	Initial metal concentration in the soil before experiment (mg/kg)
C_{ICP}	Concentration of metal in aqueous sample detected by ICP (mg/L)
$C_{Pb,soil}$	Normalised lead concentration in soil for modelling
$C_{Pb,soil0}$	Normalised lead concentration in soil after soil washing for modelling
CPC	Cetylpyridinium chloride
Cr	Chromium
Cs	Cesium
Cu	Copper
D	Dielectric constant
DC	Direct current
DF	Dilution factor
DPTA	Diethylene triamine pentaacetic acid
D_{soil}	Soil constant (porosity, tortuosity)
E	Electric field (V/m)
E_0	Electrode potential under standard condition
e^-	Electron
EDDS	Ethylenediamine-N,N'-disuccinic acid

EDTA	Ethylenediaminetetraacetic acid
EGTA	Ethylene glycol tetraacetic acid
EM	Electromigration
EOF	Electroosmotic flow
EOS	Electroosmosis
E_{PC}	Power consumed per kg Pb removed (kWh/kg)
ε_0	permitivity of a vacuum (F/m)
EW	Electrokinetic washing
Fe	Iron
H^+	Hydogen ion
H_2O	Water
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
Hg	Mercury
HNO_3	Nitric acid
HPCD	Hydroxypropyl-β-cyclodextrin
I	Electric current, A
k	Overall kinetic constant (1/hr)
$K_2Cr_2O_7$	Potassium dichromate
K_F	Freundlich isotherm constant (mg/kg)
K_L	Langmuir isotherm constant (L/mg)
Mg	Magnesium
Mn	Manganese
m_{Pb}	Mass of Pb removed (kg)
m_s	Mass of soil, kg
n	Adsorption intensity of the adsorbent for Freundlich isotherm
η	dynamic viscosity of solution
Na_2CO_3	Sodium carbonate
Na_2EDTA	disodium Ethylenediaminetetraacetic acid
$NaHCO_3$	sodium bicarbonate
$NaNO_3$	sodium nitrate
NaOH	sodium hydroxide
Ni	Nickel
NO_3^-	Nitrate ion
NTA	Nitrilotriacetic *acid*

O_2	Oxygen
OH^-	Hydroxide ion
PAHs	Polyaromatic hydrocarbons
Pb	Lead
$Pb(NO_3)_2$	lead nitrate
$Pb(OH)_2$	lead hydroxide
$Pb(OH)_3^-$	plumbites
PCA	cementol antikorodin
PCDE	plasticizers cementol delta ekstra
PFA	Pulverised fuel ash
PPF	Polypropylene fibers
pZC	Point of zero charge
Q_{max}	Maximum adsorption capacity (mg/kg)
q_t	Adsorption of Pb per unit adsorbent at time t (mg/kg)
q_e	Adsorption capacity for Pb at equilibrium (mg/kg)
RSM	Response Surface Methodology
SDS	Sodium dodecyl sulfate
Si	Silicon
SS	Stabilisation and solidification
SW	Soil washing
t	Time, minutes (For pseudo second order kinetic model)
TCE	Trichloroethane
TCLP	Toxicity Chracteristic Leaching Procedure
Ti	Titanium
u	Ionic mobility (m^2/sV)
UESR	Upward electrokinetic soil remediation
V	Voltage or electric potential difference, V
V_{HNO_3}	Volume of HNO_3 solution, (L)
V_0	Initial sorption rate, mg/(kg.min) (pseudo second order kinetic model)
V_{ES}	Volume of extraction solution after the extraction method (L)
v_{EM}	Electromigration velocity (m/s)
v_{EO}	Electroosmosis velocity (m/s)
ξ	Zeta potential
Zn	Zinc

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CHAPTER 1: INTRODUCTION

1.1 Background

Lead (Pb) has been identified as one of the top six toxic pollutants in the world (McCartor and Becker, 2010) as it can cause acute and chronic illnesses to human by damaging central and peripheral nervous systems, cardiovascular and reproductive systems as well as gastrointestinal and urinary tracts when it is inhaled and ingested (Duruibe *et al.*, 2007; Wuana and Okieimen, 2011). As a result of its extensive use, humans are exposed to Pb via several pathways. One of the pathways is soil contamination. Pb concentration as high as 751.98-138,000 mg/kg is reported in shooting range soil, dumpsite for lead-acid battery manufacturing and mining regions over the world (Adejumo *et al.*, 2010; Hashimoto *et al.*, 2010; Kim *et al.*, 2010; McCartor and Becker, 2010). Therefore, a proper treatment must be conducted for these soils.

Among the soil remediation methods available, soil washing is one of the *ex situ* remediation methods which is frequently used in treating Pb and heavy metals contaminated soil, especially for higher permeability soil that has lower silt and clay content (Dermont *et al.*, 2008; FRTR, n.d). There have been several studies on the treatment of Pb contaminated soil using different washing agents such as acids and chelating agents (Isoyama and Wada, 2007; Qiu *et al.*, 2010; Yang *et al.*, 2012; Voglar and Lestan, 2013) where positive results are reported. However, it is worth noting that the main disadvantages of soil washing is the wastewater generation and the presence of chemical agents in the wash fluid, which complicates the treatment process for spent solutions and is costly (Dermont *et al.*, 2008). Moreover, a high ratio for solution: soil in the system of 1.25-80 mL: 1 g (Isoyama and Wada, 2007; Qiu *et al.*, 2010) is another disadvantage for soil washing as the amount of spent wash solution to be treated is large.

Other than soil washing, stabilisation and solidification (SS) is another soil remediation method that is often used for treating heavy metal contaminated soils (Wuana and Okieimen, 2011). This process involves addition of cement and binding agents to the contaminated materials to reduce the mobility and migration of the contaminants (Pensaert *et al.*, 2008; Wuana and Okieimen, 2011; Falciglia *et al.*, 2014). However, it is observed that SS experiences the drawbacks of high cost cement usage and high solid waste generation (Pensaert *et al.*, 2008; Wuana and Okieimen, 2011).

In contrast, electrokinetic process is a potential soil treatment method, which uses electricity as the driving force for contaminant transport. The induction of low intensity direct current through the soil augments the transport of contaminants via two major mechanisms, namely electromigration for ion transport and electroosmosis for pore water/neutral compounds transport (Acar and Alshawabkeh, 1993; Acar *et al.*, 1995; Shenbagavalli and Mahimairaja, 2010). It is noteworthy that the transport of metal ions via electromigration is generally independent of hydraulic flow as electromigration would occur as long as an electric field is induced, regardless of the cessation of electroosmosis (Acar *et al.*, 1995) and pore flow.

In comparison to conventional soil washing which requires high amount of wash solution for high removal of heavy metals from the soil (Moutsatsou *et al.*, 2006; Zou *et al.*, 2009; Qiu *et al.*, 2010), electrokinetic process serves as an option as soil remediation method due to its ability to transport the desorbed heavy metals even in the absence of pore flow via electromigration (Acar *et al.*, 1995). Thus, the amount of wash solution needed is lower than that for normal soil washing. In addition, the ability of electrokinetic process to transport heavy metals in the absence of hydraulic and concentration gradients could also be utilised in soil pretreatment process to concentrate heavy metals into smaller soil volume before stabilisation and solidification is applied so that the solid waste generation and the amount of cement needed could be reduced.

This has created an interest to study the feasibility of electrokinetic process to be incorporated into other soil remediation methods such as soil washing and SS for maintaining/improving the treatment efficiency at low chemical solution consumption and reducing waste generation, respectively.

1.2 Research objectives

The study focuses on the incorporation of electrokinetic process into soil remediation methods. The first part of the study consists of the incorporation of electrokinetic process in soil washing as a novel two-stage electrokinetic washing in enhancing process efficiency for Pb removal at low wash solution consumption. The main objectives for this study are as follows:

i) To determine the effectiveness of two-stage electrokinetic washing as soil remediation method and the best performing wash solution in Pb removal.

ii) To evaluate the effects of operating parameters such as electric potential difference, wash solution concentration and initial Pb concentration on the process in terms of removal efficiency, effluent generation and power consumption.

iii) To optimize Pb removal efficiency of two-stage electrokinetic washing at low power consumption with minimum effluent generation.

iv) To understand the transport mechanisms involved in two-stage electrokinetic washing process.

The second part of the study involves the technical feasibility evaluation on the application of simple electrokinetic process as soil pretreatment method to provide volume reduction on contaminated soil via concentrating Pb into smaller soil volume. The main objectives of this study are:

i) To evaluate the effectiveness of electrokinetic process as a soil pretreatment method for concentrating Pb into smaller soil volume using different types of chemical solutions as wetting agents.

ii) To investigate the effect of single Pb contaminated soil and Pb/Cr co-contaminated soil on the performance of electrokinetic process in Pb electromigration.

iii) To investigate the effect of approaching electrode technique on the performance of electrokinetic process from the aspects of electric current, soil pH, Pb electromigration and power consumption.

1.3 Scope of study

The feasibility study on the incorporation of electrokinetic process into soil remediation methods in treating Pb contaminated soil was carried out using artificially contaminated soil in laboratory scale experiments. The first part of the study was the evaluation on the feasibility of two-stage electrokinetic washing in removing iron/mineral oxides adsorbed/bounded Pb from artificially contaminated soil using conventional chemical solutions. The process was conducted as an *ex-situ* soil remediation process in a laboratory scale column without pH control. The feasibility study focuses on the effect of chemical solutions and operating conditions on Pb removal efficiency, effluent generation, system stability and power consumption. Pb was chosen as the heavy metal contaminant in this study as it is reported to be one of the most recalcitrant divalent metal cation species that is adsorbed/bounded on the metal/mineral oxides surface in comparison to other metals (Violante *et al.*, 2007).

The second part of the study was the investigation on the ability of electrokinetic process to serve as soil pretreatment method in reducing the volume of Pb contaminated soil via electromigration. In this study, a sandbox design was used and the electrode rods were injected directly into the soil, which was further saturated with the chemical solution. The effect of Pb species and the presence of opposing charged competitive metals, Cr on Pb electromigration was investigated on a comparative basis. In addition, the effect of approaching electrode in Pb electromigration enhancement was also evaluated in this study.

1.4 Thesis outline

The thesis consists of five chapters, namely: i) introduction, ii) literature review, iii) methodology, iv) results and discussion, and v) conclusions and recommendations.

Chapter 1 provides the background of the study, research objectives, scope of study and the structure of the thesis.

Chapter 2 contains the literature review. The first section of this chapter is the introduction of Pb in terms of its properties, its production, applications and toxicity, as well as the current information on Pb contaminated soil and the environmental regulations. This chapter also explains the conventional soil remediation methods and their disadvantages. In addition, the introduction and process description of electrokinetic soil remediation method are also covered in this chapter. Lastly, recent studies on the application of conventional electrokinetic process as soil remediation method on heavy metals removal using different enhancement methods are also included.

Chapter 3 describes the experimental set-up and procedures for desorption tests, two-stage electrokinetic washing and electrokinetic soil pretreatment process. Besides, analytical methods such as electric current measurement and determination of pH as well as Pb concentration in the soil samples are also elaborated.

Chapter 4 presents the results and discussion of the study. This chapter is categorised into three major sections. The first section provides discussion on the characterisation of the soil and maximum Pb contamination level for the selected soil. The second section deals with the performance of two-stage electrokinetic washing in removing Pb from the soil using different types of wash solutions, and the discussions are based on the aspects of removal efficiency, effluent generation, system stability and power consumption. Also, key experimental findings on the performance of two-stage electrokinetic washing under different operating conditions are discussed. Finally, the ability of electrokinetic soil pretreatment process in electromigrating and concentrating Pb into smaller soil volume under different types of wetting agent and different Pb species are discussed in the third section.

Chapter 5 covers the conclusions of this study and some recommendations for future studies.

CHAPTER 2: LITERATURE REVIEW

This chapter consists of three main sections which discuss the usage, hazards and soil contamination from lead, the types of soil remediation methods available and the application of electrokinetic process as a soil remediation method.

2.1 Lead

Lead (Pb) is a metal element which is toxic to organisms due to its ability to bio-accumulate. Pure Pb is soft, malleable and has bluish white colour while it becomes dull grayish when exposed to air (Anonymous, 2013; Lenntech, n.d.). This metal is normally found in the earth's crust in the form of minerals such as galena, anglesite, cerussite, mimetite and pyromorphite (Inchem, 1994). General physical properties of Pb are as shown in Table 2.1.

Table 2.1: Physical properties of Pb (Inchem, 1994; Lenntech, n.d.)

Parameters	Value
Symbol	Pb
Molecular weight	207.2
Melting point, ^{o}C	327.4
Boiling point, ^{o}C (at atmospheric pressure)	1740
Specific gravity (at 20 ^{o}C)	11.34
Vapor pressure, kPa (at 1000 ^{o}C)	0.233
Solubility in water	Highly dependent on the anion of its salt. Generally soluble in acids such as HCl and HNO_3.

2.1.1 Production and application of lead

Production and consumption of Pb has been increasing worldwide since 1964 until present day (ILZSG, 2013; LDAI, n.d). Pb is mainly produced in China, Australia, USA, Peru, Canada, Mexico, Sweden, Morocco, South Africa and North Korea (Global Info Mine, n.d). Global Pb production as high as 10,654,000 tonnes was recorded in 2012 and 49.4% of the production came from ore mining and smelting (ILZSG, 2013) while recycle of scrap Pb products contributed as the secondary source for Pb production (LDAI, n.d).

Pb has been extensively used in battery manufacturing whereby about 75% of total Pb production was used for this industry (McCartor and Becker, 2010; LDAI, n.d). Pb has also been used as raw materials in industrial manufacturing products such as ammunition, bearings, cable covers, plumbing, lining, pipes, ceramic glazes, weights, caulks, dyes, pigments and pesticides (Inchem, 1994; McCartor and Becker, 2010; Wuana and Okieimen, 2011). Besides manufacturing products, it also serves as a main component to alloy with other metals in the manufacturing of maintenance free storage batteries, anodes in electro-winning processes, pipes and sheets in chemical installations and nuclear shielding, printing and high-detail casting (Wuana and Okieimen, 2011), type metals and bronze productions (Inchem, 1994). Since Pb has been used widely in various processes, they create significant pathways for Pb to enter a human body. It is therefore necessary to review the exposure risk to human beings.

2.1.2 Toxicological effect of lead on human

Pb is highly toxic metal, which can harm living organisms through cumulative poisoning. It has been identified as one of the top six toxic threats in the world (McCartor and Becker, 2010). It has also been positioned at the second place among top

20 hazardous substances by Agency for Toxic Substances and Disease Registry, ATSDR and U.S. Environmental Protection Agency, USEPA (Ahmedzeki, 2013). Pb accumulation occurs when >0.5 mg/day is absorbed, and fatal poisoning is reported for adults and children at a dosage of 500mg absorbed Pb and blood Pb levels of 1250 μg/L, respectively (Inchem, 1994).

Ingestion and inhalation are two major entry routes for human Pb poisoning (Inchem, 1994). Exposure of Pb by these routes is mainly from breathing air due to work environment, drinking water, eating food containing Pb and ingestion of Pb containing paint or Pb polluted soil (Inchem, 1994; Wuana and Okieimen, 2011) as a result of water and ground pollutions from ore mining, milling and smelting activities, automobile exhaust, and the discharges from manufacturing industries as mentioned in Sub-section 2.1.1 (Inchem, 1994; Duruibe *et al.*, 2007; McCartor and Becker, 2010; Wuana and Okieimen, 2011).

Ionic Pb, Pb oxides and hydroxides are reported to be the general forms of Pb that are released into the water body and soil (Wuana and Okieimen, 2011). These inorganic Pb compounds can cause chronic poisoning, acute poisoning and asymptomatic poisoning (Inchem, 1994). Other than death, Pb poisoning also causes poor intelligence quotient, shorten attention span, hyperactivity and mental deterioration for children (Duruibe *et al.*, 2007; McCartor and Becker, 2010; Wuana and Okieimen, 2011). Moreover, Pb also tends to cause damage to human body systems such as central nervous system, peripheral nervous system, cardiovascular system, reproductive system, gastrointestinal as well as urinary tracts (Inchem, 1994; Duruibe *et al.*, 2007; Wuana and Okieimen, 2011). The damage of these systems may lead to health disorders from the aspects of i) brain diseases (brain damage, neurological and nerve disorder/damage, reduce in reaction time, loss of memory, nausea, insomnia, anorexia, hypertension, chronic headaches); ii) dysfunctions for muscles, bones and blood circulation systems

(vomiting, pain/weakness of joints and muscles, cramps and paraesthesia, abdominal colic, inhibition on haemoglobin synthesis, anaemia, increased blood pressure, gout), iii) urinary system diseases (nephropathy, bloody urine, kidneys dysfunction), and iv) reproductive diseases such as infertility, damage to fetus and birth defects (Inchem, 1994; Duruibe *et al.*, 2007; McCartor and Becker, 2010; Wuana and Okieimen, 2011).

2.1.3 Soil contamination by lead

Soil contamination is one of the pathways that can lead to Pb ingestion and inhalation. Many cases for Pb contaminated soil are reported in 80-90's. High Pb concentration in soil has been reported in many countries such as United Kingdom, United States of America, Poland, New South Wales, Australia and France (USEPA, 1991; Markus and McBratney, 2001) in 80-90's with a maximum Pb concentration of 209,000 mg/kg. The report published by EPA in 1991 shows that the serious soil region are normally from Pb related industries such as battery soil, gold casing soil and scrap Pb soil (USEPA, 1991) besides normal mining and smelting areas (Duruibe *et al.*, 2007; Wuana and Okieimen, 2011). To date, Pb contaminated soil remains as an environmental issue. Soil contamination is still reported from various countries such as Australia, South Korea, Nigeria, Japan, China, Senegal, Mexico, Dominican Republic, Peru and Zambia with a Pb concentration of 751.98 – 138,000 mg/kg in shooting range soil, dumpsite for Pb-acid battery manufacturing and mining regions (Liu *et al.*, 2005; Adejumo *et al.*, 2010; Hashimoto *et al.*, 2010; Kim *et al.*, 2010; McCartor and Becker, 2010; Sanderson *et al.*, 2010).

High Pb concentration in soil causes severe effects to the residents nearby. Blacksmith Institute (USA) has reported several case studies on Pb contaminated sites. Among the most serious place is Dakar, Senegal where 18 children were reported dead from acute Pb poisoning due to Pb dust and soil exposure as a result of Pb-acid battery recycling activities (McCartor and Becker, 2010). Moreover, scrap metal smelting and mining activities also produce air borne particulates containing lead, which increase dermal exposure of the residents. Majority of the residents, especially children were reported to have high Pb level in blood in the contaminated areas in Haina, Dominican Republic; La Oroya, Peru; Kabwe, Zambia; and Zamfara, Nigeria (McCartor and Becker, 2010).

Pb contaminated soil is also reported in Malaysia. Scrap metal yard in Kuala Lumpur (Yang *et al.*, 2004) has been reported to have Pb concentration of as high as 1005 mg/kg. Besides that, places such as dumping sites, paddy fields and car wash in Kangar are also identified to have a concentration of 600-800 mg/kg Pb, mainly due to the use of Pb containing fertilizer and emission from vehicles near the busy roads (Nor Wahidatul *et al.*, 2012). Other equally hazardous activities in this country over the past century are mining and Pb-acid battery recycling. Therefore, soil remediation has become an absolute necessity in Malaysia in order to eliminate the sources for Pb contamination through these activities.

2.1.4. Environmental regulations for lead concentration in soil

In order to reduce and eliminate Pb poisoning issues, maximum threshold concentration has been regulated by the government for controlling and minimising soil contamination. Table 2.2 shows the threshold Pb concentration in soil in different countries. A high range of soil concentration of Pb from 60-1300 mg/kg is monitored.

Higher threshold concentration is applied for industrial areas while a more stringent concentration is applied for residential areas. For Malaysia, the threshold concentration for Pb in the soil is 400 mg/kg (residential soil) and 800 mg/kg (industrial soil).

Table 2.2: Maximum threshold value for Pb concentration in soil

Country	Threshold value, mg/kg
Alberta	800[a]
Canada	60-500[a]
France	100[c]
Germany	100[c]
India	400-1300[d]
Japan	600[a]
Korea	200-700[f]
Malaysia	400-800[b]
Netherland	580[c]
	150-600[a]
Taiwan	100[c]
UK	550c
USA	250-1000[a]
	68[c]
	107[e]

(Source: [a]Beyer, 1990; [b]DoE-Malaysia, 2009; [c]Wan Zuhairi, 2011; [d]IDEM, 2012; [e]USEPA, 2012; [f]MOE-Korea, n.d)

2.2 Popular methods for treating heavy metals contaminated soil

A number of remediation methods have been investigated by researchers for treating heavy metals contaminated soils. Among the popular methods are: i) soil washing, and ii) stabilisation and solidification (Wuana and Okieimen, 2011).

2.2.1 Soil washing

Soil washing is one of the remediation methods for heavy metals contaminated soils. It is a technology that uses liquids (water or chemical additives) and mechanical processes to scrub the soil (USEPA, 1996). In general, soil washing can be categorised

into two types: namely i) physical separation, and ii) chemical extraction (Dermont *et al.*, 2008). According to Dermont *et al.* (2008), a physical separation technique that uses gravity and flotation concepts is generally more suitable to treat soil that is contaminated with particulate and discrete metals. On the other hand, chemical extraction is more suitable for the metals that are adsorbed on soil particles in their ionic form (non-detrital metals) whereby the chemical reagents remove metals from soil to aqueous phase via dissolution and complexation processes. Soil washing has been widely studied in laboratory scales, pilot scales, as well as full scale in treating heavy metals contaminated soil (USEPA, 1996; Dermont *et al.*, 2008).

Table 2.3 summarises recent studies on soil washing via chemical extraction for remediating Pb contaminated soil. A number of chemical reagents have been applied in soil washing such as acids (Cline and Reed, 1995; Tejowulan and Hendershot, 1998; Tawinteung *et al.*, 2005; Moutsatsou *et al.*, 2006; Isoyama and Wada, 2007; Yang *et al.*, 2012), surfactants (Torres *et al.*, 2012), and chelating agents (Cline and Reed, 1995; Tejowulan and Hendershot, 1998; Abumaizar and Smith, 1999; Tawinteung *et al.*, 2005; Moutsatsou *et al.*, 2006; Zou *et al.*, 2009; Qiu *et al.*, 2010; Mohanty and Mahindrakar, 2011; Yuan *et al.*, 2012; Voglar and Lestan, 2013) and positive results on Pb removal have been reported. However, it is worth noting that chemical extraction based soil washing often involves extra cost for treatment of spent chemicals in the wash solution (Dermont *et al.*, 2008). Moreover, the use of high amount of wash solution also creates further disadvantage as the volume of spent wash solutions/wastewater generated is large (Kim *et al.*, 2012a). Table 2.3 shows that the solution: soil ratio used in soil washing is often in a range of 1.25-80. This causes generation of high volume of spent chemical solution even when treating small amount of soil, which in turn increases the treatment cost. Besides that, the efficiency of soil washing in removing heavy metals is also limited by soil texture such as silt/clay content (Dermont *et al.*, 2008).

Table 2.3: Summary of recent studies for soil washing in treating Pb contaminated soil

Heavy metals	Metal concentration, mg/kg	Soil	Wash solution	Solution: soil ratio	Best Removal efficiency, %	Duration, h	References
Pb	100-10000	Superfund soils	HCl Na$_2$EDTA CH$_3$COOH CaCl$_2$	10	92.5% 93.5% 57.3% 47.2%	24	(Cline and Reed, 1995)*
Pb HM	800 6.3-2600	Silty sand	HCl EDTA	5	HCl: Poor removal Pb: 49% HM: 53-84%	288 (24 per extraction)	(Tejowulan and Hendershot, 1998)
Pb HM	742 603-1231	Silty sand	Na$_2$EDTA	12.5 (shake flask) 300 pore volume (column experiment)	Pb: 104.6% HM: 40.7-112.1% Pb: 100% HM: 25-80%	48 (Shake flask) 300 pore volume (column experiment)	(Abumaizar and Smith, 1999)*
Pb	153-1620	Surface/ subsurface soil	EDTA HNO$_3$ Ammonium citrate	5-10 20 pore volume	85-95% 74-85%	1 20 pore volume	(Tawinteung et al., 2005)
Pb HM	64195 1030-223600	Top soil	HCl, HNO$_3$, H$_2$SO$_4$ Na$_2$EDTA	33.33	Pb: 83% HM: 46-97% Pb: 44% HM: 10-45% Pb: 6% HM: 30-93% Pb: 44% HM: 13-42%	1	(Moutsatsou et al., 2006)
Pb	1000	Surface/ subsurface soil	HCl CaCl$_2$	1.25-5	25-78%	1	(Isoyama and Wada, 2007)*
Pb HM	254.4 1.7-325.0	Silty sand	Na$_2$EDTA	20	Pb: 40.91% HM: 18.01-72.98%	16 (2 per cycle)	(Zou et al., 2009)
Pb HM	254.35 1.73-325.01	Silty sand	Na$_2$EDTA Oxalate Na$_2$EDTA/Oxalate	20 80	Pb: 27.4% HM: 2.5-53% Pb: 1.5% HM: 22-60% 99%	24 8 (2 per cycle)	(Qiu et al., 2010)
Pb Cr	26 61	Sand	Na$_2$EDTA	5	Pb: 53.87% Cr: 48.35%	6	(Mohanty and Mahindrakar, 2011)*
Pb HM	70 14-35582	Clay-loam/sand	Tap water Surfactants	3.33	Pb: 10% HM: 10-85% Pb: 0-43% HM: 20-87%	23	(Torres et al., 2012)
Pb Cd	550.10 33.93	Top soil	HCl/ Na$_2$EDTA	2-12	Pb: 73.23% Cd: 87.75%	Column washing	(Yang et al., 2012)

* Spiked soil was used; HM: Other heavy metals

2.2.2 Stabilisation and solidification

'Stabilisation and solidification' (SS) is one of the soil remediation methods for treating heavy metal contaminated soils (Wuana and Okieimen, 2011). This process involves addition of binding agents to the contaminated materials to reduce the mobility and migration of the contaminants (Pensaert *et al.*, 2008; Wuana and Okieimen, 2011; Falciglia *et al.*, 2014). SS has also been widely used for immobilisation of hazardous wastes, landfill leachate, sludge sediments and petroleum drill cuttings (Pensaert *et al.*, 2008; Wuana and Okieimen, 2011; Falciglia *et al.*, 2014). In comparison to other treatment methods, SS is applicable to most types of soil, sediment and mineral waste (Pensaert *et al.*, 2008) and it is identified by USEPA as one of the best available technologies (Voglar and Leštan, 2011; Desogus *et al.*, 2013).

Generally, the use of chemicals such as Portland cement and Pozzolanic cement together with the additives such as barite aggregates (Falciglia *et al.*, 2014), PCDE, PCA, Tween80, PPF, Akrimal (Voglar and Leštan, 2011), potassium dihydrogen phosphate, ferric chloride hexahydrate (Desogus *et al.*, 2013), PFA (Erdem and Özverdi, 2011; Kogbara *et al.*, 2013) and lime (Erdem and Özverdi, 2011) are proven to give promising results on stabilizing and immobilizing the contaminants. However, it is observed that SS tends to generate significant amount of solid waste (Wuana and Okieimen, 2011). Besides that, Pensaert *et al.* (2008) claimed that cement based SS had been an expensive process due to the high price of cement. These disadvantages often reduce the feasibility of SS.

2.3 Electrokinetic soil remediation

Electrokinetic soil remediation is a process that operates under a low magnitude direct current in the soil, as opposed to a hydraulic pressure gradient, which promotes the migration of various contaminants under coulombic forces (Shenbagavalli and Mahimairaja, 2010). This process produces an electrical gradient that acts as a driving force for the transport of various pollutants in saturated/ unsaturated soils via electrodes. As it is free from hydraulic gradient limitation, electrokinetic process is generally suitable for treating both low and high permeability soils (Shenbagavalli and Mahimairaja, 2010; Alcántara *et al.*, 2012; Giannis *et al.*, 2012). It has been reported that electrokinetic process is capable of removing a wide range of contaminants from the soil, and these contaminants include heavy metals, phenols, petroleum oils/hydrocarbons and radioactive substances (Acar *et al.*, 1995; Doering *et al.*, 2001; Korolev, 2006; Shenbagavalli and Mahimairaja, 2010; Kim *et al.*, 2011a). However, the scale up application of this treatment process is still scarce.

2.3.1 Process description

There are two mechanisms for contaminant transport in a moist soil; the first involves the migration of dissolve ions towards their respective electrodes, whilst the second mechanism occurs as water/neutral compounds transport, whereby contaminants are flushed towards the electrode chambers from anode to cathode. These mechanisms consist of two main phenomena; namely electromigration for removing metal ions, and electroosmosis for removing organic compounds (Acar and Alshawabkeh, 1993; Acar *et al.*, 1995; Reddy and Cameselle, 2009; Ma *et al.*, 2010; Shenbagavalli and Mahimairaja, 2010; Kim *et al.*, 2011a).
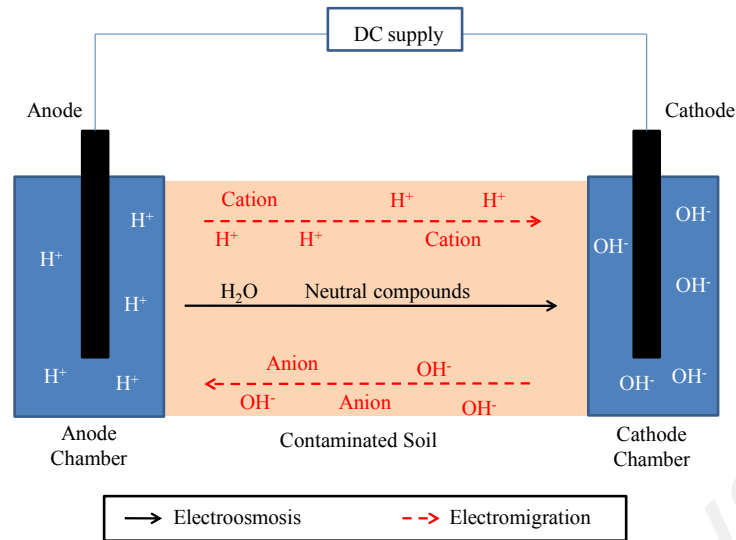
Figure 2.1: Electrokinetic process in soil treatment

Figure 2.1 illustrates the mechanisms for electrokinetic process in the soil. In general, two electrodes, namely an anode and a cathode, are introduced into the soil together with two chambers with porous wall (the anode chamber and the cathode chamber). The aqueous solutions in the chambers, which act as electrolytes/washing agents, undergo electrolysis when a direct current is induced. The hydrogen ion (H^+) is produced in the anode chamber and the hydroxide ion (OH^-) is produced in the cathode chamber during the electrolysis process, as shown in Equations (2.1) and (2.2), respectively (Acar and Alshawabkeh, 1993; Reddy and Cameselle, 2009):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E_0 = \text{-1.229V} \qquad (2.1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E_0 = \text{-0.828V} \qquad (2.2)$$
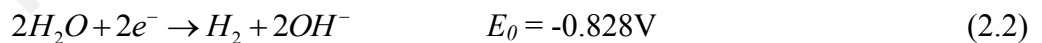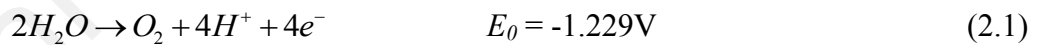
Figure 2.1 shows that the induced electric field migrates H^+ towards the cathode through the soil. As the movement of H^+ in the soil towards the cathode (acid front) is approximately 1.75 to 2 times higher than OH^- movement (base front) towards the anode (Acar and Alshawabkeh, 1993; Acar *et al.*, 1995; Chung and Kang, 1999; Gioannis *et al.*, 2008; Park *et al.*, 2009; Kim *et al.*, 2011b), a net acid front advancement from the anode region to the cathode region will progress along the soil normally,

consequently affecting the pH and properties of the soil from the anode to the cathode region.

As the acid and base fronts advance, the electrical field also induces cations and anions migration in the soil. This mechanism is known as electromigration and it governs the removal of desorbed metal ions from soil under electrokinetic process. Metal cations are transported towards the cathode and vice versa for anions, following a similar trend for the acid and base fronts, as shown in Figure 2.1. The velocity for electromigration v_{EM} (m/s) is proportional to ion mobility u, and the electric field of the system E, as shown in Equation (2.3) (Baraud *et al.*, 1997). It is important to note that, unlike electroosmosis, electromigration of the ions will still occur as long as an electric field is induced in a wet soil. This process may continue despite the cessation of electroosmosis (Acar *et al.*, 1995) and this serves as an advantage for heavy metal removal from contaminated soil.

$$v_{EM} = u.E \qquad\qquad (2.3)$$
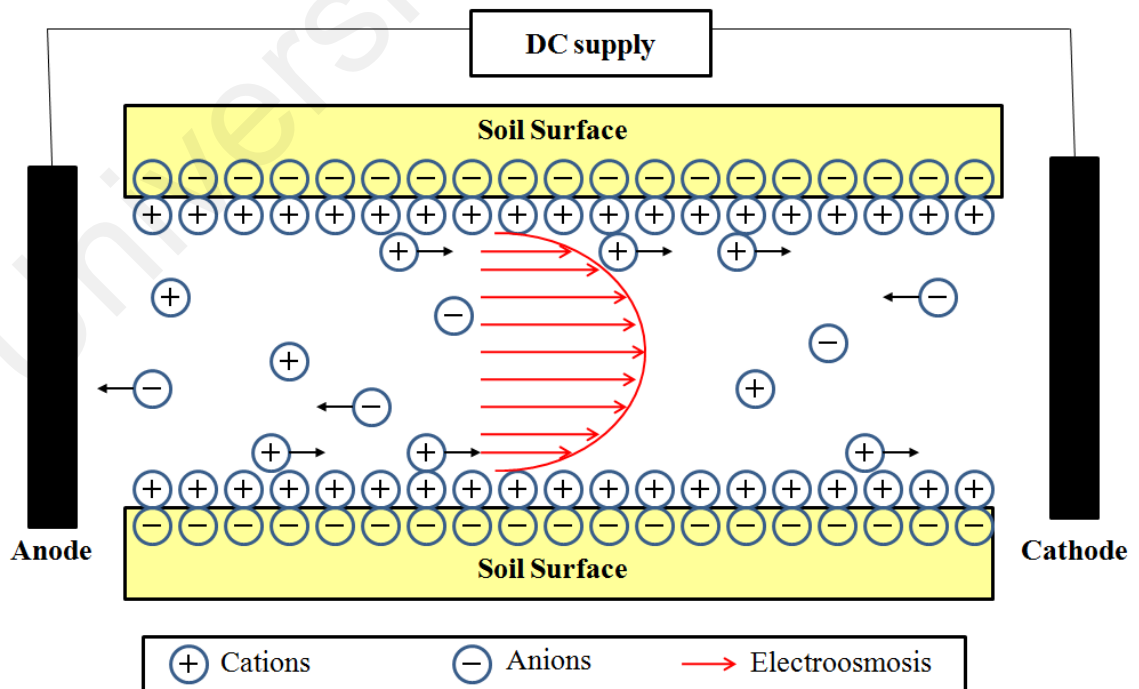
Figure 2.2: Schematic diagram for electroosmosis process

Electroosmosis is the second mechanism in electrokinetic process. This mechanism governs the transport of neutral organic compounds and water in the soil. Electroosmosis can be defined as the movement of pore water that transports neutral compounds in the soil due to the movement of ions, as shown in Figure 2.1. A schematic diagram illustrating this mechanism is shown in Figure 2.2. Soil normally contains a negative surface charge due to imperfection in the mineral lattice, which attracts cations in the soil close to the soil surface (Acar *et al.*, 1995). When an electric field is induced, the excess cations which are close to the soil surface (diffuse double layer) tend to move towards the cathode. According to Acar *et al.* (1995), the movement of cations and their associated water molecules yield a net strain on the pore fluid and thus transform into a shear force through the viscosity of the fluid. As the surface charge of the soil is normally negative, the force for the pore fluid is likely to be cationic and the transport of the pore fluid will be directed towards the cathode region, as shown in Figure 2.2. However, it is worth noting that the direction of electroosmosis strongly follows Helmholtz-Smoluchowski theory, which is dependent on the surface charge and zeta potential of the soil, as shown in Equation (2.4) where electroosmotic flow (EOF) velocity v_{EO} (m/s) is directly proportional to permittivity of a vacuum ε_0, electric field of the system E, dielectric constant of the solution D, zeta potential of the soil ξ, and is inversely proportional to dynamic viscosity of the solution, η (Lee *et al.*, 2009; Asadi *et al.*, 2013). Electroosmosis may progress from cathode to anode if the soil pH is below its point of zero charge (pZC), where ξ becomes positive values (Asadi *et al.*, 2013).

$$v_{EO} = -\frac{D\varepsilon_0\xi}{\eta}E$$

(2.4)

2.3.2 Factors affecting remediation efficiency using electrokinetic process

Electrokinetic process has been applied for removal of various heavy metals and organic compounds under different types of soil, ranging from sandy soil to clayey soil (Shenbagavalli and Mahimairaja, 2010). It is worth noting that the degree of efficacy of electrokinetic soil remediation is hardly consistent among the publications as it is highly dependent on the interactions between the nature of soil, contaminants and operating conditions/configurations. Nevertheless, it is safe to conclude that the removal efficiency for heavy metals is governed by several parameters such as i) electric potential difference/current, ii) pH conditioning, iii) chemical agents, iv) soil texture, and v) contaminant species. The effect of each parameter on the performance of electrokinetic process is discussed in the following subchapters from the view of heavy metal removal and electroosmotic flow (EOF).

2.3.2.1 Electric potential difference and current

Performance of electrokinetic process is enhanced by increasing the applied electric potential difference (voltage) and current. According to Hamed and Bhadra (1997), an applied current of 10 mA produced a water flow of 750 mL in 15 days whilst the increase in electric current to 30 mA produced the same amount of water in five days. This is mainly due to higher electric field across the soil enhances the rapid movement of cations in the diffuse double layer (Figure 2.2), consequently yielding higher shear force to the pore fluid and increases the EOF. As in line with Equations (2.3) and (2.4), the increment in electricity not only increases EOF of the system but also enhances removal efficiency for heavy metals such as Pb (Chung and Kang, 1999; Murillo-Rivera *et al.*, 2010), Ni (Reddy and Karri, 2006a), and non-metal ion fluorine (Kim *et al.*, 2009a). In addition, the removal efficiency for heavy metals can be

improved under higher electricity even though EOF is not enhanced. This is observed in the works of Zhou *et al.* (2004) and Yuan and Chiang (2008) which suggested that an increase in electric potential difference could slightly enhance the removal of copper from 81% to 85% (Zhou *et al.*, 2004) and arsenic from 35.4% to 44.8% (Yuan and Chiang, 2008) via improved electromigration even though the EOF is not significantly enhanced.

In spite of the enhancements discussed above, it is important to note that an excessively high electricity application during electrokinetic process can induce air bubble generation/foaming and soil heating, and may adversely affect soil properties, such as soil buffering capacity, glucose-induced soil respiration and urease/phosphate activities (Acar *et al.*, 1995; Colacicco *et al.*, 2010; Yeung, 2011; Pazos *et al.*, 2012). Also, the use of very high voltage gradient or current densities will increase H^+ concentration to a high level that could subsequently increase the positive charge of the soil surface, and may result in the reduction or reversal of the EOF from anode to cathode (Gioannis *et al.*, 2008). This is observed in the work of Baek *et al.* (2009) and Park *et al.* (2009) which showed EOF was enhanced under higher electricity, but in a reverse direction. This is found to inhibit the removal of cation metal Zn (Park *et al.*, 2009), but enhance removal of arsenic anion (Baek *et al.*, 2009). In addition to H^+ concentration, excessive increase in electricity also tend to increase the electrolysis rate for OH^- in the cathode, which favours metal ion precipitation near the cathode region and thus decrease the removal efficiency of metal ions from soil (Zhou *et al.*, 2005).

Other than affecting electrolysis rate, excessively high electricity may also cause insufficient residence/contact time between the wash solution and the contaminants to form soluble compounds. This consequently inhibits removal efficiency, especially for recalcitrant heavy metals. This is supported by several reported works on the removal of heavy metals/organic compounds (Reddy *et al.*, 2010) and degradation of nitrate ions on

permeable reactive barrier (Suzuki *et al.*, 2012) whereby an increase in electricity is reported to give poorer removal/degradation efficiency. Considering all the criteria mentioned above, Yeung (2011) has suggested that 1V/cm is suitable for laboratory scale studies.

2.3.2.2 pH conditioning

Electrolyte/wash solution conditioning is another method to enhance the performance of electrokinetic soil remediation. In general, two types of electrolyte conditioning are available, namely i) anolyte conditioning, and ii) catholtye conditioning. Anolyte conditioning involves pH control in the anode chamber, which strongly affects the soil pH. Preservation of soil system pH via applying high pH anolyte, could prevent low soil pH especially near the anode region. In order to achieve this condition, several chemicals are often applied in the anode chamber, as shown in Table 2.4.

Higher soil pH increases the EOF from anode to cathode due to increase in negativity in the zeta potential, as shown in Equation (2.4) (Hamed and Bhadra, 1997; Yuan *et al.*, 2006; Yuan *et al.*, 2007; Baek *et al.*, 2009; Gómez *et al.*, 2009; Kim *et al.*, 2009a). The increase in EOF enhances the removal efficiency, as reported in the works for removing organic contaminant benzo[α]pyrene (Gómez *et al.*, 2009), phenolic compounds (Cong *et al.*, 2005), arsenic (Baek *et al.*, 2009), and fluorine (Kim *et al.*, 2009a). Furthermore, anolyte conditioning is also reported to contribute in lower energy consumption for removing azo dye RB5 (Pazos *et al.*, 2007) and arsenic (Baek *et al.*, 2009).

Table 2.4: Chemicals used for pH conditioning in electrokinetic soil remediation

Conditioning	Chemical used	References
Anolyte conditioning	NaOH	(Saichek and Reddy, 2003)
		(She *et al.*, 2003)
		(Reddy and Saichek, 2004)
		(Amrate *et al.*, 2005)
		(Yuan *et al.*, 2006)
		(Pazos *et al.*, 2007)
		(Baek *et al.*, 2009)
		(Li *et al.*, 2009)
		(Pham *et al.*, 2009)
		(Wan *et al.*, 2009)
		(Kim *et al.*, 2009a)
		(Li *et al.*, 2010)
		(Kim *et al.*, 2012c)
	Na_2CO_3	(Pham *et al.*, 2009)
		(Li *et al.*, 2011)
	$Na_2CO_3/NaHCO_3$	(Yuan *et al.*, 2006)
		(Yuan *et al.*, 2007)
	Ammonium Acetate	(Murillo-Rivera *et al.*, 2010)
	Tris-acetate	(Alcántara *et al.*, 2012)
Catholyte conditioning	HNO_3	(Ribeiro *et al.*, 2005)
		(Wang *et al.*, 2006, 2007)
		(Gioannis *et al.*, 2008)
		(Baek *et al.*, 2009)
		(Park *et al.*, 2009)
		(Kim *et al.*, 2009b)
		(Kim *et al.*, 2009c)
		(Murillo-Rivera *et al.*, 2010)
		(Kim *et al.*, 2011b)
		(Almeira O *et al.*, 2012)
		(Giannis *et al.*, 2012)
	H_2SO_4	(Hansen *et al.*, 2007)
		(Pazos *et al.*, 2007)
		(Li *et al.*, 2009)
		(Li *et al.*, 2010)
	HCl	(Kim *et al.*, 2008a, 2008b)
		(Kim *et al.*, 2011b)
		(Suzuki *et al.*, 2012)
	Lactic acid	(Zhou *et al.*, 2004)
		(Zhou *et al.*, 2005)
		(Zhou *et al.*, 2006)
	Acetic acid	(Chung and Kang, 1999)
		(Kim *et al.*, 2009b)
		(Sumbarda-Ramos *et al.*, 2010)
	Acetate and citrate buffers	(Zhou *et al.*, 2004)
		(Kim *et al.*, 2009b)
		(Li *et al.*, 2012)

Even though anolyte conditioning could enhance the removal efficiency of organic contaminants by inducing higher EOF, a high pH in soil may result in low metal mobility via metal hydroxide precipitation near the cathode region. Hence, catholyte conditioning using the acids as shown in Table 2.4 is introduced in order to reduce hydroxide precipitation in the cathode region. It is found that, in general, reduction in overall soil pH increases metal ion desorption and mobility, and this increases the removal efficiency (Chung and Kang, 1999; Zhou et al., 2005; Wang et al., 2006, 2007; Gioannis et al., 2008; Baek et al., 2009; Kim et al., 2009b; Kim et al., 2011b; Almeira O et al., 2012). Other than acid buffers, soil pH could also be homogenized at low level via other operating conditions such as well-timed polarity exchange (Pazos et al., 2006; Han et al., 2010; Ma et al., 2010), circulation of high pH catholyte into the anode chamber (Lee and Yang, 2000), and using longer cathode chamber to prevent OH- migration into the soil (Rajić et al., 2012).

However, it is worth noting that low pH does not enhance organic contaminant removal. Wang et al. (2007) found that the use of HNO_3 to obtain a lower soil pH impeded p-xylene and phenanthrene transport. Furthermore, it may be noted that the decrease in soil pH causes EOF to reduce from anode to cathode, and even results in EOF reversal, as reported by Zhou et al. (2004), Zhou et al. (2005) and Baek et al. (2009). The reversal of EOF can further risk cation removal due to a counter direction of cation transport between electromigration and electroosmosis (Park et al., 2009; Kim et al., 2009b). Thus, a suitable range of pH must be used based on soil properties and the type of contaminant that needs to be removed.

Moreover, it is to be noted that low soil pH does not always increase metal desorption as the affinity of metal ions on the soil surface also governs metal desorption and removal efficiency in the electrokinetic process, as shown in the works of Kim et al. (2005b), Turer and Genc (2005), Zhou et al. (2005), Li et al. (2010), Giannis et al.

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(2009) and Giannis *et al.* (2012) for treating soil contaminated with multiple heavy metals. For example, Pb was reported to have a much higher affinity to the soil surface even under low pH conditions, and thus a low removal efficiency was observed compared to other types of metal ions (Turer and Genc, 2005; Kim *et al.*, 2005b; Giannis *et al.*, 2009).

2.3.2.3 Complexing agents

Sub-section 2.3.2.2 presents evidence that pH adjustment using acids, bases and buffer solutions affect the behaviour of the electrokinetic process whereby lower pH enhances metal cation desorption whilst a higher pH enhances the EOF and organic compounds removal. However, the use of lower pH to enhance metal desorption risks reversal of EOF at the same time. This not only retards the removal efficiency of metal cations but also causes problems when dealing with simultaneous treatments of organic compounds and metal cations. Based on this concern, studies on the utilisation of complexing agents to enhance metal desorption process without affecting the pH significantly have been conducted whereby surfactants and aminopolycarboxylates based chelating agents are often used, as summarized in Table 2.5.

Table 2.5 shows that ionic and non-ionic surfactants have been applied as the wash solutions in electrokinetic process for heavy metal removal. However, surfactants often show lower effectiveness in enhancing metal desorption than organic contaminants (Maturi and Reddy, 2006; Reddy *et al.*, 2006b; Li *et al.*, 2010; Reddy *et al.*, 2010; Alcántara *et al.*, 2012). As shown in Table 2.5, heavy metal removal efficiency demonstrated by surfactants is low, in general, at <35%. High Pb removal by Tween80 in the work of Alcantara *et al.* (2012) is mainly due to the inclusion of ethylenediaminetetraacetic acid (EDTA) in Tween80 solution as chelants. A simple

batch extraction test also shows that low Pb extraction at 40% is reported when only Tween80 is used as the extracting agent (Alcántara *et al.*, 2012), which indicates that surfactants are weak desorption agents for heavy metals.

Table 2.5: Complexing agents used in electrokinetic soil remediation for heavy metals removal

Group	Complexing agents	Contaminants	Contaminant concentration, mg/kg	Removal Efficiency, %	References
Surfactants	CPC	Arsenic	966	31.70%	(Yuan and Chiang, 2008)
	SDS	Copper	180 mg	Not mentioned	(Han *et al.*, 2010)
	Igepal CA-720	Heavy metals	1.8-38000 3.53-47000	0-30.00%	(Reddy *et al.*, 2006b) (Reddy *et al.*, 2010)
	Tergitol 15-S-7	Zinc	910	24.30%	(Park *et al.*, 2009)
	Tween 80	Lead	5000	82.40%	(Alcántara *et al.*, 2012)
		Heavy metals	1.8-38000 17.4-714.1	0-15.00%	(Reddy *et al.*, 2006b) (Colacicco *et al.*, 2010)
	HPCD	Nickel	500 42.1	0-0.93%	(Maturi and Reddy, 2006) (Li *et al.*, 2010)
		Zinc	2313-3123 2415	0-14.00%	(Li *et al.*, 2009) (Li *et al.*, 2010)
		Heavy metals	<0.5-21300 1.8-38000	Negligible	(Reddy and Ala, 2005) (Reddy *et al.*, 2006b)
Chelating agent	EDTA	Arsenic	966 953-972 0.54-183.90	44.80% 77.00% 39.80%	(Yuan and Chiang, 2008) (Yuan *et al.*, 2009) (Kim *et al.*, 2012c)
		Cesium	514 Not mentioned Not mentioned	59.30% 57.90% 57.90%	(Kim *et al.*, 2009c) (Kim *et al.*, 2008a) (Kim *et al.*, 2008b)
		Cobalt	238 Not mentioned Not mentioned	84.60% 83.50% 83.50%	(Kim *et al.*, 2009c) (Kim *et al.*, 2008a) (Kim *et al.*, 2008b)
		Copper	438 13.25-220.25 180 mg	73.00% 17.40% Not mentioned	(Zhou *et al.*, 2004) (Kim *et al.*, 2012c) (Han *et al.*, 2010)
		Lead	5000 1000 4432 11.49-504.61	82.40% 72.30-83.80% 36.28% 23.90%	(Alcántara *et al.*, 2012) (Zhang *et al.*, 2014) (Amrate *et al.*, 2005) (Kim *et al.*, 2012c)
		Heavy metals	<0.5-21300 18-270 7.7-94080 3.53-47000 17.4-714.1	Low removal 1.60-13.20% 2.00-80.00% 0-80.00% 28.00-84.00%	(Reddy and Ala, 2005) (Kim *et al.*, 2011b) (Gioannis *et al.*, 2008) (Reddy *et al.*, 2010) (Colacicco *et al.*, 2010)
	NTA	Cadmium	145	95.00%	(Giannis *et al.*, 2009)
		Copper	1005	60.00%	(Giannis *et al.*, 2009)
		Lead	455	25.00%	(Giannis *et al.*, 2009)
	DPTA	Cadmium	145	70.00%	(Giannis *et al.*, 2009)
		Copper	1005	20.00%	(Giannis *et al.*, 2009)
		Lead	455	20.00%	(Giannis *et al.*, 2009)
		Heavy metals	<0.5-21300	Low removal	(Reddy and Ala, 2005)
	EGTA	Cadmium	145	65.00%	(Giannis *et al.*, 2009)
		Copper	1005	10.00%	(Giannis *et al.*, 2009)
		Lead	455	15.00%	(Giannis *et al.*, 2009)
	EDDS	Cadmium	4000	≈50.00%	(Suzuki *et al.*, 2014)
		Lead	7366.67	≈45.00%	(Suzuki *et al.*, 2014)

In contrast, aminopolycarboxylates based chelating agents emerge as superior chemicals in enhancing heavy metals desorption from soil through the formation of water soluble complexes (Yeung and Gu, 2011). Among the agents, EDTA is widely applied in electrokinetic soil remediation, as shown in Table 2.5. EDTA is reported to provide higher metal removal efficiency than unenhanced systems (Amrate *et al.*, 2005; Reddy and Ala, 2005; Gioannis *et al.*, 2008; Yuan and Chiang, 2008; Han *et al.*, 2009; Yuan *et al.*, 2009; Colacicco *et al.*, 2010). As a chelant for anion complex formation, EDTA is observed to form complexes more effectively with metal ions than organic contaminant PAHs, especially when treating real contaminated soil (Colacicco *et al.*, 2010; Reddy *et al.*, 2010). Nevertheless, EDTA is still reported to be capable of removing organic contaminants, such as diesel (Han *et al.*, 2009) and PAHs (Reddy *et al.*, 2010) via soil mineral dissolution and change in charge of solid particle which releases PAHs (Reddy *et al.*, 2010).

In spite of outperforming an unenhanced electrokinetic system, EDTA generally has a lower metal removal rate than acidic agent such as citric acid, acetic acid, oxalic acid, HNO_3 and HCl due to its weaker acidity for metal desorption process (Kim *et al.*, 2008a, 2008b; Kim *et al.*, 2009c; Kim *et al.*, 2011b). Moreover, as a result of complex formation, EDTA causes an accumulation of metal ions in the soil matrix at an early stage of the treatment due to the counter migration of positive metal ions from the anode region and negatively charged metal complexes from the cathode region (Giannis *et al.*, 2009). This phenomenon results in lower metal removal efficiency.

The performances of chelants are also dependent on the applied electricity, pH condition and soil properties (Gioannis *et al.*, 2008; Yuan and Chiang, 2008; Kim *et al.*, 2009c; Kim *et al.*, 2011b; Alcántara *et al.*, 2012). A higher voltage may result in improved EDTA performance in comparison to citric acid (Yuan and Chiang, 2008). Besides that, the effectiveness of EDTA is also strongly dependent on the pH of the

system as EDTA has poor solubility under acidic condition, which consequently affects the complexation process in the soil (Alcántara *et al.*, 2012; Harris, 2013). Moreover, the difference in soil properties also causes the variation in the performance of EDTA. For example, Gioannis *et al.* (2008) claimed that EDTA displays superior performance in relation to citric acid as citric acid preferentially forms H-citrate complex which reduces the availability of citrate for metal complexes. On the other hand, poorer EDTA performance when compared to citric acid was observed in another study when Fe(III) was present in the soil. EDTA forms highly stable complex with Fe(III), which reduces EDTA availability for contaminants (Kim *et al.*, 2011b). It may also be suggested that the nature of target metal for remediation also governed the effectiveness of EDTA (Reddy and Ala, 2005; Kim *et al.*, 2011b), NTA, DTPA and EGTA as chelants (Giannis *et al.*, 2009).

2.3.2.4 Acidic based agents

Acidic based agents have been utilised as catholyte for pH control, as discussed in Sub-section 2.3.2.2. Besides that, due to the acidic characteristic of these agents, they are often used in processing fluids (wash solutions) for desorbing heavy metals. Strong acid HNO_3 is frequently utilized by researchers to reduce pH in cathode region and cathode chamber. When HNO_3 is applied in electrokinetic process, it depolarizes the cathode and enhances metal ion desorption/deprecipitation, especially near the cathode region (Chung and Kang, 1999; Wang *et al.*, 2006, 2007; Gioannis *et al.*, 2008; Park *et al.*, 2009; Kim *et al.*, 2009b; Giannis *et al.*, 2012). However, an excessive low soil pH may cause reversal of EOF towards anode chamber, which is in opposite direction for the electromigration for metal cations (Ribeiro *et al.*, 2005; Gioannis *et al.*, 2008; Baek *et al.*, 2009; Park *et al.*, 2009; Kim *et al.*, 2009b). This may reduce the removal

efficiency, as reported by Park *et al.* (2009), where Zn is found to accumulate in the middle region of the soil, as a result of reverse EOF. Furthermore, excessive use of HNO_3 in catholyte beyond the optimum concentration of >0.12 M is found to give undesirable effect in cathode chamber's pH, as a result of NO_3^- reduction (Almeira O *et al.*, 2012).

Besides providing better desorption condition, other acids such as HCl, acetic acid and citric acid also contribute to desorption via complexation with heavy metals. HCl provides Cl^- ions for formation of water soluble metal complexes (Kim *et al.*, 2011b) besides enhancing soil acidity. This is reported to give higher removal efficiency for Ni, Cu, Zn and Pb at 67-69.5% than HNO_3 at 7.9-42%, as shown in the work of Kim *et al.* (2011b). Besides strong acid, weak acids such as acetic acid and citric acid are also often used as buffer solutions for controlling pH (Park *et al.*, 2007; Shen *et al.*, 2007; Gioannis *et al.*, 2008; Kim *et al.*, 2009b; Sumbarda-Ramos *et al.*, 2010; Kim *et al.*, 2011b; Li *et al.*, 2012) and solubilizing agent/processing fluids (Chung and Kang, 1999; Yuan and Chiang, 2008; Kim *et al.*, 2008a, 2008b; Kim *et al.*, 2009c; Kim *et al.*, 2009d; Han *et al.*, 2010; Murillo-Rivera *et al.*, 2010; Pazos *et al.*, 2012).

It is noted that the performance of acid based agents is strongly case dependent. For example, acetic acid is reported to show higher removal efficiency than citric acid for removing Co, Cs (Kim *et al.*, 2008a, 2008b; Kim *et al.*, 2009c) and Pb (Murillo-Rivera *et al.*, 2010). It is claimed that acetic acid attacks and dissolves hydrous oxides in the soil and creates lower pH condition than citric acid (Kim *et al.*, 2008a, 2008b; Kim *et al.*, 2009c). Besides that, Murillo-Rivera *et al.* (2010) also suggested that acetic acid, which results in higher negativity of zeta potential of soil could increase the permeability of the soil and thus improve Pb removal efficiency. When citric acid was applied, Pb-citrate complex of low mobility was formed that was subsequently adsorbed on soil carbonate content, hindering Pb removal (Murillo-Rivera *et al.*, 2010).

Furthermore, citric acid is also reported to have lower Cu removal efficiency than H_2SO_4, as a result of possible reactions in the oxidation-reduction process when bipolar electrode plates were used (Hansen *et al.*, 2007).

However, contradictory observation is reported by Li *et al*. (2012) whereby citric acid is claimed to be more effective when treating Cr contaminated soil, as it enhanced desorption and formed more stable complexes than acetic acid. In addition, citric acid also performs better than EDTA and HNO_3 when treating sandy soil (Kim *et al.*, 2008a, 2008b; Kim *et al.*, 2009c; Murillo-Rivera *et al.*, 2010; Kim *et al.*, 2011b), even though metal-EDTA complexes have higher stability than citrate complexes (Kim *et al.*, 2011b). The reduction of available EDTA in the system, as a result of complexation with other metals, such as Fe(III) in the soil and inability of NO_3^- on metal complexation, are suggested as the main reasons for citric acid to outperform EDTA and HNO_3, respectively (Kim *et al.*, 2011b). However, the characteristics of contaminants influence the effectiveness of citric acid as well. This is reported by Yuan and Chiang (2008) that EDTA performed better than citric acid in mobilising As from As-Fe soil, especially under higher applied voltage.

2.3.2.5 Soil texture

Soil texture is another important factor that causes changes in electrokinetic phenomena. It influences the performance of wash solutions in electrokinetic process in terms of electroosmosis and contaminant removal efficiency (Reddy and Saichek, 2003). Several soil properties are reported to affect the performance of electrokinetic process such as particle size, buffering capacity and organic matter/carbon content (Yang and Liu, 2001; Reddy and Saichek, 2003; Kim *et al.*, 2006; Gioannis *et al.*, 2008; Sumbarda-Ramos *et al.*, 2010; Alcántara *et al.*, 2012).

The size of soil particles affects electroosmosis. Elecroosmosis was found to be effective when treating sandy soil by electric field applied under zero hydraulic gradient whilst no EOF was recorded by clayey soil, due to high permeability of sandy soil (Sumbarda-Ramos *et al.*, 2010). Other than particle size, soil buffering capacity is also responsible for governing the effectiveness of electroosmosis in soil especially for low permeability soil (Saichek and Reddy, 2003b, as cited in Alcántara *et al.*, 2012). This observation is reported by Kim *et al.* (2006) based on Hadong clay, which has higher buffering capacity, yielded higher EOF than low buffering capacity kaolin. Reddy and Saichek (2003) also suggest that glacial till soil with high carbonate content and buffering capacity provides higher electroosmosis than kaolin when 3% Tween80 is applied as wash solution due to soil's ability to maintain negative zeta potential. This is reported to enhance the removal efficiency for phenanthrene in glacial soil. On the other hand, soil with high buffering capacity generally shows poor heavy metal removal efficiency, as a result of ineffective soil acidification (Reddy *et al.*, 2006b; Gioannis *et al.*, 2008) for metal desorption.

In addition, soil with higher organic matter content is also found to give lower removal efficiency, especially for organic contaminants such as phenenthrene, as a result of its stronger binding on the organic matter (Reddy and Saichek, 2003). This conforms to the work of Alcantara *et al*. (2012) who reported that the removal efficiency for Pb and phenanthrene for sandy soil was lower than that for kaolin clay (73.5-82.4% vs 93.3-95.1%) under similar operating conditions, as the organic matter content for sandy soil was higher than that for kaolin clay. Furthermore, Yang and Liu (2001) who worked on remediation of trichloroethane, TCE contaminated soil using electrokinetic-fenton process further claimed that higher organic matter content not only causes lower TCE removal efficiency via adsorption on the organic matter, but also

reduces TCE destruction efficiency via extra consumption of hydroxyl radicals on the organic matters.

2.3.2.6 Contaminant species

The effectiveness of electrokinetic soil remediation on heavy metal removal is also dependent on the types of metals. For example, Pb is reported as one of the most recalcitrant metal species to adsorb/bind on soil mineral surface (Violante *et al.*, 2007). Its strong affinity for soil often causes relatively low removal efficiency in comparison to other metals such as Cd and Zn when a co-contaminated soil is treated (Turer and Genc, 2005; Kim *et al.*, 2005b; Giannis *et al.*, 2009; Giannis *et al.*, 2012). This is also well demonstrated in the works of Zhou *et al.* (2005) and Li *et al.* (2010) who claimed that low removal was achieved for Ni and Cu in comparison to Zn, as a result of their higher affinity to bind on high clay (soil particle size < 2μm) containing soil as well as high iron containing red soil (Violante *et al.*, 2007). In addition, Turer and Genc (2005) also suggested that competitive migration of metal species in a co-contaminated soil affected the removal efficiency in comparison to soil containing single contaminant. The presence of significant amount of Zn and Cu in the soil reduced Pb removal efficiency from 48% to 32% (Turer and Genc, 2005). However, it is worth noting that metal mobility could be enhanced by using proper chemical solutions/complexing agents in electrokinetic process. For example, Cu has lower mobility than Ni (Violante *et al.*, 2007) and it often showed lower removal efficiency than Ni when HNO_3 and EDTA were used as the wash solutions (Kim *et al.*, 2011b). However, Cu removal efficiency (69.8%) was reported to increase compared to Ni (49.4%) when citric acid was used (Kim *et al.*, 2011b).

2.3.3 Incorporation of electrokinetic process with soil washing/ flushing

Electrokinetic process has also been incorporated into soil washing/flushing for improving heavy metal removal efficiency. The different types of electrokinetic washing/flushing are discussed in the sub-sections below.

2.3.3.1 Electrokinetic flushing

Electrokinetic flushing is an electrokinetic process which is aided by a hydraulic pump for transporting the wash solution through the soil, as shown in Figure 2.3. This configuration is reported to provide significant enhancement in removal efficiency than normal electrokinetic process, especially when treating higher permeability sandy soil at lower remediation time (Kim *et al.*, 2008a, 2008b; Reddy *et al.*, 2010). Kim *et al.* (2008a) reported that electrokinetic flushing enhanced the removal of Co and Cs by about 25% and 35%, respectively, in comparison to normal electrokinetic process in a five day treatment period. This is also in line with the work of Kim *et al.* (2008b) which claimed that an enhancement of 30% was achieved in four days as flushing process detached the adhered Co and Cs from soil surface by pressure flushing. The removal enhancement by flushing is also highly dependent on soil permeability and treatment duration whilst it is less dependent on wash solution injection rate (Kim *et al.*, 2008a).
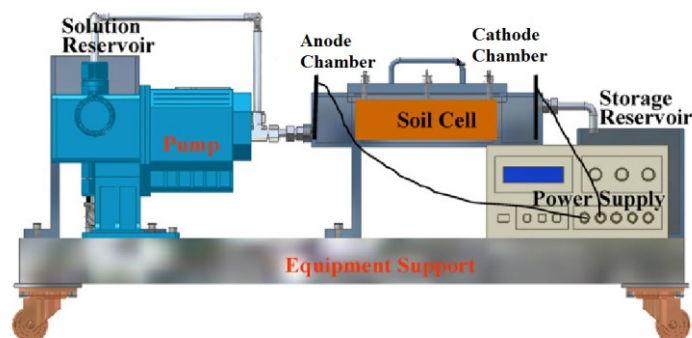
Figure 2.3: Electrokinetic soil flushing equipment (Kim *et al.*, 2008b)

In terms of effluent generation, electrokinetic flushing produced more effluent than that for a normal electrokinetic process, where a solution: soil ratio of 2.4 mL/g was recorded for the former whilst 1.6 mL/g for the later, as reported by Kim *et al.* (2008a). In another study, Kim *et al.* (2008b) observed effluent generation to the extent of 96.5 mL/day in electrokinetic flushing in comparison to normal electrokinetic process, which showed 53.4 mL/day. Nevertheless, the authors also claimed that electrokinetic flushing only produced an effluent volume of less than 10% of that for soil washing. This observation was also reported by Kim *et al.* (2008a) that a much higher solution: soil ratio of 47.1 mL/g was needed for soil washing in order to achieve high removal efficiency in comparison to electrokinetic flushing at 2.4 mL/g.

2.3.3.2 Vertical electrokinetic flushing

Electrokinetic flushing has also been conducted in vertical configuration. Figure 2.4 illustrates two types of vertical configurations, namely i) downward configuration, and ii) upward configuration. Unlike normal electrokinetic configuration, a downward configuration consists of an anode which is installed on the top of the soil tank and a cathode at the bottom. Downward configuration is claimed to minimize accumulation of contaminants in the middle of soil while preventing generation of waste solution via anode chamber contamination, as a result of possible reverse EOF at low soil pH condition (Kim *et al.*, 2009c). In terms of removal efficiency, Kim *et al.* (2009c) reported that the use of vertical electrokinetic flushing achieved high removal efficiency of 98.30% and 88.80% for Co and Cs, respectively. Moreover, the effluent generated by this configuration was also reported to be much lower, at 2.4 mL/g soil in comparison to normal soil washing at 30 mL/g.
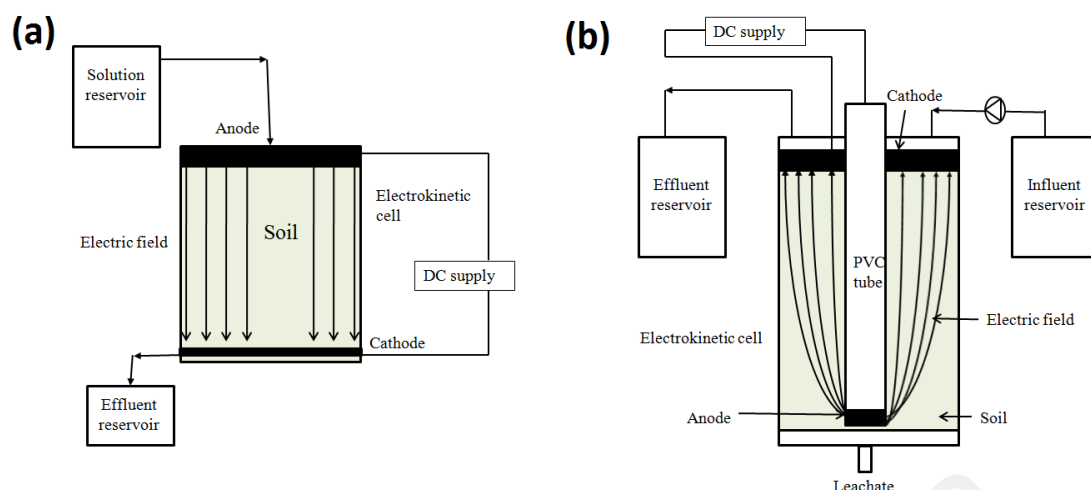
Figure 2.4: Vertical Electrokinetic Soil Washing: (a) Downward configuration (Kim *et al.*, 2009c); (b) Upward configuration (UESR)

Other than downward module, the feasibility of upward electrokinetic soil remediation (UESR) has also been investigated using a cathode at the top and anode at the bottom, as shown in Figure 2.4b. Upward contaminant transport is claimed to produce minimal site disturbance and reduces overall treatment cost as contaminants tend to accumulate on the surface of the cathode, which can be further treated easily (Wang *et al.*, 2006, 2007). UESR has been applied in electrokinetic process on the removal of heavy metals such as As, Cd, Cr, Cu, Pb, Ni, Zn (Wang *et al.*, 2006, 2007; Giannis *et al.*, 2012) and organic contaminant such as p-xylene, pyrene, phenanthrene and other PAHs (Wang *et al.*, 2007; Lima *et al.*, 2011; Giannis *et al.*, 2012). In general, heavy metals electromigrate upwards and are concentrated in the cathode region or precipitated on the cathode (Wang *et al.*, 2006; Giannis *et al.*, 2012). The removal of heavy metals via effluent is also noticed, especially when HNO_3 is used as the wash solution instead of non-acidic distilled water (Wang *et al.*, 2006, 2007; Giannis *et al.*, 2012).

In contrast, the migration of organic compounds is dominated by pore water movement. This was well documented in the works of Wang *et al*. (2007) and Giannis *et al*. (2012) which reported that p-xylene and pyrene were transported by electroosmosis and leachate flow, respectively. The mobility for organic compounds was higher when distilled water was used as the wash solution due to favourable soil zeta potential for electroosmosis (Wang *et al.*, 2007). In addition, light non-aqueous phase liquid phenanthrene could be removed in UESR by the upward movement of pore solution flow in the system that provided additional upward force towards the cathode at the upper surface (Wang *et al.*, 2007; Giannis *et al.*, 2012). Nevertheless, the removal of heavy metals and PAHs by UESR is also dependent on the diameter and height of the cell (Wang *et al.*, 2006, 2007), which could be correlated with current density and contaminant solubilities in water (Wang *et al.*, 2006, 2007; Giannis *et al.*, 2012).

The concept of UESR has also been applied together with conventional horizontal electrode configuration, known as 2D crossed electric field, and has been observed as having a positive influence on chromium removal (Zhang *et al.*, 2010). With regard to electromigration enhancement by horizontal electrodes, the risk of chromium diffusion into deep soil layers and groundwater is found to be minimized by the application of a UESR. This is mainly due to the fact that UESR transports Cr(VI) anions upward, counteracting the downward gravitational and concentration gradient migration (Zhang *et al.*, 2010). Therefore, improved remediation efficiency is obtained in comparison to any individual application of horizontal and vertical configurations.

2.3.3.3 Electrokinetic washing

Other than the use of flushing in electrokinetic process, soil washing has also been incorporated with electrokinetic process for the removal of heavy metals and radionuclides from soil (Kim *et al.*, 2012b), concrete (Kim *et al.*, 2009d) and ashes (Kim *et al.*, 2013; Liao *et al.*, 2014). This process is normally applied in two different stages involving initial washing and the electrokinetic process. The washing is applied to provide desorption condition and initial contaminant removal. Then, the soil/concrete/ash is further transferred into an electrokinetic equipment for further removal process. An example of electrokinetic washing equipment and the summary of these studies are as shown in Figure 2.5 and Table 2.6, respectively.
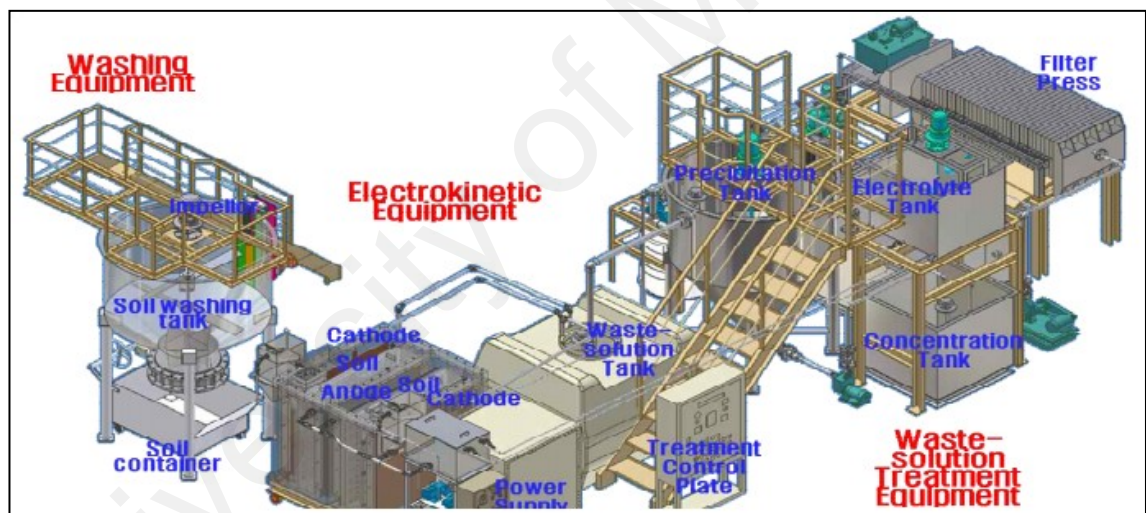
Figure 2.5: Example of electrokinetic washing equipment (Kim *et al.*, 2012b)

The use of electrokinetic washing is reported to provide treatment for ash to non-hazardous waste via reduction in the reactive fraction of heavy metals. This is well reported in the work of Liao *et al.* (2014) which applied initial Pb contaminated ash washing using deionized water before the application of electrokinetic process. The initial washing provided significant impact especially on Pb mobility, whereby it removed chloride ions in the ash and this prevented inhibition of Pb fraction changes into less reactive forms during electrokinetic process. A comparison on Toxicity

Characteristic Leaching Procedure (TCLP) further proved that electrokinetic washing process recorded better performance than normal electrokinetic process as TCLP detection for Pb was found to decrease from 16.5mg/L to 0.746 mg/L and 15.2 mg/L, respectively (Liao *et al.*, 2014). A normal electrokinetic process failed to remove Pb, which was strongly bound to the carbonate content.

Table 2.6: Summary on the application of electrokinetic washing process

References	Medium	Contaminant	Process condition	Removal efficiency	Remarks
(Kim *et al.*, 2009d)	Concrete	Cs Co	Washing Wash solution: 3 M HCl Solution: concrete ratio: 1.5 Duration: 4 h Electrokinetic process Wash solution: 0.01 M Acetic acid Duration: 14.83 days	Washing Cs: 76.83% Co: 85.0% Electrokinetic: Cs: 99.6% Co: 99.7%	Acid washing reduces pH and $CaCO_3$ content on the concrete. This enhances Co and Cs desorption. Solution: soil ratio (mL:g) Washing: 1.5 Electrokinetic: 2.7-2.8 Electrokinetic washing: 7.2
(Kim *et al.*, 2012b)	Soil	Cs	Washing Wash solution: HNO_3 2 times scrubbing Electrokinetic process Wash solution: 0.1 M HNO_3 Duration: 60 days	Washing: 75-85% Electrokinetic: >95.0%	Longer duration needed when treating higher Cs concentration ash
(Kim *et al.*, 2013)	Radioactive ash	^{137}Cs ^{134}Cs	Washing Wash solution: HNO_3 Solution: ash ratio: 1 Duration: 2 h 3 times washing Electrokinetic process Wash solution: water/HNO_3 Duration: 10 days	Washing: 87-89% Electrokinetic: 93.9-94.0%	Electrokinetic process provides further removal of Cs to achieve the clearance concentration level Longer duration needed when treating higher Cs concentration ash
(Liao *et al.*, 2014)	Municipal solid waste incineration ash	Pb Cd Cr Cu	Washing Wash solution: deionized water Solution: ash ratio: 20 Duration: 0.5 h Electrokinetic process Wash solution: deionized water Duration: 168 h	Not stated Metals transform to strongly binded species	Enhancement given by washing is dependent on the fraction of contaminants. E.g. removal of metals bounded with carbonate content could be enhanced by washing process.

Furthermore, electrokinetic washing is also found to have favourable impact in remediating radionuclides polluted concrete and soil. Kim *et al*. (2009d) claimed that the use of electrokinetic process after concrete washing could further enhance the removal efficiency by 14.7-23.3% in comparison to normal washing. Application of initial washing by 3 M HCl was reported to break down the carbonate content in concrete and provided lower pH condition for desorption. The use of subsequent electrokinetic process could boost the overall removal of Co and Cs to >99% in comparison to single electrokinetic process, which only gave <1% Co and <65% Cs removal. This was also agreed by Kim *et al.* (2012b) and Kim *et al.* (2013) who showed that initial soil washing in multiple cycles could provide early conditioning and removal of the radioactive waste, ranging from 75% to 89% while subsequent application of electrokinetic process could further enhance the removal to below guideline concentration level.

However, electrokinetic washing is often applied in two different stages and processes. This causes a relatively high chemical consumption and effluent generation than normal soil washing and electrokinetic process. An example is given in the work of Kim *et al*. (2009d) where electrokinetic washing showed a high solution: concrete ratio of 7.2 mL/g, as a result of spent solution that is generated from soil washing and electroosmosis. In contrast, the use of normal soil washing and electrokinetic process only needed a ratio of 1.5 mL/g and 2.7-2.8 mL/g, respectively. Thus, a study on the other types of equipment process/configuration is required in order to enhance the feasibility of electrokinetic washing by maintaining high removal efficiency at lower wash solution consumption.

2.4 Summary of literature review

Soil washing and SS have been proven as effective methods for treating heavy metal contaminated soils. However, such processes have major shortcomings such as high chemicals consumption and high solid waste generation, which in turn increase the treatment cost. As discussed in Sub-section 2.2.1, high solution: soil ratio used in soil washing is responsible in increasing the cost for spent wash solution treatment. For SS, a high amount of waste solid generated increases the cost for landfill and cement as well.

In contrast, electrokinetic process is an effective method in remediating heavy metals contaminated soil and it is applicable for both high and low permeability soils. Its ability to promote migration of heavy metals even in the absence of pore flow (Acar *et al.*, 1995) makes it an attractive option along with other remediation technologies to improve the removal efficiency of heavy metals at lower chemical solution consumption.

Electrokinetic process has been incorporated into soil washing to enhance the removal process for heavy metals from soil, concrete and ash, as discussed in Sub-section 2.3.3.3. However, it is worth noting that the wash solution consumption, which is the main disadvantage of soil washing, is not reduced by the introduction of electrokinetic process. In order to reduce spent wash solution generation while maintaining the removal efficiency, a different configuration for electrokinetic washing process, namely two-stage electrokinetic washing was introduced in this study for remediating Pb contaminated soil. This configuration involves the incorporation of soil washing and electrokinetic process in a single equipment, but operating at two different stages. The use of spent wash solution as catholyte after initial soil washing can reduce wash solution consumption while maintaining the removal efficiency for electrokinetic washing. The details of this process are elaborated in Section 4.4.

Other than incorporating in soil washing, electrokinetic process can also be applied as a soil pretreatment method to reduce contaminated soil volume before applying other treatment process such as SS due to its ability to migrate heavy metals even in the absence of pore flow. Thus, high chemical solution consumption can be prevented at the latter stage. This is investigated in the present study by using minimum chemical solution as wetting agent to saturate the soil, desorb the heavy metals and concentrate them into smaller soil volume under the influence of electric field. The details of the study are further discussed in Section 4.5.

CHAPTER 3: METHODOLOGY

This chapter discusses the methodologies used in the study. The chapter consists of five main sections, which are: i) materials, ii) equipment and apparatus, iii) experimental procedures, iv) analytical methods, and v) precautionary steps and minimisation of error.

3.1 Materials

3.1.1 Chemicals

The main chemicals used could be categorized into three major groups, namely i) heavy metals, ii) wash solutions/wetting agents, and iii) analytical chemicals. The heavy metals used in this study were lead nitrate, $Pb(NO_3)_2$ and potassium dichromate $K_2Cr_2O_7$, both of which were supplied in solid powder. The wash solutions investigated in this study were supplied in the forms of: i) HCl 37 wt% solution, ii) H_2SO_4 98 wt% solution, iii) HNO_3 67 wt% solution, iv) acetic acid 99% solution, v) EDTA 0.5 M solution at pH 8-9, vi) citric acid monohydrate crystal powder, and vii) $NaNO_3$ powder. The wash solutions of desired concentrations were prepared by diluting with/dissolving in distilled water prior to use. Other chemicals, which were used for analytical purpose are as summarized in Appendix A. The chemicals used were of analytical grade and were supplied by R&M Chemicals, Malaysia. These chemicals were used without any further treatment.

3.1.2 Soil

The soil was collected from first aquifer layer of the soil in Hulu Langat area, Selangor, Malaysia. The soil was pretreated by removing rocks, dried branches and grass and was dried in open air for one week. This soil was classified as sandy soil according to USDA Soil Classification as it has 92% sand content, with 8% silt and clay. The properties of uncontaminated soil such as cation exchange capacity (CEC), specific gravity, and organic matter content, were analysed based on the procedures as shown in Appendices B1-B3. The metal content in the soil was analyzed using USEPA 3050b, as discussed in Section 3.4.2.2. General properties of the uncontaminated soil used in this study are discussed in Section 4.2.

3.2 Equipment and apparatus

3.2.1 Electrokinetic washing system

Figure 3.1 illustrates the set-up for electrokinetic washing. The set-up fabricated was at a laboratory scale. The soil column was made of PTFE and had an inner diameter of 4 cm and 15 cm length. It was installed with four passive electrodes so that the voltage drop across the soil could be monitored when necessary. Two ends of the column were connected to two chambers, namely anode chamber and cathode chamber, each having a size of 4 cm diameter and 7.4 cm length. The column and chambers were separated by filter papers which functioned as selective barriers to prevent soil movement into the chamber. The other ends of the chambers were connected with the graphite electrode discs (diameter 4.9 cm; thickness 1 cm), as shown in Figure 3.2. These electrodes were connected to a direct current supply (Atten APS3003S-3D). The chambers were further connected with tubing and the overflow levels for both chambers were held at the same height in order to prevent extra effluent generation via hydraulic

head difference. The configuration of the setup for electrokinetic washing is as shown in Figure 3.1.
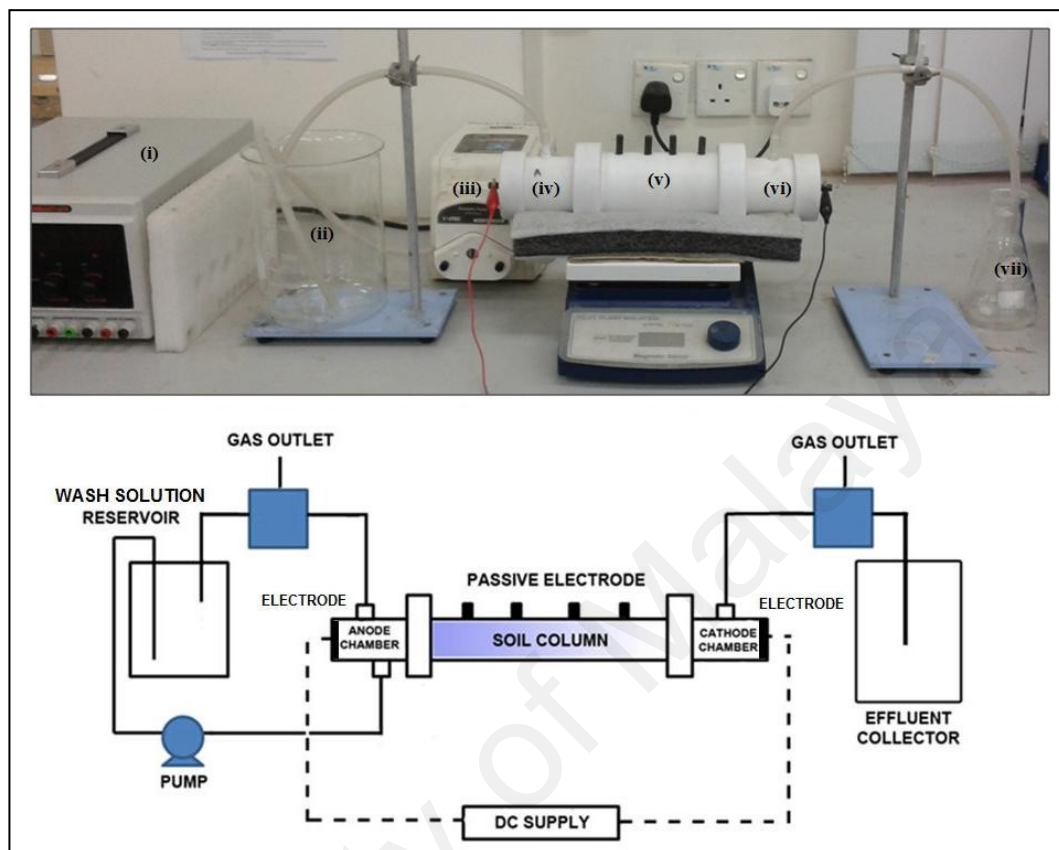
Figure 3.1: Experimental setup for electrokinetic washing system: (i) direct current supply, (ii) wash solution reservoir, (iii) peristaltic pump, (iv) anode chamber, (v) soil column, (vi) cathode chamber, (vii) overflow tube/effluent collector
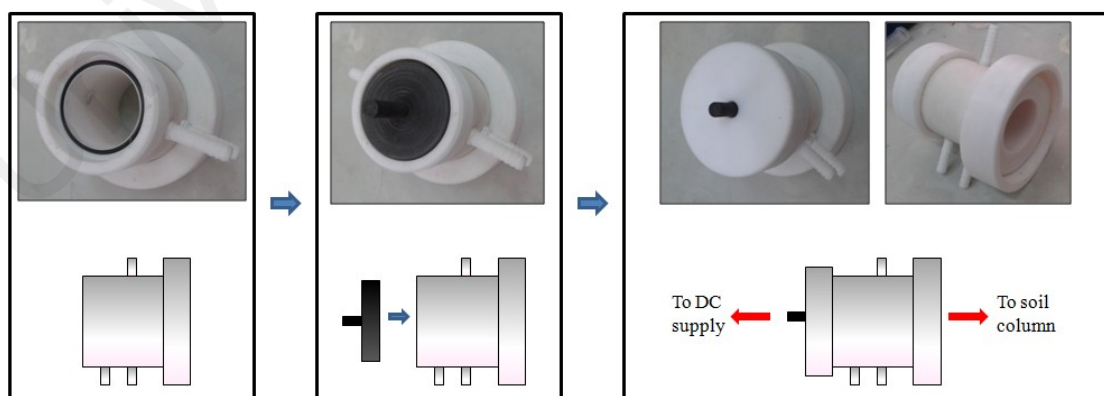
Figure 3.2: Connection of graphite electrode into the wash solution chamber

3.2.2 Electrokinetic soil pretreatment system

The ability of the electrokinetic process to serve as a soil pretreatment method for concentrating heavy metals into smaller soil volume was investigated in a simple system. This system consisted of a polypropylene sand box with a dimension of 8.5 cm x 6.2 cm x 5 cm. In this study, wash solution chamber was absent. Instead, the electrodes were in direct contact with the soil so that a consistent electrode environment/condition could be established for both fixed electrode tests and approaching electrode tests. Six graphite rods with dimension of 0.7 cm diameter and 4 cm length were used as the electrodes. They are positioned at left, middle and right of the sandbox, as shown in Figure 3.3, which indicates anodes, approaching electrodes and cathodes, respectively. A pair of anodes (positioned at S1) and cathodes (positioned at S4) were used in this study to enhance the effective electric field in the soil. These electrodes are connected to the direct current supply, as shown in Figure 3.3.
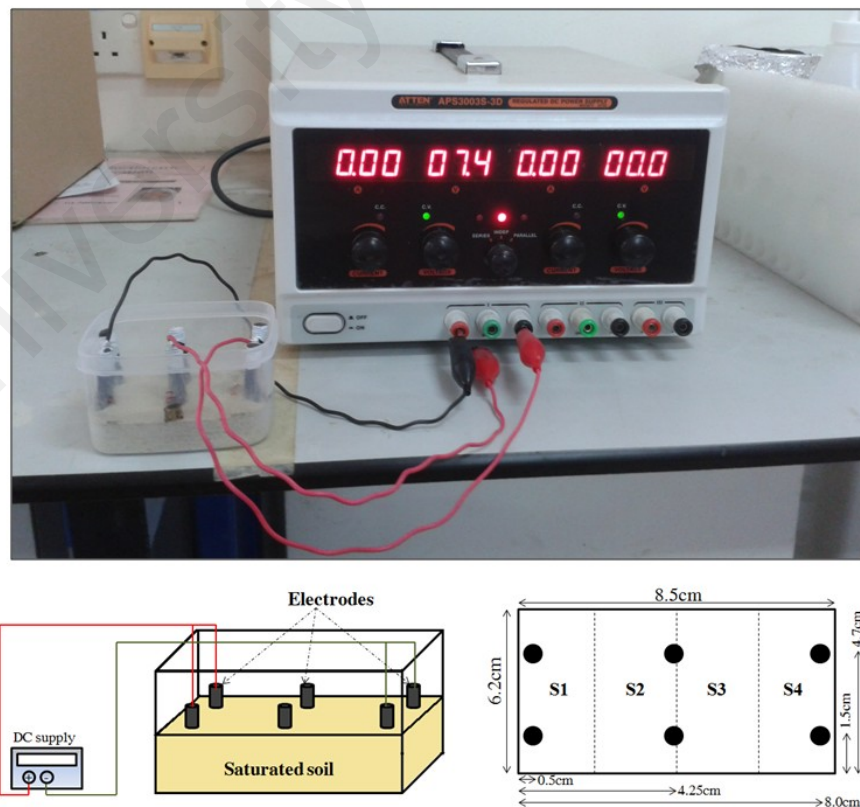
Figure 3.3: Experimental setup for soil pretreatment system using electrokinetic process

3.2.3 Analytical instruments

CRISON Multimeter MM26+ was used for measuring pH. The electrical properties such as current and electric potential difference were measured by Multimeter Sunwa TE-832B. For metal ion concentration, Inductive Couple Plasma – Optical Emission System (ICP-OES) Perkin-Elmer Optima 7000DV was used for analysis. The other analytical equipment used for soil characterisation were as follows: Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX), Fourier Transform Infrared Spectroscopy (FTIR), and X-Ray Diffraction (XRD).

3.3 Experimental procedures

3.3.1 Degree of soil contamination

The ability of the soil studied to be contaminated by Pb was justified. The study was conducted using shake flask adsorption test at a soil particle size of <0.85 mm. Based on some preliminary experiments (Ng *et al.*, 2016), Pb was favoured to adsorb on the soil at solution pH 5. Thus, the maximum Pb contamination level was investigated at solution pH 5. The tests were carried out by contacting 10 g of soil with 200 mL of Pb solution with a concentration of 150 ppm in a conical flask. The mixture was homogenized using an orbital shaker operating at a speed of 175 rpm for 6 h under room temperature. Aqueous sample was taken at different time interval and was filtered through 0.45 μm syringe filter. These samples were then acidified with 0.1 M HNO_3 and Pb concentration in the aqueous samples was analysed by ICP-OES. The adsorption of Pb by the soil was determined using Equation (3.1). The adsorption capacity and kinetics were further evaluated by fitting the results for Pb adsorption into different kinetic models, namely pseudo first order kinetic model, pseudo second order kinetic model, Elovich model, second order kinetic model, film diffusion mass transfer kinetic

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model and double exponential model. Pb speciation in the soil was determined using Tessier's Method (Tessier *et al.*, 1979; Gworek and Mocek, 2003; Venkateswaran *et al.*, 2007). The detailed procedure for this method is discussed in Appendix B4.

Adsorption isotherm study was carried out by contacting 4 g of soil with 100 mL of solution, with Pb concentration of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L. The tests were conducted for 5 h in an orbital shaker at a rotational speed of 175 rpm under room temperature. Aqueous sample was taken after the experiment and was filtered through 0.45 μm syringe filter. Then, the sample was acidified using 0.1 M HNO$_3$ and Pb concentration in the aqueous sample was analysed using ICP-OES. Pb adsorption by the soil was calculated using Equation (3.1). The results obtained were fitted into different isotherm models to determine the adsorption mechanism.

$$\text{Adsorption by soil, mg/kg} = \frac{\text{Initial Pb in the solution - final Pb in the solution (mg)}}{\text{mass of soil used (kg)}} \qquad (3.1)$$

3.3.2 Soil spiking

Artificially contaminated soil was used in this study instead of real contaminated soil. The former was more suitable for use in laboratory experiments as the results obtained had less effect on the variation in contamination levels. Artificially Pb contaminated soil at desired contamination level was prepared by spiking the pretreated soil at a particle size of <0.85 mm with Pb(NO$_3$)$_2$ solution at pre-calculated concentration. The contaminated soil was then homogenized using a trowel/spatula and was air-dried for one week with occasional mixing. The contaminated soil was again homogenized with trowel/spatula and the Pb concentration in the soil was determined. The soil was then stored in a dark and closed space prior to use.

For Pb and Cr co-contaminated soil, the contamination was carried out by spiking the soil with solution containing $Pb(NO_3)_2$ and $K_2Cr_2O_7$. The mixture was spiked according to the procedure mentioned above. The concentration for Pb and Cr was determined and the soil was stored in a dark and closed space prior to use.

3.3.3 Screening for wash solutions

Chemical agents such as acids (Tawinteung *et al.*, 2005; Isoyama and Wada, 2007; Yang *et al.*, 2012) and chelating agent EDTA (Tawinteung *et al.*, 2005; Qiu *et al.*, 2010; Yang *et al.*, 2012; Voglar and Lestan, 2013) are widely used in soil washing to remove Pb. These groups of agents have also been applied to an electrokinetic process to remove Pb, as mentioned in Chapter 2. It is to be noted that the effectiveness of a wash solution is soil dependent, as discussed in Sub-sections 2.3.2.3 and 2.3.2.4. For example, EDTA showed high Pb removal in the works of Reddy and Ala (2005) and Gioannis *et al.* (2008), but low removal in the work of Kim *et al.* (2011b). Another example was citric acid, whereby it was reported to give high Pb removal from dredged marine sediment (Kim *et al.*, 2011b) but low removal for treating industrial harbor soil (Gioannis *et al.*, 2008). As the performance of wash solution is strongly soil dependent, a preliminary screening of wash solution was necessary before they were further applied in electrokinetic washing.

The screening process was conducted using shake flask desorption experiments. The tests were initiated by contacting 10 g of dry 1000 mg/kg Pb contaminated soil with 100 mL of wash solution in a conical flask. Three groups of wash solutions were investigated, namely i) strong acids (HCl, H_2SO_4, HNO_3), ii) weak acids (acetic acid, citric acid), and iii) chelating agent EDTA at a concentration of 0.001 M, 0.01 M and 0.1 M. The mixtures were homogenised using a mechanical shaker at a rotational speed

of 150 rpm for 24 h under room temperature. Following that, aqueous sample was taken from each test and was filtered through 0.45 μm syringe filter to remove the suspended particles in the solution. Pb concentration in the aqueous sample was analyzed using ICP-OES after acidifying with 0.1 M HNO$_3$. The desorption efficiency achieved by each wash solution was determined using Equation (3.2). The best wash solution from each group that gave the highest desorption efficiency with minimum physical nuisance was selected for further application in electrokinetic washing.

$$\text{Desorption Efficiency, \%} = \frac{\text{Mass of Pb detected in aqueous phase, mg}}{\text{Initial mass of Pb in soil, mg}} \times 100 \qquad (3.2)$$

3.3.4 Two-stage electrokinetic washing

A mass of 250 g Pb contaminated soil was compacted into the soil column. The soil was packed slowly and an average soil voidage of 0.47 was obtained. The procedure in determining soil voidage is discussed in Appendix B5. The two ends of the column were then connected to the anode chambers and cathode chamber, with filter papers in between them to prevent soil movement into the chamber. The graphite electrode discs were further installed to the other end of the chambers, as shown in Figure 3.1.

The experiment was conducted in two stages, namely i) initial washing, and ii) electrokinetic process. Initial washing was carried out by pumping the wash solution from a reservoir into the anode chamber from the bottom of the chamber at a speed of 15mL/min using a peristaltic pump while the cathode chamber was left empty. Due to the hydraulic head gradient between the chambers, the wash solution was transported through the soil column and filled up the cathode chamber. This process not only provided soil wetting and desorption condition but also early flushing of desorbed Pb into the cathode chamber. As the overflow levels for both chambers were the same, soil

washing process attenuated with time as a result of the reduction in hydraulic head gradient. It eventually stopped when the cathode chamber was completely filled up. At this point, a constant electric potential difference (voltage) was applied across the soil for 24 h via the graphite electrodes in the chambers as a second driving force to further transport the desorbed Pb from the soil into the cathode chamber under room temperature. The electric current across the soil and effluent generation/electroosmotic flow (EOF) were observed throughout the experiment. The study for two-stage electrokinetic washing was conducted in two main sections, namely i) effect of wash solution, and ii) effect of operating parameters. The details of the experimental parameters in both sections are as shown in Table 3.1.

Table 3.1: Experimental parameters for two-stage electrokinetic washing

Effect of wash solution		
Variable	**Parameter**	**Value**
Independent variables	i) Types of wash solutions	0.01 M $NaNO_3$* 0.1 M HNO_3 0.1 M citric acid 0.01 M EDTA
Constant variables	i) Initial Pb concentration, mg/kg ii) Experimental duration, h iii) Electric potential difference, V	1000 24 15
Main dependent variables	i) Removal efficiency, % ii) Effluent generation, mL iii) System stability iv) Power consumption, kWh/kg Pb removed	
Effect of operating parameters**		
Independent variables	i) Electric potential difference, V ii) Wash solution concentration, M iii) Initial Pb concentration, mg/kg	7.5-30 0.001-0.1 400-1000
Constant variables	i) Types of wash solution ii) Experimental duration, h	Citric acid 24
Main dependent variables	i) Removal efficiency, % ii) Effluent generation, mL iii) Power consumption, kWh/kg Pb removed	

* Reference test: Soil washing was initiated using distilled water as the wash solution. When electricity was applied, $NaNO_3$ was added into the anode reservoir/chamber as background electrolyte to increase the conductivity in the anode chamber for completing the electric circuit in the soil column.
** Conducted using Response Surface Methodology based on Box-Behnken Design

Experiments for normal soil washing in treating 250 g contaminated soil were conducted for removal efficiency comparisons only. The experiment for normal soil washing was conducted by repeating the procedures as discussed above (Sub-section 3.3.4), but without the application of electricity.

3.3.5 Electrokinetic soil pretreatment process

Table 3.2: Experimental parameters for electrokinetic soil pretreatment process

Experiments for single contaminated soil		
Variable	**Parameter**	**Value**
Independent variables	i) Types of wetting agents	0.01 M NaNO$_3$ 0.1 M citric acid 0.1 M EDTA
	ii) Electrode switching time	Nil or 12 h
Constant variables	i) Voltage gradient, V/cm	1
	ii) Experimental duration, h	24
	iii) Volume of wetting agent, mL	35 (Saturated with soil)[*]
	iv) Initial Pb concentration, mg/kg	750
Main dependent variables	i) Normalised Pb concentration at different soil sections, C/C$_0$	
	ii) Electric current generated, mA	
	iii) Soil pH	
	iv) Power consumption, kWh	
	v) Removal efficiency at pretreated region, %	
Experiments for co-contaminated soil		
Independent variables	i) Types of wetting agents	0.01 M NaNO$_3$ 0.1 M citric acid 0.1 M EDTA
Constant variables	i) Voltage gradient, V/cm	1
	ii) Experimental duration, h	24
	iii) Electrode switching time, h	12 (Best wash solution only)
	iv) Volume of wetting agent, mL	35 (Saturated with soil)[*]
	v) Initial Pb concentration, mg/kg	400 (mainly in PbCrO$_4$ form)
	vi) Initial Cr concentration, mg/kg	800 (Cr(VI))
Main dependent variables	i) Normalised concentrations of Pb/Cr at different soil sections, C/C$_0$	
	ii) Electric current generated, mA	
	iii) Soil pH	
	iv) Power consumption, kWh	
	v) Removal efficiency at pretreated region, %	

[*] Preliminary test was conducted to determine the maximum amount of wetting agent that can be uphold by the soil a.k.a soil saturation. Wetting agent was slowly added into a specific amount of soil until the formation of liquid layer on the soil surface. In the soil studied, 35mL of wetting agent is needed to saturate the soil. Further addition of wetting agent will form a liquid layer on the top of the soil.

The equipment as discussed in Sub-section 3.2.2 was used in this study. A mass of 100 g contaminated soil was compacted into the sand box. Three pairs of electrodes (diameter: 0.7 cm; length: 4 cm) were directly injected into the soil and were connected to a direct current supply. The system configuration is as shown in Figure 3.3. Then, the wash solution, a.k.a wetting agent in this study, was sprinkled from the top of the soil. When the soil was saturated with the wetting agent, constant voltage gradient of 1 V/cm (7.5 V) was applied for 24 h under room temperature. During the experiment, 1-2 mL of distilled water was added from time to time to maintain the soil saturation condition and to compensate water losses via evaporation and electrolysis. The electric current across the soil was closely monitored throughout the experiment. For approaching electrode tests, the anode (approaching anode) or cathode (approaching cathode), depending on the direction of heavy metal migration, was switched to the middle electrode (Figure 3.3) at the 12th hour of the experiment and the electric potential difference was adjusted to maintain a voltage gradient of 1 V/cm (3.75 V). The study was conducted for two types of contaminated soils, namely i) single Pb contaminated soil, and ii) Pb and Cr co-contaminated soil. The details of the experimental conditions for each study are as shown in Table 3.2.

3.3.6 Response surface methodology

Response Surface Methodology (RSM) was used to evaluate the effects of operating parameters in the study. RSM is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems for which a response on outcome is influenced by several variables (Montgomery, 2001). The use of RSM and Analysis of Variance (ANOVA) could provide an approximation for the true functional relationship between the set of independent variables and the responses in the

form of a polynomial equation as shown in Equation (3.3), where y is the response, β is the regression coefficient, x is the independent parameters (Montgomery, 2001). The equation is useful to navigate through the effects of the independent variables on the responses not only from the aspect of individual effect but also the interaction effects between these parameters.

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \tag{3.3}$$

In this study, RSM based on Box-Behnken Design (BBD) was conducted by the aid of Design Expert software (Design Expert 6.0.1). BBD is a spherical three level design by combining 2^k factorial design with incomplete block design. It is most efficient in terms of the number of required runs in comparison to Central Composite Design as this design requires fewer numbers of experiments (Montgomery, 2001). The details in number of experiments required and the combination level on the parameters are discussed in Sub-section 4.4.4. Based on ANOVA analysis, the numerical models generated from the analysis were used to analyse the importance of the parameters and their interaction effects.

3.4 Analytical methods

In general, the analysis could be categorised into three main sections, which are: i) electrical properties, ii) properties in soil phase and iii) supporting analysis. The details for the analytical procedures involved in each section were discussed in the following sub-sections.

3.4.1 Electric current

The electric current that passed through the soil was measured by connecting the ammeter (Multimeter Sunwa TE-832B) in series between the direct current supply and the anode/cathode. Three reading were taken and the average value for the electric current was used in results analysis. The current density was calculated using Equation (3.4).

$$\text{Current density} = \frac{\text{Electric current detected, mA}}{\text{Cross sectional area for the soil column, cm}^2} \qquad (3.4)$$

3.4.2 Soil properties

After the experiment, the soil was divided into several sections, i.e. five sections for two-stage electrokinetic washing and four sections for electrokinetic soil pretreatment study and they were dried before the analysis. The pH and metal concentration (Pb and Cr) in the soil at each soil section were analysed using different methods.

3.4.2.1 Soil pH

Soil pH was determined using USEPA SW-846 Method 9045D at room temperature. The soil sample was mixed with distilled water at a soil: water ratio of 1 g : 2.5 mL. The suspension was homogenised for five minutes. Then, the mixture was left undisturbed for 1 h to settle the suspended particles. The pH of the supernatant was then determined by CRISON Multimeter MM26+ at room temperature.

3.4.2.2 Pb concentration in soil

Two types of Pb species were investigated in this study, namely: i) metal oxides adsorbed/bounded Pb ($Pb(NO_3)_2$) and ii) water insoluble Pb ($PbCrO_4$). For the former, KSTM method (Kim *et al.*, 2005b) was used as it gives similar high recovery as USEPA 3050b method at faster extraction time with simpler procedure. This method was discussed in detail by Kim *et al.* (2005b) whereby the soil was dried at 105 ^{o}C. Following this, a mass of 5 g dry soil was contacted with 50 mL 0.1 M HCl in a conical flask and the mixture was agitated at a rotational speed of 100 rpm under 30 ^{o}C for 1 h. The supernatant was then filtered and was analyzed using ICP-OES.

For water insoluble Pb species, USEPA 3050b method was used. This method involved acid digestion using HNO_3, H_2O_2 and HCl. The digestion was conducted in a fume hood. 1 g of soil sample was placed in a digestion vessel. Then, 10 mL of HNO_3 solution at a HNO_3: distilled water ratio of 1:1 was added and the vessel was covered with a watch glass. The mixture was then heated to 95±5 ^{o}C on a hot plate and was refluxed for 10-15 minutes without boiling. Following this, the sample was allowed to cool down and 5 mL of concentrated HNO_3 was added into the vessel. The mixture was again refluxed for 30 minutes. This step was repeated until no brown fume was given off by the sample. The solution was then evaporated to approximately 5 mL and was cooled down.

Digestion was continued by adding 2 mL of water and 3 mL of 30% H_2O_2 into the sample. The vessel was then covered with a watch glass and the sample was warmed for peroxide reaction. Warming was continued until effervescence subsided and the vessel was cooled down. These steps were repeated by adding 1 mL of 30% H_2O_2 into the sample until the general appearance of the sample was unchanged. Following this, the solution was again being reduced to approximately 5 mL by evaporation.

Finally, 10 mL of concentrated HCl was added to the sample and the mixture was heated at 95±5 °C at reflux condition for 15 minutes with a watch glass cover. Then, the digestate was cooled down and was filtered through a filter paper and the supernatant was collected in a 100 mL volumetric flask. The volume of the supernatant was adjusted to 100 mL and the Pb concentration in the supernatant sample was analysed by ICP-OES. Pb concentration in the soil can be calculated based on Equation (3.5), where C_{ICP} is the Pb concentration in the supernatant sample detected by ICP (mg/L), DF is the dilution factor, V_{ES} is the volume of extraction solution/supernatant after the digestion (L), and m_s is the mass of soil sample used (kg). The Pb removal efficiency achieved by the system and normalised concentration for Pb were further determined using Equations (3.6) and (3.7), respectively, where C is the Pb concentration left in the soil after the experiment (mg/kg) and C_0 is the initial Pb concentration in the soil (mg/kg).

$$\text{Pb concentration in soil, C, mg/kg} = \frac{C_{ICP}(DF)(V_{ES})}{m_s} \tag{3.5}$$

$$\text{Removal efficiency, \%} = \frac{C_0 - C}{C_0} \times 100 \tag{3.6}$$

$$\text{Normalised concentration} = \frac{C}{C_0} \tag{3.7}$$

3.4.2.3 Cr concentration in soil

Cr concentration in the soil sample was determined from two aspects: i) Cr(total), and ii) Cr(VI). Cr(total) in the soil, which consisted of Cr(III) and Cr(VI) was determined from the aqueous sample obtained from acid digestion USEPA 3050b via ICP analysis, as discussed in Sub-section 3.4.2.2. The removal efficiency and normalised concentration of Cr at different soil sections was determined using Equations (3.6) and (3.7), respectively.

Cr(VI) concentration in the soil after the experiment was determined using alkaline digestion as specified in USEPA 3060A. A mass of 2.5 g soil was mixed with 50mL of digestion solution containing 20 g/L NaOH and 30 g/L Na_2CO_3. The mixture was further mixed with approximately 400 mg of $MgCl_2$ and 0.5 mL of 1.0 M KH_2PO_4/K_2HPO_4 buffer. Following this, the mixture was stirred for five minutes before it was heated to 90-95 $^{\circ}C$ for 60 minutes with continuous stirring. After the heating process, the mixture was gradually cooled down to room temperature under continuous stirring. The aliquot was collected by filtering the mixture through a filter paper. The pH of the aqueous sample was further adjusted to 2-3 using HNO_3 before it was diluted to 100 mL in a volumetric flask. The Cr(VI) concentration in the aqueous sample was then determined by ICP-OES.

3.4.3 Pb deposition efficiency

Deposition efficiency can be defined as the percentage of Pb that was recovered as solid deposit on cathode from the contaminated soil. This was analysed for two-stage electrokinetic washing process whereby the deposit on the cathode surface was taken and dissolved in 150 mL of 0.1 M HNO_3 in a conical flask for 24 h under vigorous stirring. The cathode was also immersed in another beaker with 150 mL of 0.1 M HNO_3 for 24 h to dissolve the deposit that was left over on the cathode surface. Following this, both of the aqueous samples were diluted and analysed for Pb concentration using ICP-OES to identify the amount of Pb that was deposited on the cathode. Deposition efficiency was calculated using Equation (3.8), where V_{HNO_3} is the volume of HNO_3 solution used (L) and m_s is the mass of soil used in the experiments (kg).

$$\text{Deposition Efficiency, } \% = \frac{\sum C_{ICP}(DF)V_{HNO_3}}{m_s C_0} \times 100 \qquad (3.8)$$

3.4.4 Aqueous properties

The properties in aqueous phase were evaluated only for two-stage electrokinetic washing as electrokinetic soil pretreatment study did not involve wash solution chamber. The wash solution was removed from the chambers after the experiments. Aqueous samples from effluent, wash solution reservoir, anode chamber, and cathode chamber were collected for further analysis for the purpose of supporting the results only. The main properties monitored were pH and Pb concentration. The pH was determined by contacting a calibrated CRISON Multimeter MM26+ directly with the aqueous samples collected. Pb concentrations in the samples mentioned above were also determined via ICP-OES after diluting with 0.1 M HNO_3 solution.

3.5 Precautious steps for chemicals handling

The precautionary steps taken in the handling of chemicals and solutions are as follow:

 i. Mask and gloves were worn during the preparation of acids and other chemical solutions.

 ii. The acid solutions were prepared in fume cupboard.

 iii. The used glassware and experimental apparatus were cleaned by soaking with detergent and rinsing with water. They were then soaked in 2 M HNO_3 for 1 h. Then, another rinsing was carried out using distilled water. Following this, they were dried before used.

 iv. All the chemicals were stored in a dark place to prevent any possible degradation caused by light.

3.6 Minimisation of error

The analytical instrument such as pH meter and ICP-OES were calibrated before each experiment to minimise systematic error. The experiments and soil analysis were at least duplicated to validate the results and the average values with standard errors were reported in this thesis. In addition, readings for pH and metal concentrations were triplicated during the analysis and average readings were taken with an error of within ±4%.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Study outlines

The study consists of two major sections, namely, i) characterisation study for the soil, and ii) incorporation of electrokinetic process in soil remediation methods, as shown in Figure 4.1. The first major section (Section 4.2) is devoted mainly to the properties of the soil, the contamination mechanism as well as the maximum Pb contamination level for the soil. Then, a study on screening of the wash solutions for desorbing Pb from the soil was carried out in order to determine the most efficient wash solution from different groups of chemical agents (Section 4.3). These solutions were further utilised as chemical agents/wash solutions in electrokinetic soil remediation process, which is the second major section of this study (Sections 4.4 and 4.5).
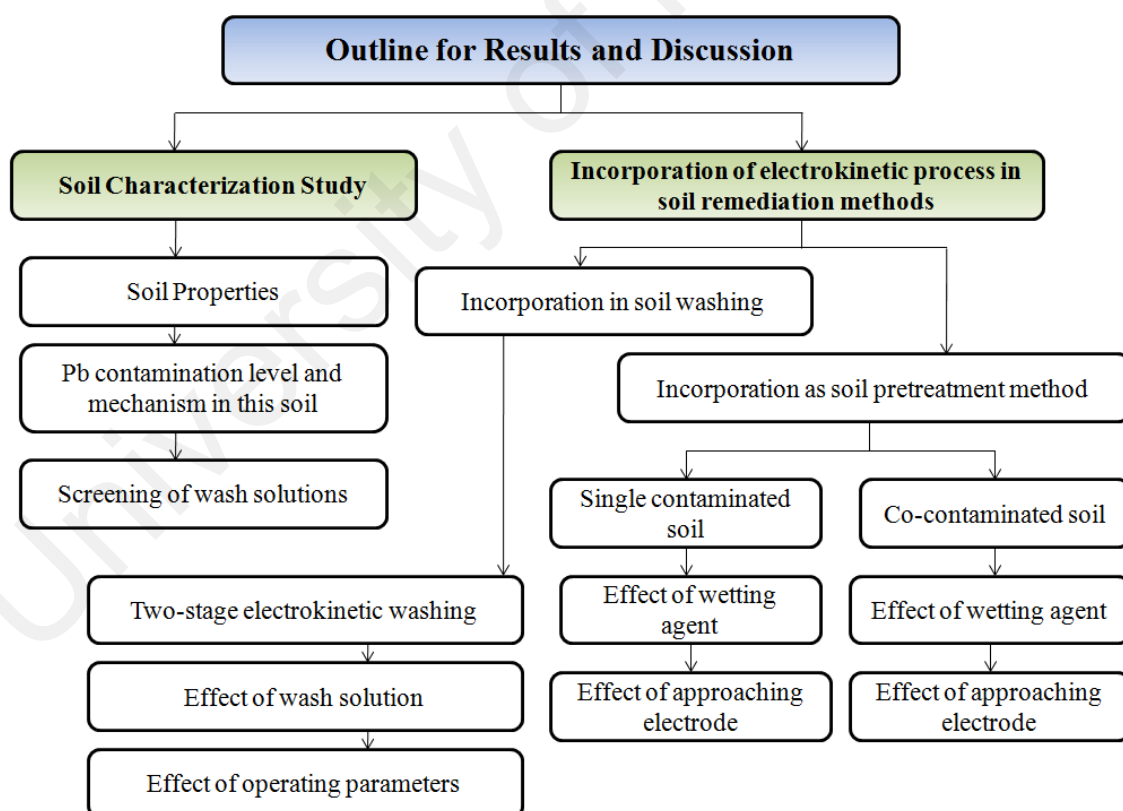
Figure 4.1: The outline for Chapter 4: Results and Discussion

The study on the incorporation of electrokinetic process in soil remediation techniques consists of two parts: i) incorporation of electrokinetic process in soil washing as a two-stage electrokinetic washing process, and ii) incorporation of electrokinetic process as a soil pretreatment method to concentrate heavy metals and reduce contaminated soil volume. The details of these studies are further elaborated in their respective sections (Sections 4.4 and 4.5).

4.2 Soil characterisation

4.2.1 Soil properties

Table 4.1: Characteristic of the natural soil used in this study

Soil properties	Value	Methods
pH	3.97	USEPA SW-846 Method 9045D
Specific gravity	2.5	ASTM D 854 - Water pycnometer method
Cation exchange capacity (meq/100g)	5.1	Ammonium acetate method
Organic matter content, % LOI	1.4%	Loss of weight on ignition
Soil metal content, (mg/kg)		**Methods**
Iron, Fe (mg/kg)	3719	
Aluminium, Al (mg/kg)	2400	
Magnesium, Mg (mg/kg)	635	USEPA 3050b (Acid digestion). Aqueous samples obtained from the acid digestion were analyzed using ICP-OES
Manganese, Mn (mg/kg)	185	
Zinc, Zn (mg/kg)	18	
Lead, Pb (mg/kg)	11	

The soil used in this work was taken from Hulu Langat, Malaysia. The properties of the natural soil such as soil pH, specific gravity, cation exchange capacity, organic matter content and metal content were determined using standard methods after passing through a sieve with mesh number of 20. Table 4.1 shows that the sandy soil had a pH of 3.97 with cation exchange capacity and organic matter content of 5.1 meq/100g and 1.4%, respectively. The soil had high iron and aluminium content, which served as good adsorbent to entrap heavy metals (Violante *et al.*, 2007).
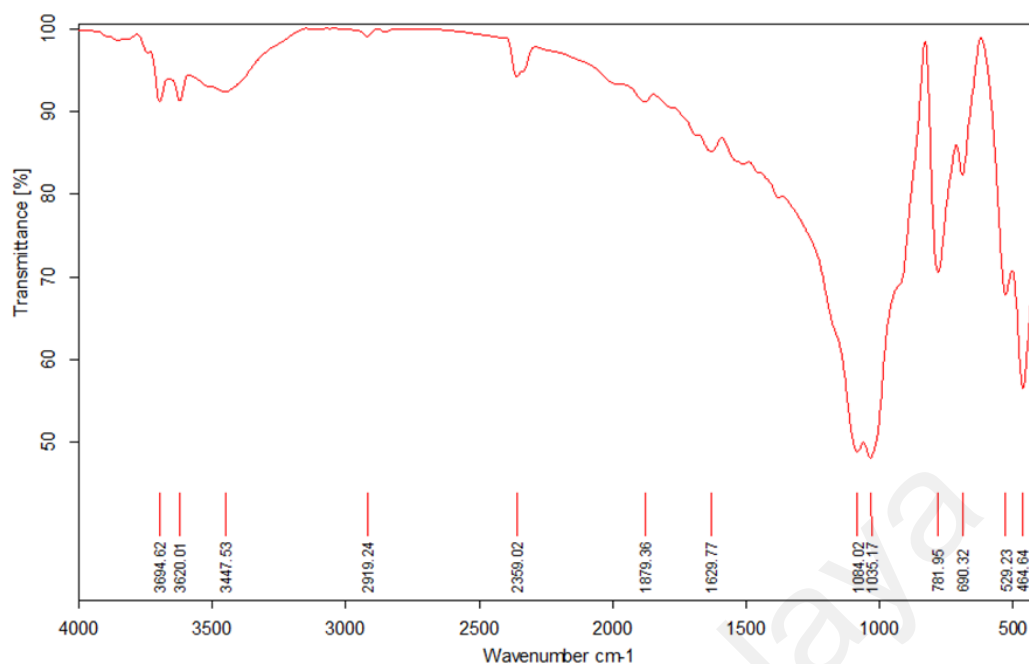
Figure 4.2: FTIR spectrum for the uncontaminated soil
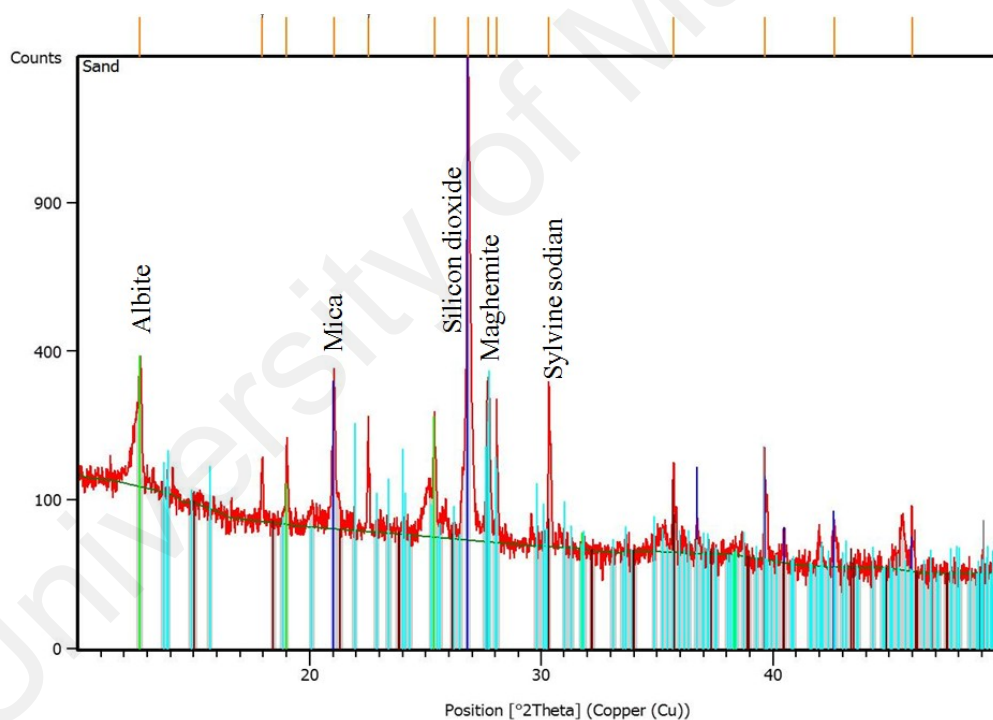
Figure 4.3: XRD spectrum for the uncontaminated soil

Studies of Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) on the soil further revealed the metal species available on the soil. The FTIR spectrum for the soil as shown in Figure 4.2 indicates that iron oxides in the soil are found at 464.64 cm^{-1}, 529.23 cm^{-1}, 690.32 cm^{-1} and 781.95 cm^{-1}, which correspond to Fe-O stretch peaks (Rubim *et al.*, 2001; Sahoo *et al.*, 2010; Avram *et al.*,

2011). The XRD spectrum as shown in Figure 4.3 further suggests that the iron oxide species is maghemite (Isometric $Fe_{21.333}O_{32}$, XRD displacement 0.001), with the presence of other metal species such as silicon dioxide (SiO_2, XRD displacement 0.158), aluminosilicate such as feldspar albite ($AlNaO_8Si_3$, XRD displacement -0.053), mica ($(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$, XRD displacement 0.119), and sylvine, sodian ($Cl_1K_{0.9}Na_{0.1}$, XRD displacement -0.171).

4.2.2 Degree of contamination and the mechanisms

The degree of contamination for Pb in the soil studied was determined. Preliminary study shows that Pb was favoured as an adsorbate on soil surface at a solution pH of 5 in comparison to lower pH values (Ng *et al.*, 2016). On the other hand, precipitation of $Pb(OH)_2$ occurred at pH 6 and above, and this was also reported in the work of Niu *et al.* (2013). Thus, maximum Pb contamination level for this soil was investigated at solution pH 5 via adsorption capacity test. The change in Pb concentration in soil with time at pH 5 is as shown in Figure 4.4. The figure reveals that rapid adsorption occurs at initial stage once the solution is in contact with the soil and equilibrium is achieved in less than 1 h. Similar equilibrium time was also observed when iron oxides and maghemite nanotubes were applied as adsorbents for removing Pb (Lai and Chen, 2001; Boujelben *et al.*, 2009; Mohapatra *et al.*, 2009; Cheng *et al.*, 2012; Ahmedzeki, 2013), Cd (Mohapatra *et al.*, 2009; Ahmedzeki, 2013), Zn (Mohapatra *et al.*, 2009), Cu, Ni and Cr (Hu *et al.*, 2006). Fast adsorption rate could be mainly due to external surface adsorption mechanism as the adsorption sites were available on the soil surface (Hu *et al.*, 2006). The adsorption data could be fitted into pseudo second order rate equation (Equation 4.1) with an R^2 value of 0.9969 whilst it failed to fit into other kinetic models. This kinetic model was also in line with other research publications on iron coated sand (Mohapatra *et al.*, 2009; Ahmedzeki, 2013) and maghemite nanotubes

(Roy and Bhattacharya, 2012) for Pb adsorption. From this model, the adsorption capacity/maximum Pb contamination level for the soil was determined as 1000mg/kg, as shown in Figure 4.4.

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_e}t$$

(4.1)
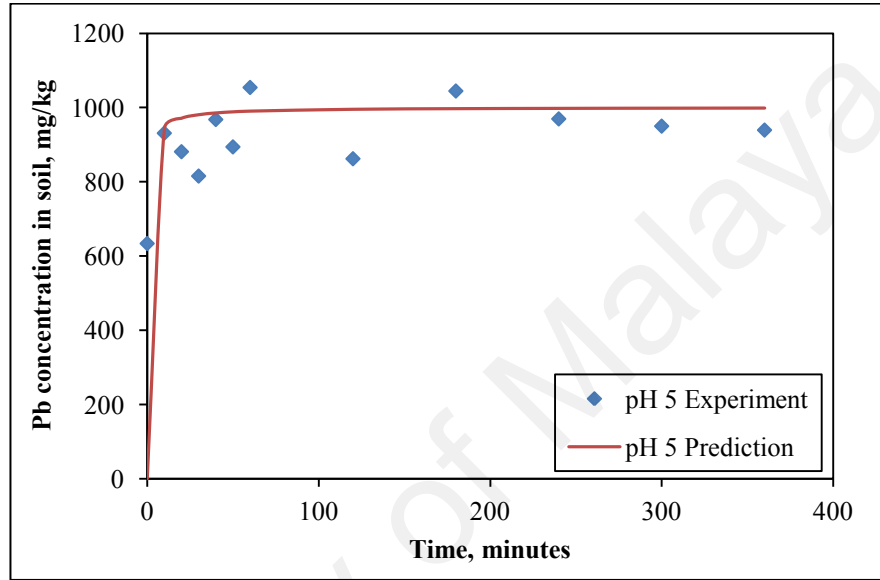
Figure 4.4: Change in Pb concentration in soil with time at solution pH 5 and the curve fitting using pseudo second order kinetic model

The contamination mechanism of Pb was investigated by fitting the experimental data to different isotherm models. Table 4.2 shows that Langmuir isotherm has the best fit with R^2 value of 0.9954 while the maximum adsorption capacity, Q_{max} was determined as 909.091mg/kg. Several studies also reported that the adsorption of Pb on iron oxides coated sand and maghemite nanotubes followed Langmuir adsorption isotherm (Lai and Chen, 2001; Boujelben *et al.*, 2009; Mohapatra *et al.*, 2009; Roy and Bhattacharya, 2012). Langmuir isotherm is valid only for monolayer adsorption on a surface containing finite number of identical sites without transmigration of adsorbate in the plane of the surface (Dada *et al.*, 2012). Thus, it is suggested that Pb adsorption on this soil conforms to another published work that proposed monolayer adsorption of Pb on the iron coated sand (Mohapatra *et al.*, 2009)

and maghemite nanotubes (Roy and Bhattacharya, 2012). In this study, significant presence of iron and other minerals such as aluminosilicate in the soil served as binding sites for Pb adsorption on the soil particles and no further binding was detected after saturation, indicating the occurrence of monolayer adsorption process.

Table 4.2: Adsorption isotherms for Pb adsorption on soil under solution pH 5

Isotherm	Slope	Intercept	R^2	Q_{max}	K_L	n	K_F	β
Langmuir	0.0011	0.0047	0.9954	909.091	0.234	-	-	-
Freundlich	0.2058	2.5791	0.9876	-	-	4.859	13.185	-
Dubinin-Radushkevich	7.00E-07	6.6726	0.8887	790.4481	-	-	-	7.00E-07

It is believed that the type of soil used in this work poses the risk for Pb contamination, depending on the surrounding activities as Pb could be adsorbed on the soil surface easily when Pb solution is in contact with the soil. The adsorption process takes place through monolayer adsorption on the iron (maghemite) and other minerals on the soil surface such as aluminosilicates during the contact. This was further justified through the study of Pb speciation in the soil using Tessier's Method (Tessier *et al.*, 1979; Gworek and Mocek, 2003; Venkateswaran *et al.*, 2007) whereby the results showed that >96% of the Pb in the soil was in Fe-Mn oxide bounded, carbonate bounded and exchangeable forms whilst the Pb species in organic matter bounded and residual form was low and negligible. Maximum Pb contamination level for this soil was determined as 900-1000 mg/kg, which is much higher than the maximum threshold concentration of 400mg/kg in Malaysia (DoE-Malaysia, 2009). Thus, it is taken as soil for investigation.

4.3 Screening of wash solutions
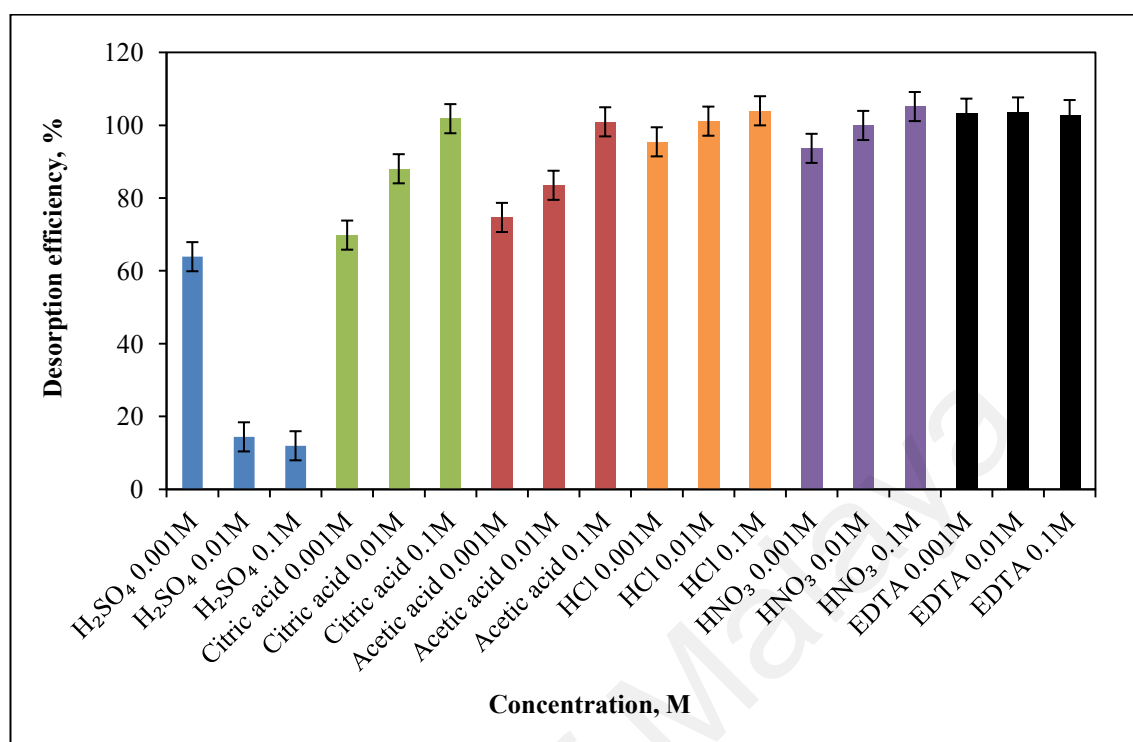
Figure 4.5: Desorption efficiency of Pb from soil using different types of wash solutions

Performance of wash solution was evaluated from Pb desorption efficiency from the soil by contacting excess volume of wash solution (100 mL) with artificial Pb contaminated soil (10 g). The wash solutions used in this study were HCl, HNO_3, H_2SO_4, citric acid, acetic acid and EDTA. Figure 4.5 shows that EDTA could desorb nearly all Pb from the soil effectively regardless of EDTA concentration from 0.001-0.1 M. The use of high EDTA concentration was not necessary as an EDTA: Pb mole ratio of ≈2 (at 0.001 M EDTA concentration) was adequate to completely removed Pb from the soil. On the other hand, the acids also showed positive results. However, the desorption efficiency was highly dependent on the acid concentration. Generally, higher acid concentration gave higher desorption efficiency as it provided lower pH condition, which favoured Pb desorption/dissolution (Carlon *et al.*, 2004). In terms of the nature of acids, strong acids such as HCl and HNO_3 showed better performance than weaker citric acid and acetic acid. However, as the acid concentration increased to 0.1 M, complete

desorption was achieved for all types of acids. The acids not only enhanced Pb desorption but also served as complexation agents (citrate, acetate, chloride) for enhancing Pb solubility in aqueous phase (Chung and Kang, 1999; Kim *et al.*, 2011b). Nevertheless, an exception is observed for H_2SO_4 whereby the increase in acid concentration from 0.001 M to 0.01 M and 0.1 M reduces the desorption efficiency from 63.87% to 14.39% and 11.94%, respectively, as shown in Figure 4.5. This was mainly due to the formation of water insoluble $PbSO_4$ at high H_2SO_4 concentration (Reger *et al.*, 2010).

Wash solutions were screened for further application in electrokinetic washing based on the highest desorption efficiencies achieved. Generally, 0.1 M HNO_3, 0.1 M citric acid, and 0.01 M EDTA showed highest desorption efficiencies among the chemical agents. In contrast, other chemical agents showed disadvantages not only in terms of desorption efficiency but also in other operational aspects. Strong acids such as HCl and H_2SO_4 were not selected as HCl could produce harmful chlorine gas (Cl_2) in the electrokinetic process (Giannis and Gidarakos, 2005) while H_2SO_4 was poor in Pb desorption. On the other hand, among the organic acids, acetic acid was not considered as it not only did not show superior desorption efficiency than citric acid but also caused strong odour to the soil during the experiments and this is not desirable for large scale treatment. Hence, 0.1 M HNO_3, 0.1 M citric acid and 0.01 M EDTA were selected for further study in electrokinetic washing process.

4.4 Two-stage electrokinetic washing

4.4.1 Introduction

Two-stage electrokinetic washing is a configuration where soil washing and electrokinetic process are operated at two different stages in a single equipment. Sub-section 2.3.3.3 suggests that the use of electrokinetic process after soil washing could further enhance the removal efficiency of heavy metals to below regulatory concentration. However, this generates a huge amount of spent wash solution in comparison to both normal soil washing as well as normal electrokinetic process (Kim *et al.*, 2009d). In contrast, two-stage electrokinetic washing that utilises spent wash solution as the catholyte in cathode chamber could reduce wash solution consumption while maintaining the removal efficiency for electrokinetic washing.

Figure 4.6 illustrates the process flow diagram of a two-stage electrokinetic washing for Pb removal. This process is carried out in two stages: i) initial soil washing, followed by ii) electrokinetic process. Soil washing is initiated by filling up the anode chamber with the wash solution while the cathode chamber is left empty. Due to the hydraulic gradient between the two chambers, the solution diffuses into the soil, wets the soil, desorbs and transports Pb into the empty cathode chamber. Soil washing stops when the cathode chamber is fully filled up. At this stage, electrokinetic process is introduced as the second stage of the treatment, which serves as another driving force to further transport the remaining desorbed Pb towards the cathode chamber, as shown in Figure 4.6. The desorption process can also be enhanced as electromigration generally reduces Pb concentration polarization at soil: solution interface in the absence of pore flow. Furthermore, as the spent wash solution is utilised as catholyte, the amount of wash solution used in the process is reduced in comparison to the electrokinetic washing as discussed in Section 2.3.3.3.
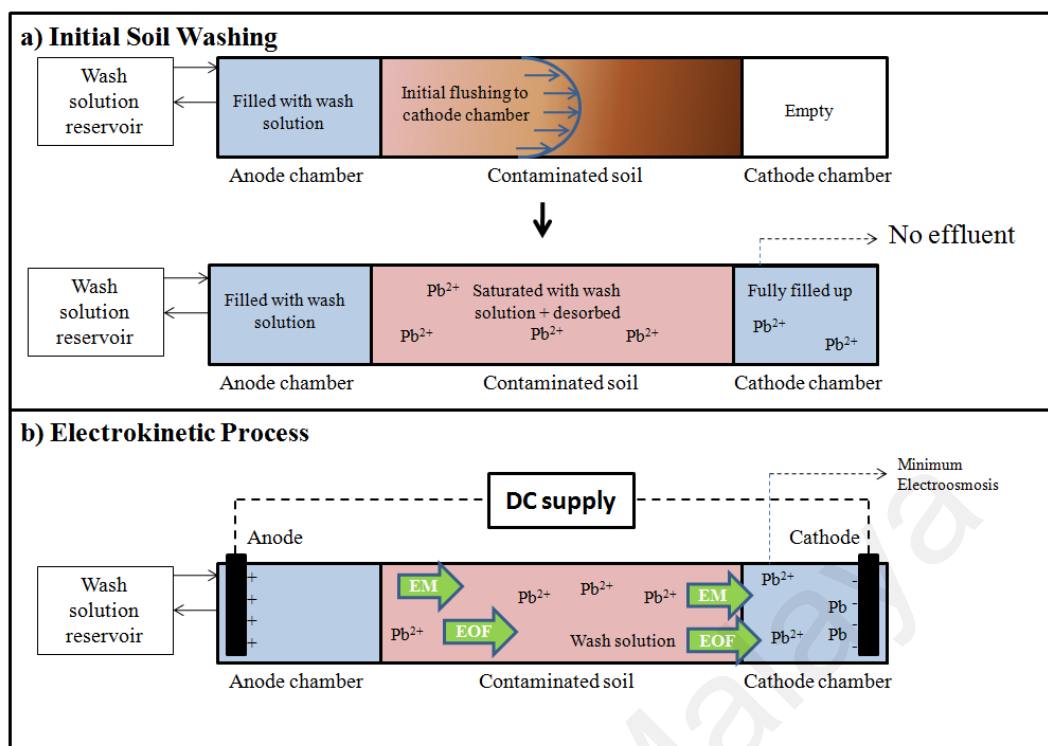
Figure 4.6: Schematic diagram of two-stage electrokinetic washing process

4.4.2 Efficiency comparison
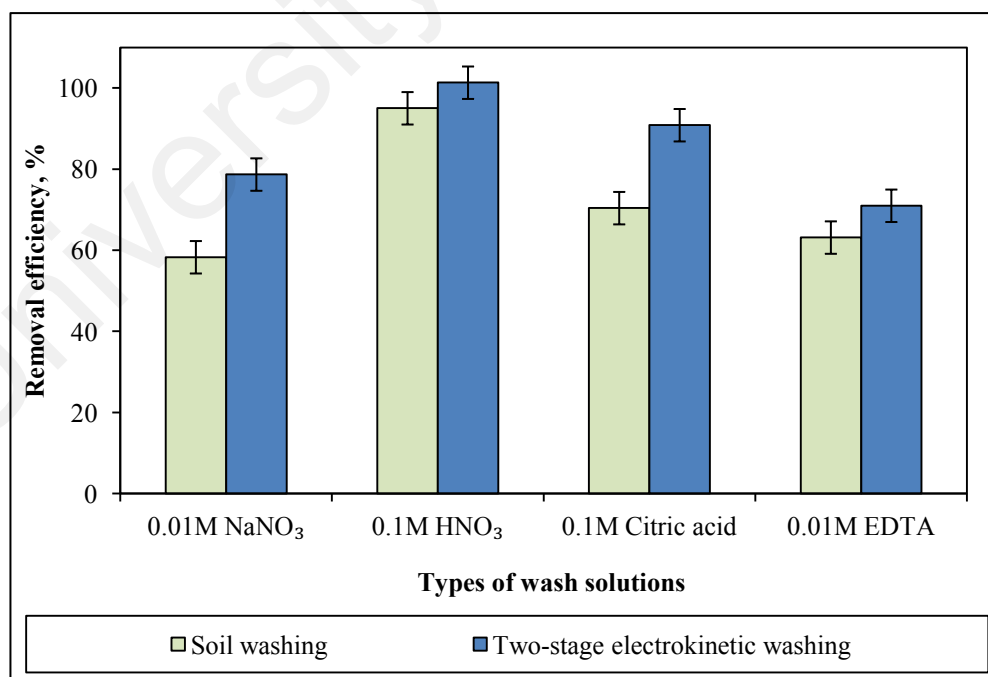
Figure 4.7: Comparison on Pb removal efficiency between soil washing and two-stage electrokinetic washing

Figure 4.7 illustrates that two-stage electrokinetic washing provided higher Pb removal efficiency than normal soil washing whereby an enhancement of 4.98-20.45% was obtained. The use of electricity across the soil provided electromigration and electroosmosis as the driving forces to remove Pb from the soil to the cathode chamber. In addition, the removal of desorbed Pb from the soil by electromigration also prevented local concentration polarisation and maintained Pb desorption from soil: solution interface, which further aided the removal process. However, the enhancement presented by the two-stage electrokinetic washing is wash solution dependent, as shown in Figure 4.7. Electrokinetic washing generally provided higher enhancement when $NaNO_3$ and citric acid were used as the wash solution. In contrast, the enhancements were relatively less significant in the tests that utilized HNO_3 and EDTA.

4.4.3 Effect of wash solution on two-stage electrokinetic washing

The type of wash solutions used was found to significantly affect the performance of two-stage electrokinetic washing, as discussed in Sub-section 4.4.2. Thus, the effect of wash solutions on the process was further evaluated not only for removal efficiency but also for other aspects such as effluent generation, stability of the system and power consumption.

4.4.3.1 Removal efficiency

Figure 4.7 shows that the removal efficiencies for two-stage electrokinetic washing follows a trend of HNO_3 > citric acid > $NaNO_3$ > EDTA. This trend is in line with the order of soil pH, as shown in Figure 4.8a whereby lower soil pH provides higher removal efficiency. Compared to non-acidic $NaNO_3$, low soil pH of ≈2.5 created

by HNO_3 and citric acid was found to enhance Pb desorption from the soil (Yang *et al.*, 2006). This not only increased Pb removal via soil washing but also provided better Pb mobility for electromigration in soil column, resulting in higher removal efficiency. Among the acids, HNO_3 which is a strong acid showed higher removal efficiency than weaker citric acids in soil washing.
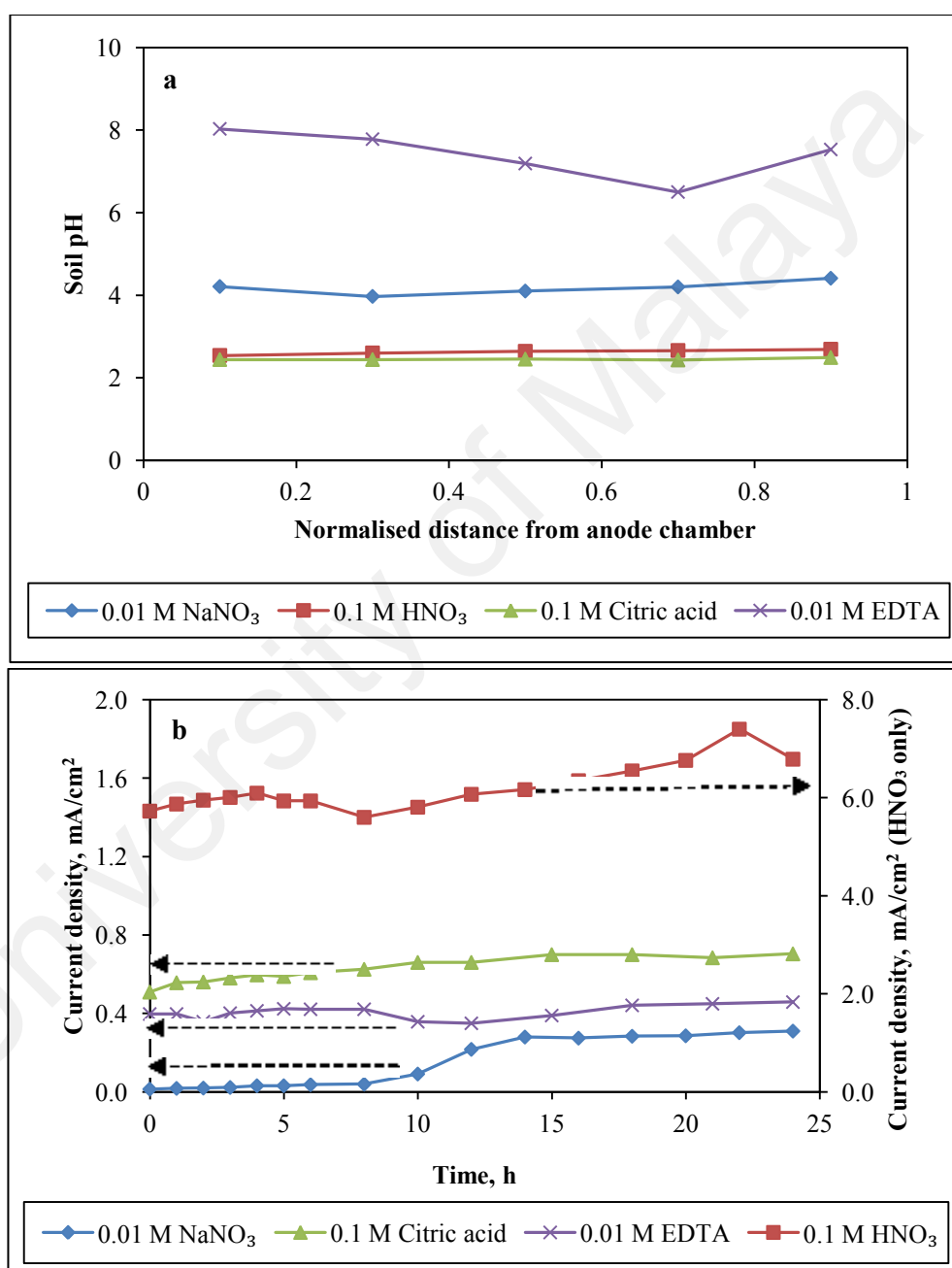
Figure 4.8: Properties of two-stage electrokinetic washing process using different types of wash solutions: a) soil pH; b) current density across the soil

Other than soil pH, the current density across the soil from anode to cathode is another factor that affected Pb transport in electrokinetic process, especially for acid based agents. Figure 4.8b shows that the current density across the soil is generally stable with no significant drop during the experiments. This is perhaps due to the relatively short experimental time in comparison to other studies (Amrate *et al.*, 2005; Kim *et al.*, 2011b). The magnitude of current density in the process was governed by the ionic strength and desorption efficiency provided by the wash solutions, in the order of HNO_3> citric acid > EDTA > $NaNO_3$. Figure 4.8b shows that the acids have higher current density than EDTA and $NaNO_3$ as they are in higher concentration and they can enhance metal desorption/dissolution by providing low pH condition (Mellis *et al.*, 2012). This in turn increased dissolved ions concentration and reduced electrical resistance in the overall system. In terms of removal efficiency, Figure 4.7 shows that HNO_3 is found to provide nearly complete Pb removal, as a result of its high desorption capacity for metals and low electrical resistance for electromigration. On the other hand, a complete removal was not achieved by weaker citric acid. Instead, it enhances the removal efficiency from 70.39% to 90.84%, as shown in Figure 4.7. However, it is worth noting that similar efficiency enhancement of 20.4% is also observed when $NaNO_3$ is used as a wash solution even though it has lower current density, as shown in Figures 4.7 and 4.8b. Nevertheless, a relatively higher amount of effluent at 492.9mL was generated by $NaNO_3$ via electroosmosis than that for citric acid (65.9mL) and this could be one of the reasons for high removal efficiency enhancement in $NaNO_3$ test. The effect of wash solution on effluent generation is further elaborated in Sub-section 4.4.3.2.

On the other hand, a different trend was observed when 0.01 M EDTA was applied. Figure 4.7 shows that EDTA has the lowest removal efficiency in a two-stage electrokinetic washing as a result of lower enhancement by electrokinetic process.

Unlike $NaNO_3$, HNO_3 and citric acid, the main mechanism for Pb removal in EDTA test was water soluble complex formation as Pb desorption and mobility was generally poor at a high soil pH of 7-8 (Figure 4.8a) due to possible $Pb(OH)_2$ precipitation (Niu *et al.*, 2013). The presence of iron and other mineral content in the soil may compete with Pb for EDTA complex formation, which may reduce the availability of EDTA for Pb to form complex (Kim *et al.*, 2011b). This phenomenon may cause lower Pb removal in comparison to acidic based solutions. In addition, anionic Pb-EDTA complexes were formed at this pH (Niinae *et al.*, 2008; Zhang *et al.*, 2014) and their migration towards the anode in electrokinetic process may also cause low enhancement in removal efficiency. This is observed from the analysis of Pb residual in the soil sections, as shown in Figure 4.9d.

Figure 4.9 shows that, in general, lower Pb residual is observed in any soil section in a two-stage electrokinetic washing in comparison to the tests that utilised soil washing only due to the removal enhancement by electromigration and electroosmosis. This was true for all wash solutions in this study except for EDTA test where more Pb residual was detected near the anode region (normalised distance from anode chamber <0.5) in the two-stage electrokinetic washing than in soil washing. Unlike soil washing, which showed one way Pb transport, a higher Pb concentration near anode region in two-stage electrokinetic washing indicated the transport of Pb-EDTA complexes towards anode. This was further justified where Pb concentration of 3.476 mg/L was detected in anode chamber whilst this was not detected in $NaNO_3$, HNO_3, and citric acid tests. Counter migration of anionic Pb-EDTA towards the anode chamber could be the main reason for the delay in Pb removal from the soil and this eventually showed low enhancement in removal efficiency. This trend was also reported by Yang and Lin (1998). Nevertheless, it is worth noting that majority of Pb removed was still accumulated in the cathode chamber in comparison to anode chamber at the end of the

experiment. The electromigration of anionic Pb-EDTA complexes towards the anode may be slowed down by the electroosmosis, which was in opposite direction, as reported in the work of Villen-Guzman *et al.* (2015).
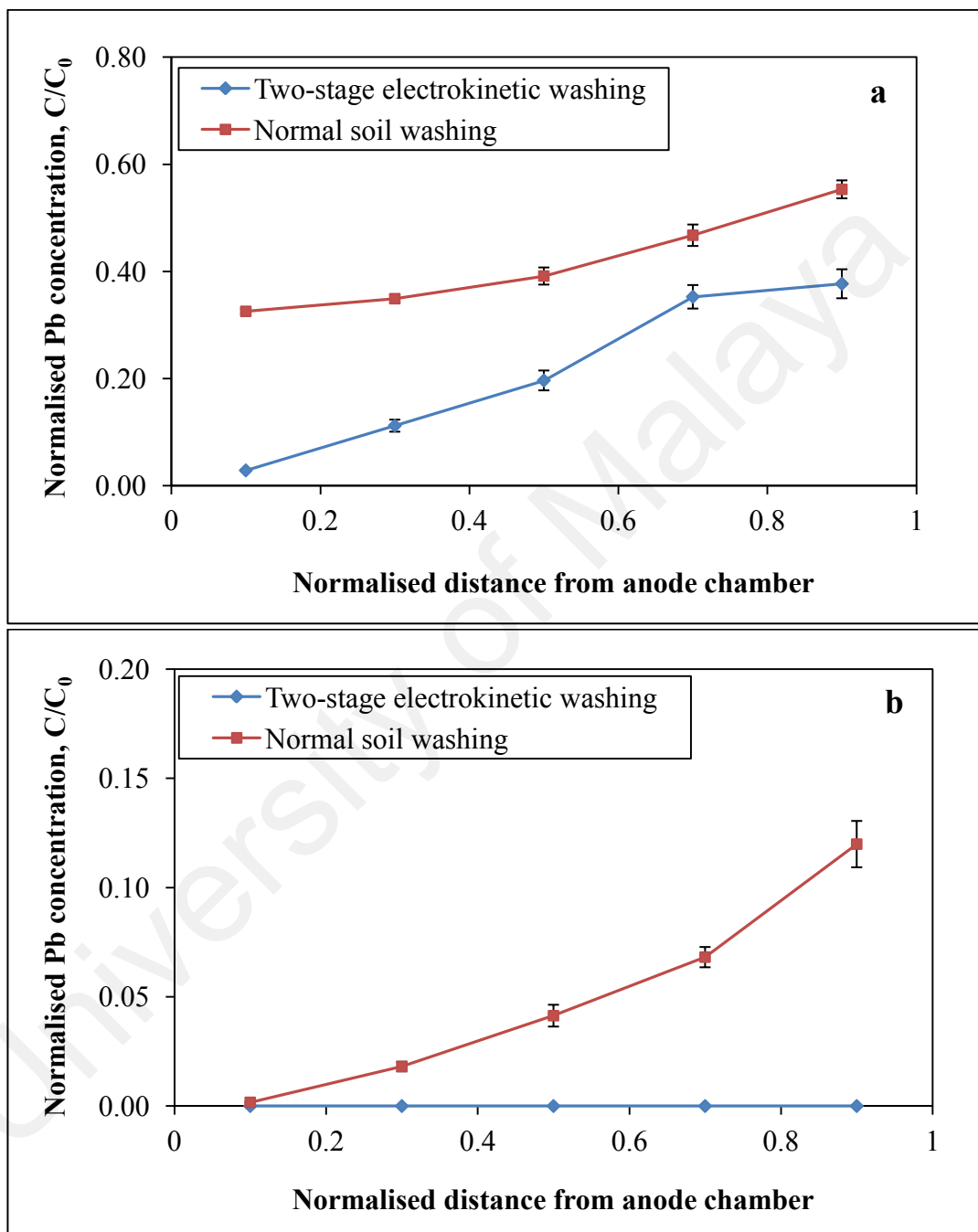
Figure 4.9: Normalised Pb concentration at different soil sections after the experiments using different types of wash solutions: a) 0.01 M NaNO$_3$, b) 0.1 M HNO$_3$, c) 0.1 M citric acid, d) 0.01 M EDTA.
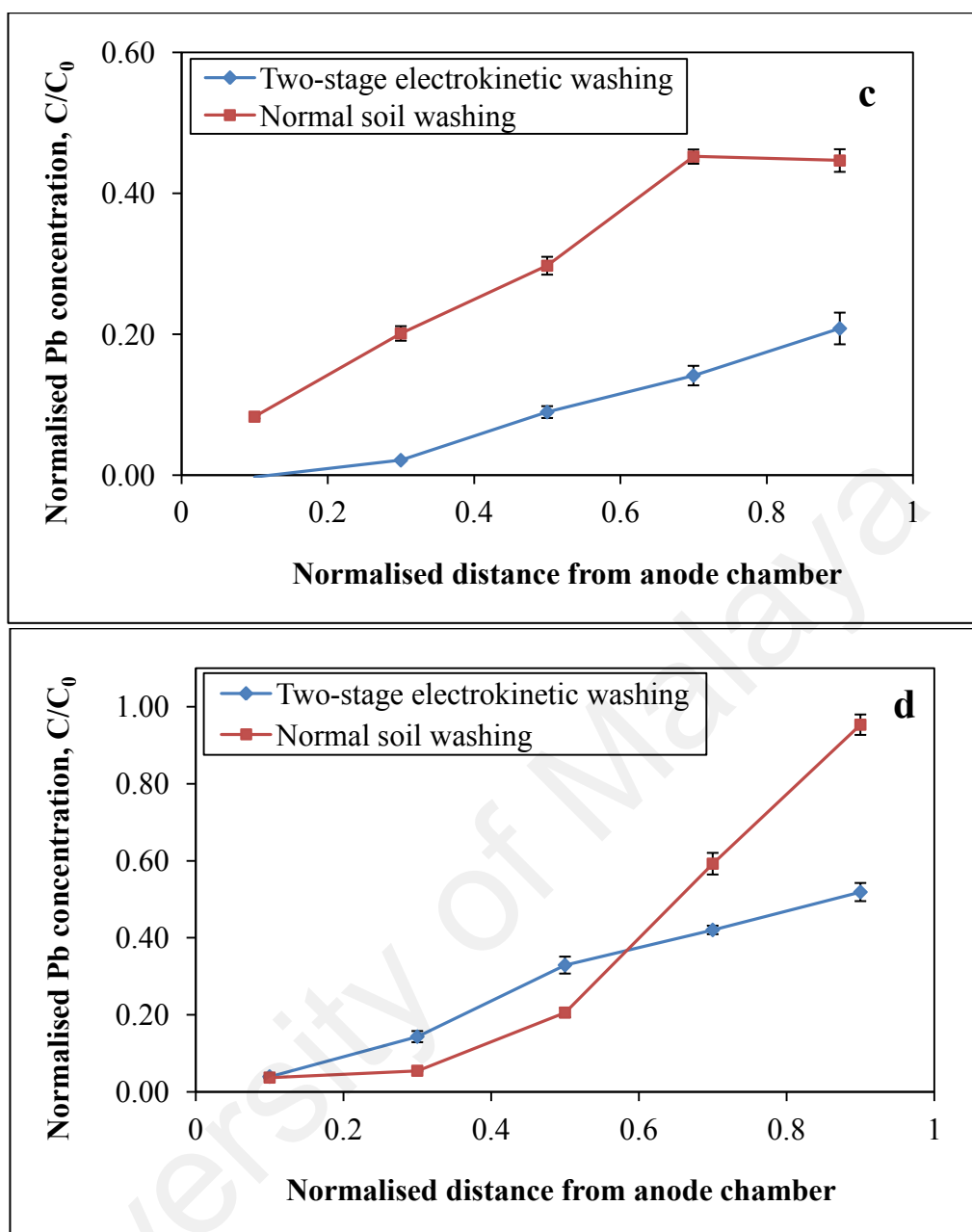
Figure 4.9, continued'

4.4.3.2 Effluent generation

Application of electrokinetic process was found to cause extra effluent generation due to the presence of electroosmosis. The extra effluent generated is collected in an effluent collecter, as shown in Figure 3.1. Figure 4.10 illustrates that the amount of effluent generated under a constant electric potential difference of 15V follows a trend of 0.01 M $NaNO_3$ > 0.1 M HNO_3 > 0.1 M citric acid > 0.01 M EDTA.
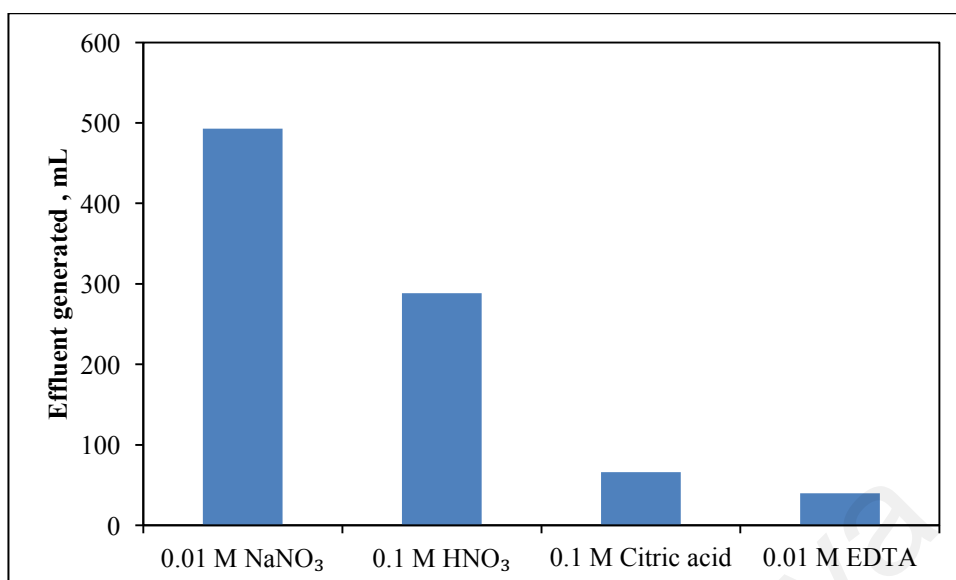
Figure 4.10: Volume of effluent generated under different types of wash solutions

Figure 4.10 illustrates that the volume of effluent generated via electrosmosis is dependent on the types of wash solutions used. It was found that $NaNO_3$ generated the highest amount of effluent at 492.9 mL. This could be due to this test which utilised 0.01 M $NaNO_3$ as wash solution showed a higher average soil pH at 4.2 (Figure 4.8a) compared to HNO_3 and citric acid. Higher soil pH condition resulted in higher negativity of soil zeta potential (Acar and Alshawabkeh, 1993; Reddy and Saichek, 2003; Baek *et al.*, 2009; Lee *et al.*, 2009). According to Helmholtz-Smoluchowski theory, as shown in Equation (2.4) (Lee *et al.*, 2009; Asadi *et al.*, 2013), higher effluent generation was expected as electroosmosis was proportional to the negativity of soil zeta potential. Besides that, the use of $NaNO_3$ as electrolyte was also reported to favour electroosmotic flow (Alcántara *et al.*, 2008b; as cited in Alcántara *et al.*, 2012).

On the other hand, 0.1 M HNO_3 also generated high effluent volume via electroosmosis at 288.5 mL during the experiment. However, it was worth noting that HNO_3 test showed lower effluent generation than $NaNO_3$ test even though it recorded higher electric current. This was probably caused by relatively low soil pH condition at about ≈2.5 in HNO_3 test, as low pH was reported to reduce and even reverse the

direction of electroosmosis in electrokinetic soil treatment (Zhou *et al.*, 2004; Zhou *et al.*, 2005; Baek *et al.*, 2009) as a result of reduction in negativity of soil zeta potential. Thus, according to Helmholtz-Smoluchowski theory (Lee *et al.*, 2009; Asadi *et al.*, 2013), electroosmotic force was expected to be smaller than that in $NaNO_3$.

Similar reason could be applied for citric acid test. In comparison to $NaNO_3$ and HNO_3, 0.1 M citric acid shows relatively low effluent generation at 65.9 mL, as shown in Figure 4.10. This was attributed to the low electric current and low pH condition. As citric acid provided similar low soil pH as in HNO_3 test, it showed weaker electroosmosis than $NaNO_3$. Under similar soil pH condition, citric acid only provided about 10% of current density as in HNO_3. As electroosmosis was found to be higher at higher current density (Yang and Long, 1999; Kim *et al.*, 2005a), lower amount of effluent was collected in citric acid test. In contrast, lowest volume of effluent is collected at 39.8 mL when 0.01 M EDTA is employed as the wash solution even though it has high soil pH, as shown in Figure 4.10. This trend was in agreement with other sandy soil treatments using electrokinetic process where EDTA showed lower electroosmosis rate than citric acid (Kim *et al.*, 2008a, 2008b). This could be due to electromigration of anionic EDTA complexes in opposite direction to electroosmosis/cation transport, which may compress electrical double layer, as suggested by Colaccico *et al*. (2010). Thus, lower electroosmosis rate was observed.

The presence of electroosmosis may affect the removal enhancement given by electrokinetic process. An example is given for $NaNO_3$ and citric acid. Figure 4.7 shows that two-stage electrokinetic washing provides similar Pb removal enhancement of ≈20% when both $NaNO_3$ and citric acid are used as the wash solutions, even though citric acid has higher Pb desorption efficiency from soil washing and lower resistance for electromigration. In this case, electroosmosis flow of 492.9 mL (≈5.6 pore volume) in $NaNO_3$ test may provide additional flushing effect in the system in which 43% of Pb

was removed out of the cathode chamber/system via effluent in comparison to citric acid test, which only showed 2% removal via 65.9mL of effluent. From this observation, it can be suggested that both electromigration and electroosmosis were responsible in enhancing Pb removal efficiency in two-stage electrokinetic washing, especially when 0.01 M $NaNO_3$ was applied. In contrast, for citric acid, similar enhancement in removal efficiency could be achieved at lower effluent generation, as discussed in Sub-section 4.4.3.1. This mechanism will be considered as one of the criteria for selection of the best wash solution for the two-stage electrokinetic washing as the effect of electroosmosis could be controlled by the current intensity and the nature of wash solution (Murillo-Rivera *et al.*, 2010).

4.4.3.3 System stability – anode chamber
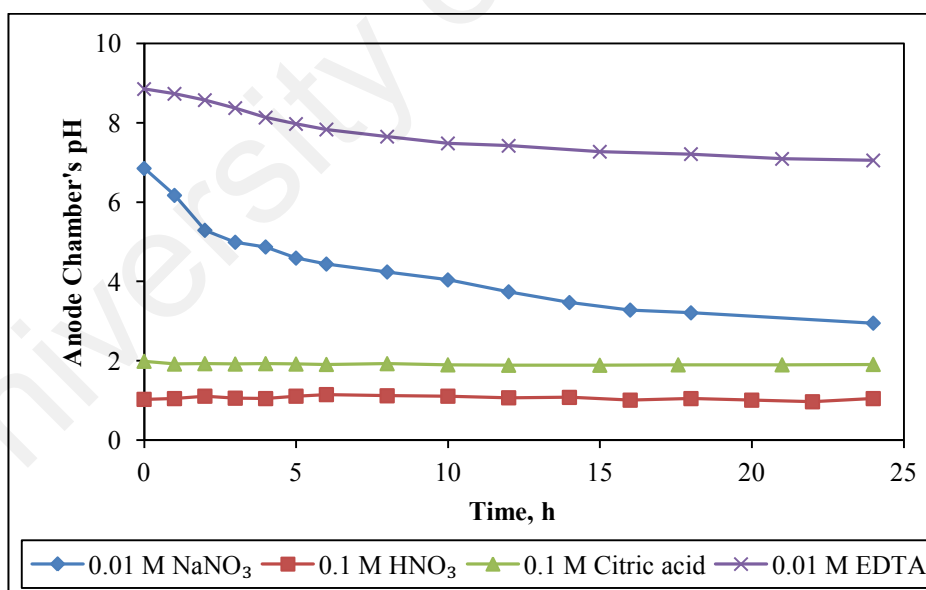
Figure 4.11: pH of wash solutions in anode chamber at different time

System stability in anode chamber during two-stage electrokinetic washing was analysed from two aspects, namely anode chamber pH and physical appearance of anode. Figure 4.11 reveals that the application of electricity caused a decrease in anode chamber pH from 6.85 to 2.95 and 8.85 to 7.05 when $NaNO_3$ and EDTA were used,

respectively. The pH drop in anode chamber was mainly due to electrolysis of water at anode which generated H^+ ions, as explained by Equation (2.1) (Acar and Alshawabkeh, 1993). It was also found that the pH drop was slower in EDTA test as EDTA solution which had an initial pH of ≈ 9 acted as a buffer solution. Among them, the electrolysis and acid front in $NaNO_3$ test provided slight acidification for soil in the anode region (normalised distance from anode: 0.1-0.5), reducing the pH from an average of 4.71 to 4.09. In contrast, stable low pH values are observed for acidic wash solutions, as shown in Figure 4.11. The increase in H^+ concentration in anode chamber via electrolysis showed less variation in pH as the H^+ content in the chamber was already at a high concentration.
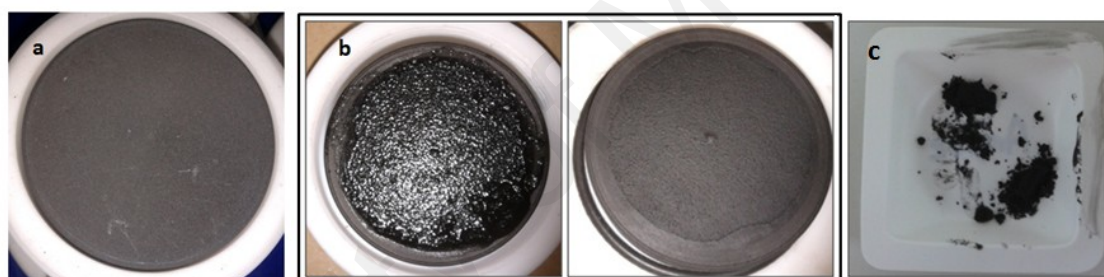
Figure 4.12: Physical appearance of graphite anode in 0.1 M HNO_3 test: (a) before the experiment; (b) after the experiment; (c) carbon particles collected in anode chamber

As for electrode stability, it was found that graphite anode was stable throughout the experiments when $NaNO_3$, citric acid and EDTA were used as the wash solution. However, when 0.1 M HNO_3 was used, corrosion of graphite anode was observed. Figure 4.12b shows that in contrast to the original anode (Figure 4.12a), the used anode had corroded. Carbon particles were also collected in the wash solution in the anode chamber after the experiment, as shown in Figure 4.12c. The carbonaceous particles could be graphite oxides as they could be produced in the presence of HNO_3 under strong oxidizing condition (Brodie, 1859, as cited in Hummers and Offeman, 1958), which was achieved in the anode chamber. Thus, it was suggested that HNO_3 was

unsuitable as the wash solution in electrokinetic washing when graphite was used as an electrode.

4.4.3.4 System stability – cathode chamber

Similar evaluation for system stability was conducted for cathode chamber. Figure 4.13 shows that the pH in the cathode chamber increases from 4.18 to 9.85 and 4.87 to 11.93 when $NaNO_3$ and EDTA are used, respectively. Wash solution pH in the cathode chamber was reduced to a range of 4-5 after soil washing process as the soil was acidic. When electric current was induced, water was electrolysed in the cathode chamber and OH^- was produced, as shown in Equation (2.2) (Acar and Alshawabkeh, 1993). Thus, the pH in cathode chamber increased. It was observed that pH rise in EDTA test was faster as it had relatively higher current and lower EOF in comparison to $NaNO_3$. The high cathode chamber's pH in this test eventually increased the soil pH in the cathode region (normalised distance from anode: 0.5-0.9) from 5.34 to 7.07.
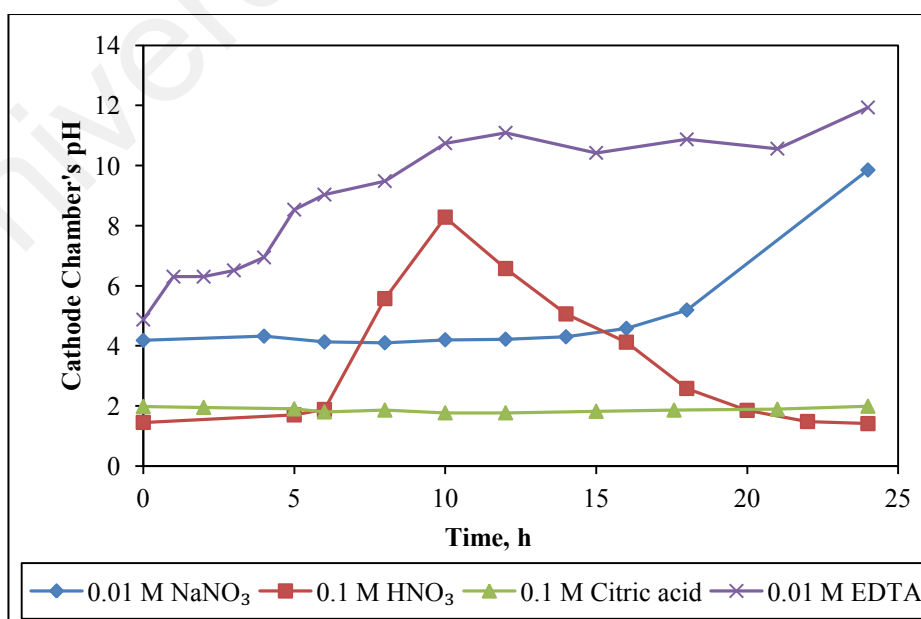
Figure 4.13: pH of wash solutions in cathode chamber at different time

In contrast, the use of citric acid maintains low pH in cathode chamber close to its initial pH at 2, as shown in Figure 4.13. Due to its acidic characteristic, citric acid served as a buffer solution to prevent pH rise in the cathode chamber throughout the experiment. However, different behaviour was noticed for HNO_3. Figure 4.13 reveals that HNO_3 provides a pH of < 2 in cathode chamber until the 6th hour. Then, a rapid increase in pH occurred and a maximum pH of 8.28 was achieved at the 10th hour. This unusual trend was also noticed by Almeira O et $al.$ (2012) when HNO_3 concentration was higher than 0.12M. It was suggested that under high HNO_3 concentration, NO_3^- in cathode chamber underwent reduction and more OH^- ions were produced, as shown in Equations (4.2-4.5) (Almeira O et $al.$, 2012). Excessive OH^- prevailed over the H^+ ions in the cathode chamber, which increased the chamber's pH. However, it was worth noting that the pH was again decreased after 10th hour and eventually reduced to 1.41, as a result of electroosmosis and acid front after the consumption of NO_3^- in the cathode chamber.

$$NO_3^- + 2e^- + H_2O \rightarrow NO_2^- + 2OH^-$$

(4.2)

$$2NO_3^- + 16e^- + 12H_2O \rightarrow 2NH_3 + 18OH^-$$

(4.3)

$$2NO_3^- + 10e^- + 6H_2O \rightarrow N_2 + 2OH^-$$

(4.4)

$$NO_3^- + 7H^+ \rightarrow NH_4 + 3OH^-$$

(4.5)

With regard to physical appearance of the cathode, no corrosion on graphite cathode was observed. Instead, Pb and other metal ions were found to deposit on cathode surface during electrokinetic washing process. This phenomenon, known as electrodeposition, provided Pb recovery as solid from the spent wash solution in the cathode chamber. The electrodeposition was strongly dependent on the types of wash solution, whereby acid-based agents yielded Pb deposition efficiency as high as 60%-70% whilst EDTA showed lower deposition efficiency at 46.41%. For $NaNO_3$, the deposition

efficiency only accounted for the precipitates that deposited on the cathode and the observed Pb deposition efficiency was 18.56%.
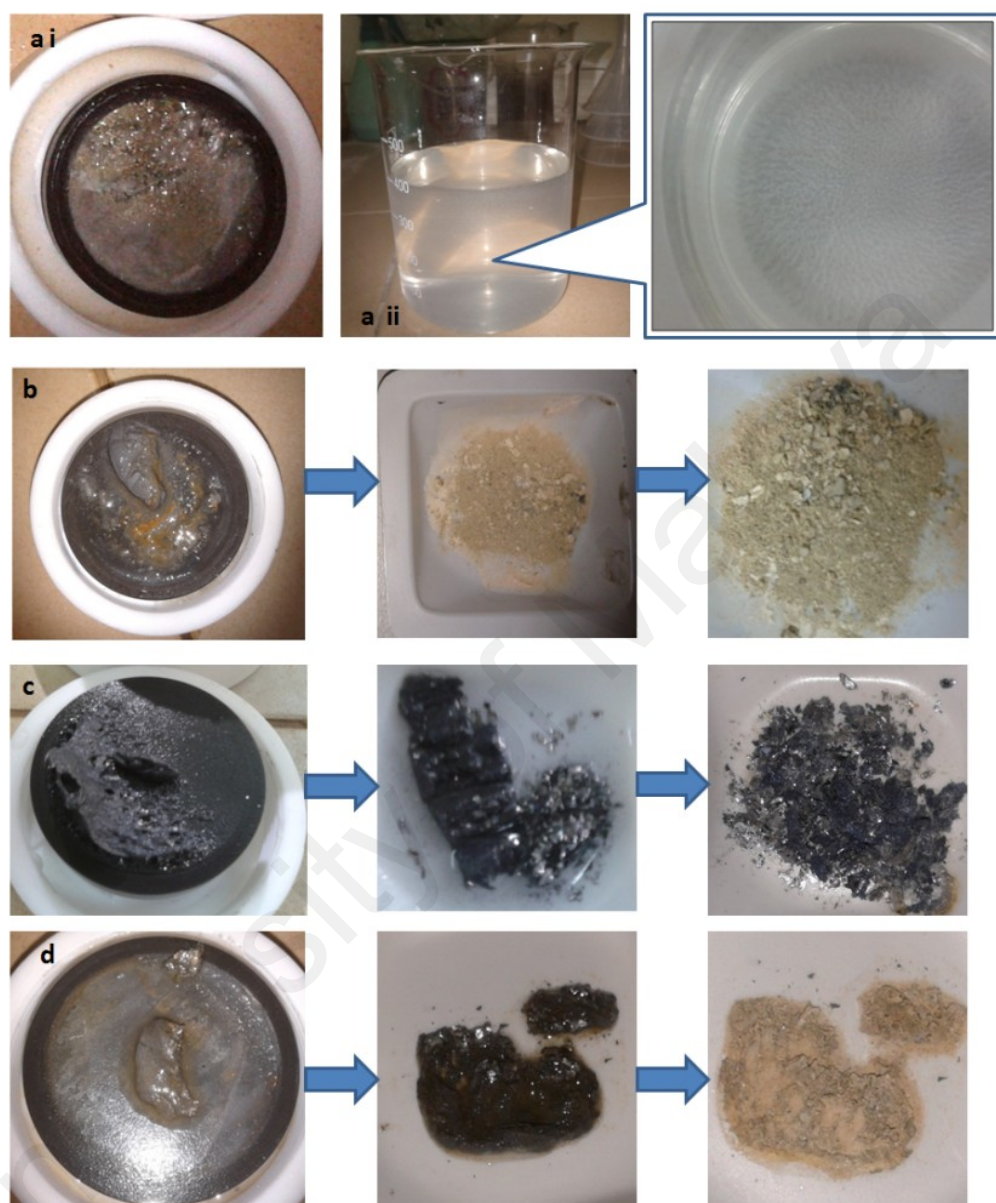
Figure 4.14: Physical appearance of cathode and deposits after the experiments: a) 0.01 M $NaNO_3$; b) 0.1 M HNO_3; c) 0.1 M citric acid; d) 0.01 M EDTA

Figure 4.14 shows that the physical appearance of deposits is dependent on the types of wash solution used. The figure reveals that when $NaNO_3$ is used, white/brownish precipitates are deposited on the cathode surface (Figure 4.14a-i) and some of the precipitates are suspended in the effluent (Figure 4.14a-ii). The white precipitate was identified as $Pb(OH)_2$ as a result of high pH in the cathode chamber. This was supported by a test which showed that Pb was detected in the sample of 0.1 M

HNO$_3$ solution after the white precipitate was dissolved in the solution. In contrast, soft and malleable grey solids were deposited on cathode surface when HNO$_3$, citric acid and EDTA were used. The solids in HNO$_3$ and EDTA tests were identified as mainly Pb as the colour of the deposit changed from grey to whitish yellow when they were dried in open air for one week, indicating Pb oxidation in the presence of moisture and oxygen. The illustrations are as in Figures 4.14b and 4.14d. On the other hand, Figure 4.14c shows a mixture of black and silver deposits is obtained on the cathode surface when citric acid is used. The colour of the deposits remained the same after drying at room temperature, suggesting a mixture of metals was deposited. This is verified through SEM analysis for soil surface, as shown in Figure 4.15. Unlike other tests which showed similar soil texture to virgin soil after the experiment, citric acid provided smoother soil surface, supporting the extraction of Pb and other metals from the soil. This is further justified through SEM-EDX analysis which shows that the deposits are primarily Pb, with the presence of other elements such as aluminium (Al) and titanium (Ti), as shown in Figure 4.16.

Natural soil
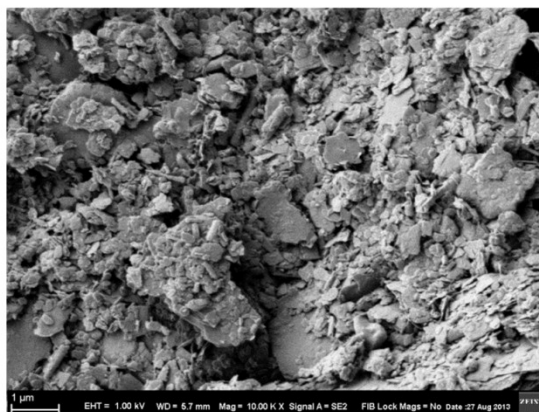
Spiked soil
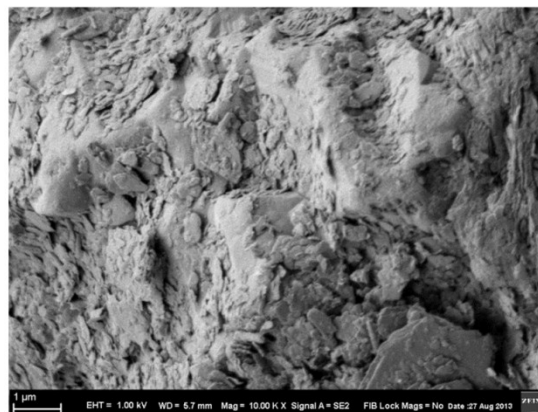
NaNO$_3$
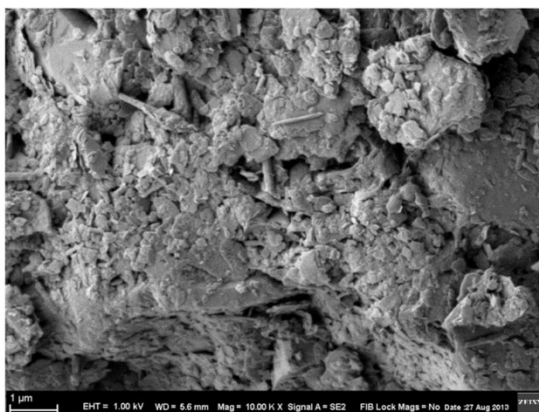
HNO$_3$
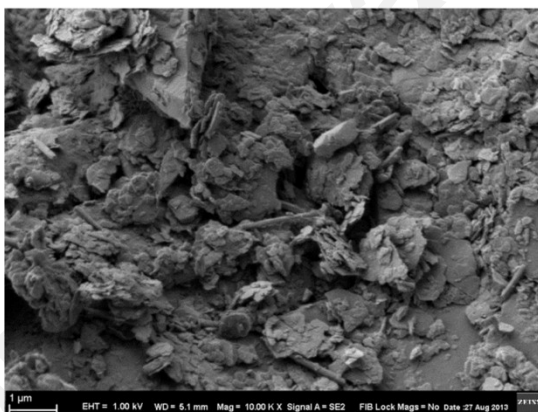
Citric acid
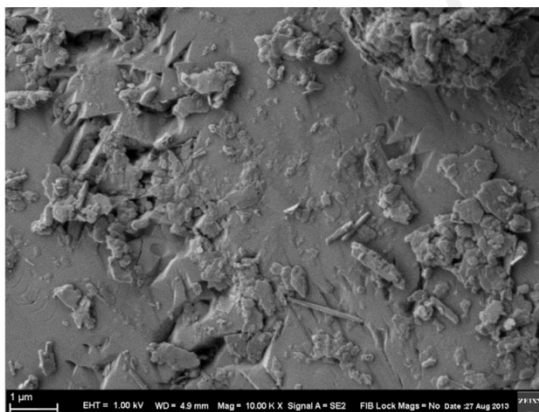
EDTA
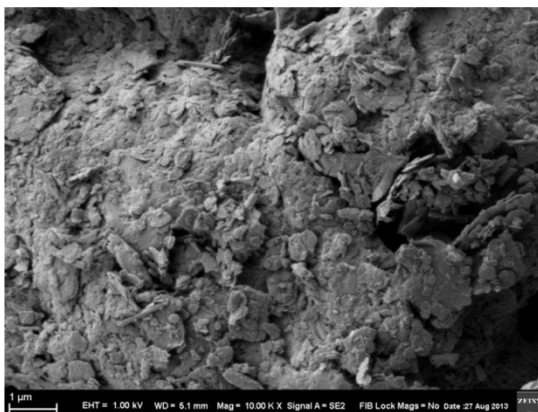
Figure 4.15: SEM images for the soil samples after the experiments of two-stage electrokinetic washing under different types of wash solutions
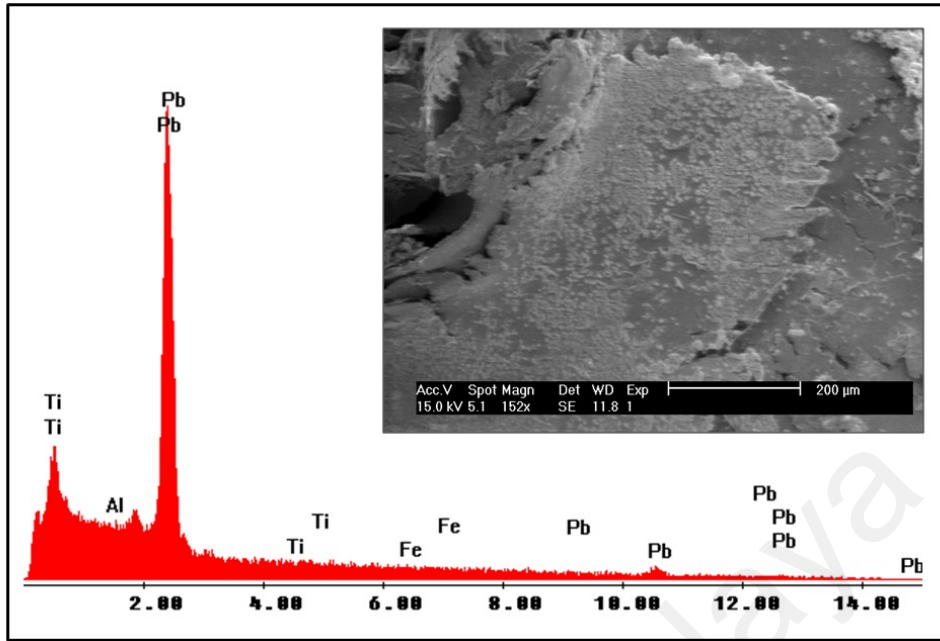
Figure 4.16: SEM-EDX analysis for the deposits obtained after two stage electrokinetic washing using 0.1 M citric acid

4.4.3.5 Power consumption

Application of two-stage electrokinetic washing process results in additional electric power consumption in the electrokinetic process (Stage 2) and this contributes to additional operating cost in comparison to normal soil washing. Power consumption can be expressed in terms of average power consumed by electrokinetic process per unit mass of Pb removed in electrokinetic washing system. This was calculated using Equation (4.6), where E_{PC} is the power consumed per kg Pb removed (kWh/kg), m_{Pb} is the mass of Pb removed (kg), V is the electric potential difference used (V), I is the current across the soil (A), and t is the time (h).

$$E_{PC} = \frac{1}{m_{Pb}} \int_0^t VI.dt \qquad (4.6)$$

Table 4.3 shows that acidic wash solutions consume more electric power in electrokinetic washing process but yield higher removal efficiency than the other two. Among the acidic wash solutions, citric acid only consumed 10% of the power than that of HNO_3 test for achieving high removal efficiency at 90.84%. In contrast, even though HNO_3 provides 99.99% Pb removal efficiency in two-stage electrokinetic washing, its relatively small removal enhancement of 4.98% compared to soil washing at high power consumption makes it less attractive as a wash solution in two-stage electrokinetic washing.

Table 4.3: Power consumption for two-stage electrokinetic washing under different types of wash solutions

Wash solution	0.01 M NaNO$_3$	0.1 M HNO$_3$	0.1 M citric acid	0.01 M EDTA
Removal efficiency by two-stage electrokinetic process, %	78.67	99.99	90.84	70.97
Power consumption, kWh/kg Pb removed	3.09	114.47	12.93	10.43

4.4.3.6 Selection of best wash solutions

Table 4.4: Performance of two-stage electrokinetic washing on Pb removal using different types of wash solutions

Wash solution	0.01 M NaNO$_3$	0.1 M HNO$_3$	0.1 M citric acid	0.01 M EDTA
Removal Efficiency, %	78.67	99.99	90.84	70.97
Removal enhancement by electrokinetic process, %	20.40	4.98	20.45	7.84
Effluent generation, mL	492.9	288.5	65.9	39.8
Final current, mA	3.90	85.30	8.85	5.76
Average soil pH	4.18	2.63	2.45	7.41
Final pH in anode chamber	2.95	1.05	1.91	7.05
Final pH in cathode chamber	9.85	1.41	1.99	11.93
Electrode condition	Stable	Corrosion	Stable	Stable
Power consumption, kWh/kg Pb removed	3.09	114.47	12.93	10.43
Transport way	One way	One way	One way	Counter migration

Table 4.4 summarizes the performance of each wash solution studied in two-stage electrokinetic washing process based on the experimental results. Among the four wash solutions used in this work, citric acid was found to be the best wash solution in removing Pb from the soil in a two-stage electrokinetic washing. It could enhance the removal efficiency of Pb than normal soil washing by 20.45% at lower electroosmosis/effluent generation in comparison to $NaNO_3$. HNO_3 is not suitable as wash solution in two-stage electrokinetic washing as it showed insignificant removal enhancement than soil washing. Moreover, it also caused variation in cathode chamber pH, corroded graphite anode and increased power consumption. In contrast, citric acid did not exhibit such problems. Furthermore, citric acid also provides stable one way Pb migration into the cathode chamber in comparison to EDTA, which complicates the transport mechanisms via Pb counter-migration.

Two-stage electrokinetic washing using 0.1 M citric acid has been proven to successfully maintain high removal efficiency at 90.84% with low wash solution consumption at a solution: soil ratio of ≤1 mL: 1 g (≈247 mL: 250 g), where the wash solution used consisted of the solution in soil column, cathode chamber and the effluent generated via electroosmosis (wash solution in anode chamber is not considered as it has negligible Pb concentration). However, the effluent generated, at 65.9 mL, can be considered to be significantly high, and this was not desirable for the objective of this study. Hence, the effects of operating parameters such as electric potential difference and wash solution concentration on the system performance were further investigated using citric acid as the wash solution in order to suppress electroosmosis while maintaining the removal efficiency as these parameters had significant influence on electroosmosis and electromigration, according to Equations (2.3) and (2.4) (Baraud *et al.*, 1997; Lee *et al.*, 2009; Asadi *et al.*, 2013).

4.4.4 Effect of operating parameters

Equations (2.3) and (2.4) show that the velocities for electromigration and electroosmosis are highly dependent on the electricity that passes through the soil. Besides that, the concentration of wash solution in the system, which is citric acid in this study, also governs the effectiveness of both soil washing and electrokinetic processes in terms of Pb desorption. Thus, it is necessary to study the effect of these parameters on the performance of two-stage electrokinetic washing.

The effects of electric potential difference (A, range from 7.5-30 V), wash solution concentration (B, range from 0.001-0.1 M) and initial Pb concentration (C, range from 400-1000 mg/kg) on the system performance was investigated in order to minimize electroosmosis (effluent generation) while maintaining high removal efficiency at low power consumption. The study was investigated using Response Surface Methodology based on Box-Behnken Design. A total of 17 experiments were carried out with five replicates for the centre point experiment to analyze the error. The experimental design and results for i) removal efficiency, ii) effluent generated, and iii) power consumption are as shown in Tables 4.5 and 4.6, respectively.

Table 4.5: Parameters and levels of the experiments

Parameters	Code	Level		
		-1	**0**	**1**
Electric potential difference, V	A	7.5	18.75	30
Wash solution concentration, M	B	0.001	0.0505	0.1
Initial Pb concentration, mg/kg	C	400	700	1000

Table 4.6: Experimental results using Response Surface Methodology based on Box-Behnken Design

Run No.	A, Electric potential difference, V	B, Wash solution concentration, M	C. Initial Pb concentration, mg/kg	Removal efficiency, %	Effluent generation, mL	Power consumption, kWh/kg Pb removed
1	18.75	0.0505	700	86.29	2.25	25.45
2	7.50	0.001	700	53.99	0	1.06
3	18.75	0.1	400	78.60	27.7	51.17
4	30.00	0.0505	1000	96.98	115.3	45.04
5	7.50	0.1	700	77.38	0	4.22
6	7.50	0.0505	1000	82.93	0	1.69
7	18.75	0.001	1000	84.52	0	6.23
8	18.75	0.0505	700	82.78	4.35	25.55
9	18.75	0.1	1000	90.79	27	21.49
10	18.75	0.0505	700	84.85	1.5	24.82
11	18.75	0.001	400	58.24	0	14.11
12	30.00	0.001	700	83.72	0	21.98
13	18.75	0.0505	700	85.19	3	25.37
14	30.00	0.1	700	94.62	103.35	79.53
15	18.75	0.0505	700	84.07	6.25	26.68
16	7.50	0.0505	400	61.12	0	5.82
17	30.00	0.0505	400	88.34	43.5	92.48

4.4.4.1 ANOVA analysis

Analysis of Variance (ANOVA) was carried out to evaluate the significance and fitness of the operating parameters to the numerical model generated based on the experimental results obtained (Nosrati *et al.*, 2011). In general, the models were evaluated based on the criteria as shown below:

i)   The model must be significant (Prob >F of less than 0.0001),

ii) The terms that have Prob >F of less than 0.05 are significant terms for the model (95% confidence level),

iii) Insignificant lack of fit (Prob >F of more than 0.05),

iv) Difference between Predicted R^2 and Adjusted R^2 of less than 0.2 (Nosrati *et al.*, 2011),

v)   Signal to noise ratio (Adeq Precision) of more than 4. (Long *et al.*, 2013)

Table 4.7: ANOVA for removal efficiency

Source	Sum of Square	DF	Mean Square	F Value	Prob > F	
Model	2319.02	8	289.88	79.22	< 0.0001	significant
A	973.29	1	973.29	265.99	< 0.0001	
B	463.91	1	463.91	126.78	< 0.0001	
C	593.75	1	593.75	162.27	< 0.0001	
A^2	9.45	1	9.45	2.58	0.1467	
B^2	142.09	1	142.09	38.83	0.0003	
AB	39.00	1	39.00	10.66	0.0114	
AC	43.36	1	43.36	11.85	0.0088	
BC	49.63	1	49.63	13.56	0.0062	
Residual	29.27	8	3.66			
Lack of Fit	22.42	4	5.60	3.27	0.1388	not significant
Pure Error	6.85	4	1.71			
Cor Total	2348.30	16				
Std. Dev.	1.91		R-Squared	0.9875		
Mean	80.85		Adj R-Squared	0.9751		
C.V.	2.37		Pred R-Squared	0.9025		
PRESS	229.07		Adeq Precision	31.56		

Table 4.7 shows an example of ANOVA for removal efficiency. The results show that the model is significant as there is only less than 0.01% chance that the "Model F-value" this large could occur due to noise. The significant terms for the models are of A, B, C, B^2, AB, AC and BC. The lack of fit analysis indicates the model has insignificant lack of fit. The "Lack of fit F-value" of 3.27 implies that the lack of fit is not significant relative to the pure error as there is 13.88% lack of fit "F-value" in the model this large could occur due to noise; hence this model is acceptable for this study. The term "Adeq. Precision" of 31.56 and the difference between Predicted R^2 and Adjusted R^2 of 0.0726 further justify the suitability of the model for space navigation. ANOVAs for the effluent generated and power consumption were also analysed based on these criteria and the ANOVA tables were summarized in Appendix C. Based on the analysis as discussed above, the coded numerical models obtained are as shown in Equations (4.7) to (4.9). The values for A, B and C are in the range of -1 to 1, which is the level of the parameters studied, as shown in Table 4.5.

$$\text{Removal Efficiency, } \% = 84.28 + 11.03A + 7.62B + 8.62C - 1.5A^2 - 5.8B^2$$
$$- 3.12AB - 3.29AC - 3.52BC \tag{4.7}$$

$$\text{Effluent generated, mL} = 3.47 + 39.70A + 13.68B - 0.18C + 24.2A^2 - 1.83B^2$$
$$+ 12.03C^2 + 25.84AB + 17.95AC + 12.16A^2B + 18.13A^2C \tag{4.8}$$
$$- 13.86AB^2$$

$$\ln(\text{power consumption/kg Pb removed}) = 3.24 + 1.5A + 0.65B - 0.42C - 0.61A^2$$
$$- 0.39B^2 + 0.021C^2 - 0.024AB + 0.13AC - 0.068A^2C \tag{4.9}$$

The numerical models generated are further analysed via the diagnostic plots. Linear plots for normal probability and predicted versus actual results as shown in Figures 4.17 and 4.18, respectively, indicate that the models generated by ANOVA are suitable for results analysis, as the predicted results by the models are close with the experimental results.
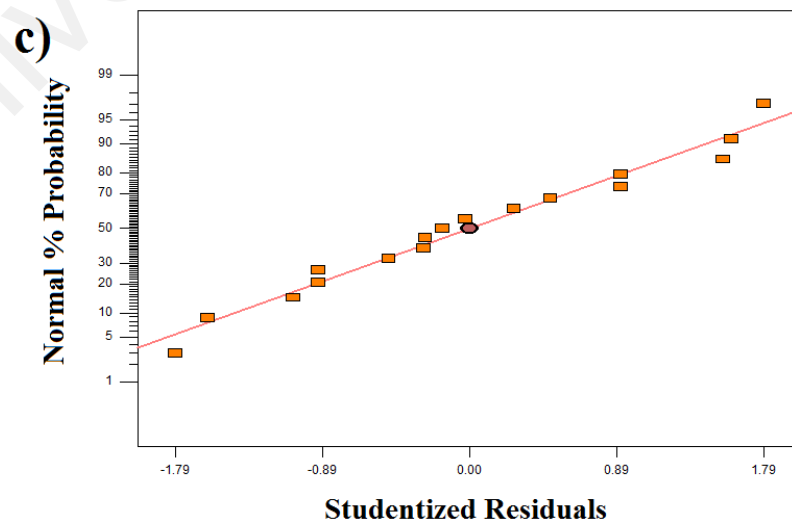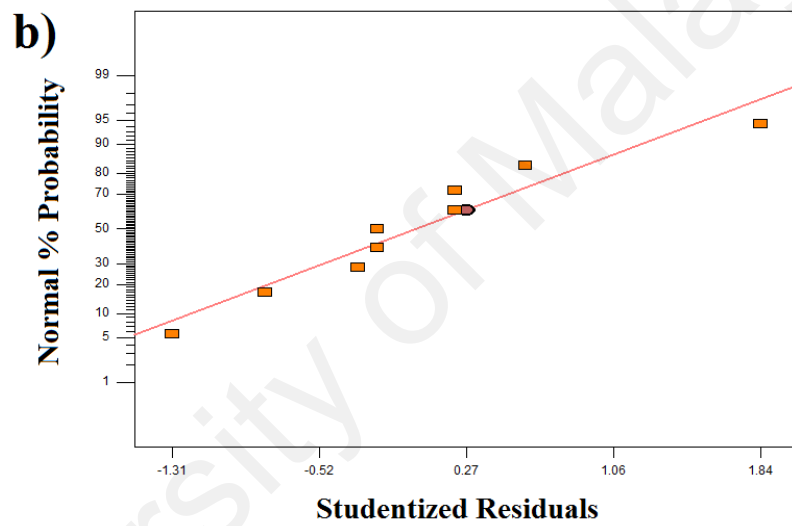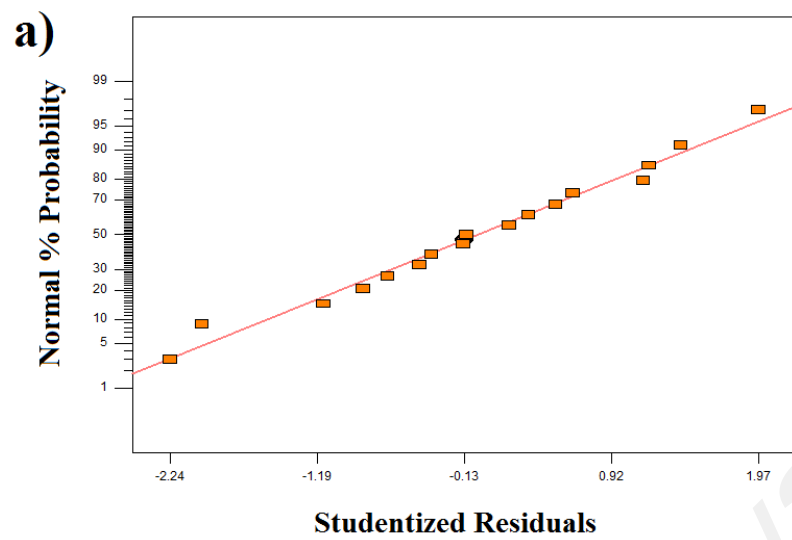
Figure 4.17: Normal probability plot for: a) removal efficiency; b) effluent generated; c) power consumption
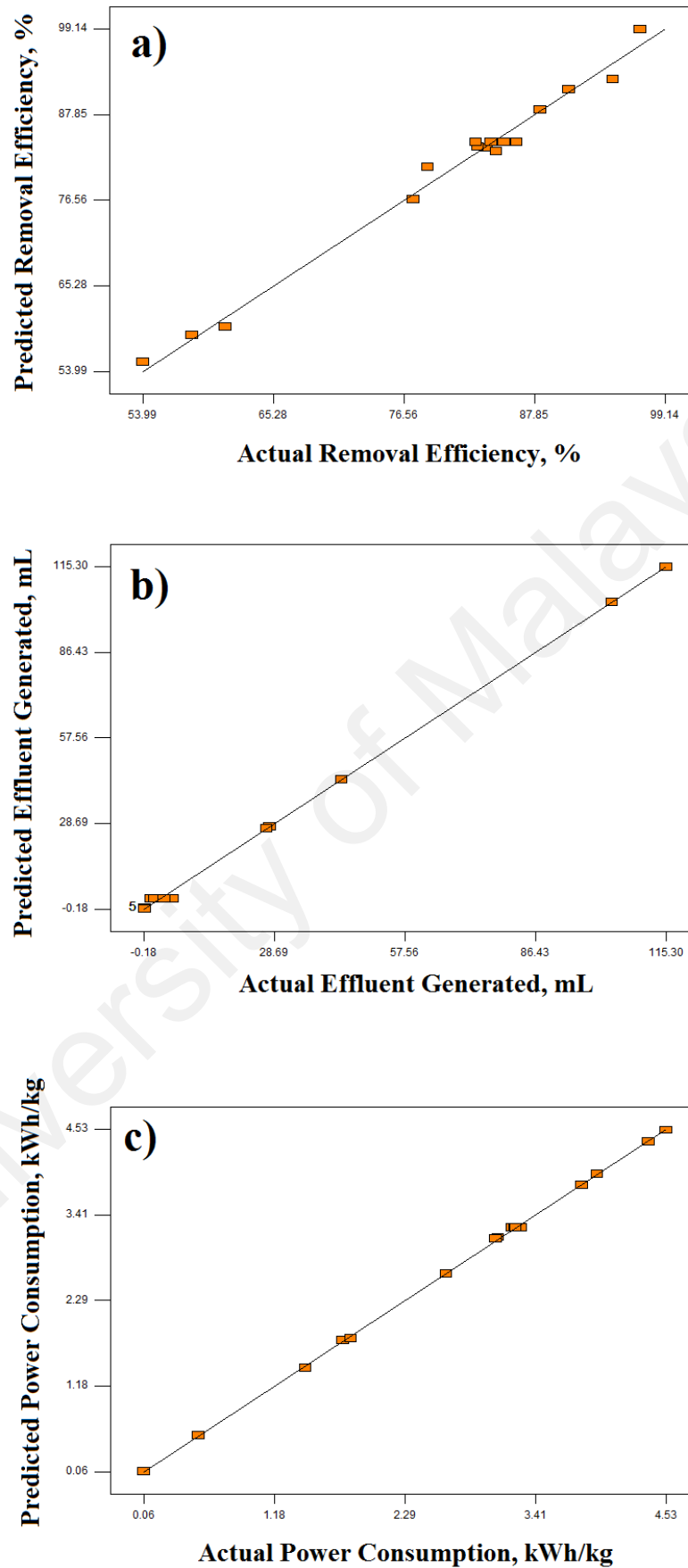
Figure 4.18: Predicted results vs actual results plot for: a) removal efficiency; b) effluent generated; c) power consumption

4.4.4.2 Removal efficiency

Figure 4.19 illustrates the response surface plots for removal efficiency under different parameters based on the mathematical model as shown in Equation (4.7). It was found that the increases in electric potential difference, wash solution concentration and initial Pb concentration created positive impact on the removal efficiency. Figures 4.19a and 4.19b show that the removal efficiency is proportional to electric potential difference, regardless of wash solution concentration and initial Pb concentration. Figure 4.19a reveals that an increase in electric potential difference from 7.5 V to 30 V enhances the removal efficiency steadily from 53.99% to 83.72% and 77.38% to 94.62% when the wash solution concentration used are 0.001 M and 0.1 M, respectively. According to Equations (2.3) and (2.4), the use of high electric potential difference could promote high removal efficiency, as a result of higher electric field strength and electric current through the soil for better electromigration as well as electroosmosis. This trend is in agreement with other works on the removal of heavy metals such as Cu (Zhou *et al.*, 2004), Ni (Reddy and Karri, 2006a) and As (Yuan and Chiang, 2008) whereby higher removal efficiency and electromigration were reported when higher electric potential difference was used.

In addition, wash solution concentration also showed positive impact on the removal efficiency. As shown in Figures 4.19a, when the electric potential difference is constant, the increase in wash solution concentration from 0.001 M to 0.1 M steadily enhances the removal efficiency. When other parameters are held constant, the presence of higher citric acid concentration provided higher amount of H^+ ions for enhancing Pb desorption via low pH condition (Chaari *et al.*, 2008; Mohapatra *et al.*, 2009; Kim *et al.*, 2011b). Moreover, it also prevented the increase of pH in cathode chamber, which might reduce Pb electromigration via Pb hydroxide precipitation, especially near the cathode region (Kim *et al.*, 2011b). In addition, citric acid also can increase Pb

solubility via water soluble complex formation (Niinae *et al.*, 2008). Citric acid could promote dissolution of Fe and Al, which were the main binding sites for Pb on soil surface, as shown in Figure 4.16. All of the mechanisms mentioned above could contribute to better Pb desorption and removal efficiency. However, it is noted that the effect of wash solution concentration is more significant at low electric potential difference, as shown in Figure 4.19a. As the electric potential difference was increased from 7.5 V to 30 V, the enhancement caused by the increment in wash solution concentration from 0.001 M to 0.1 M was decreased from 23.39% to 10.9%. Moreover, the effect of wash solution is optimum at a concentration of 0.075 M for any electric potential difference used, as shown in Figure 4.19a. Further improvement on the removal efficiency can only be achieved by increasing the electric potential difference for better electromigration/electroosmosis rate while improving H^+ generation via electrolysis to enhance Pb desorption. Thus, it is suggested that high removal efficiency could be attained by fine tuning the electric potential difference and wash solution concentration. This is important when both efficiency and cost are to be considered.

The study also suggested that two-stage electrokinetic washing is suitable for the soil with high contamination level as higher removal efficiency is achieved at higher initial Pb concentration when other parameters are held constant, as illustrated in Figures 4.19b and 4.19c. This was mainly due to the fact that higher amount of Pb was removed under high initial Pb concentration. In terms of Pb residual in the soil, initial Pb concentration did not show significant effect. This was supported by the residual Pb concentration in the soil after 24 h experiment. The residual Pb concentration in the soil remained close when different initial Pb concentrations (400 mg/kg vs 1000 mg/kg) were used but other parameters were held constant. Examples are given in four cases, namely, i) Tests 11 vs 7 (171 mg/kg vs 163 mg/kg), ii) Tests 3 vs 9 (88 mg/kg vs 97 mg/kg), iii) Tests 17 vs 4 (48 mg/kg vs 32 mg/kg), and and iv) Test 16 vs 6 (160 mg/kg

vs 180 mg/kg). This proved that even though higher removal efficiency could be achieved, the amount of residual Pb was less dependent of initial Pb concentration.
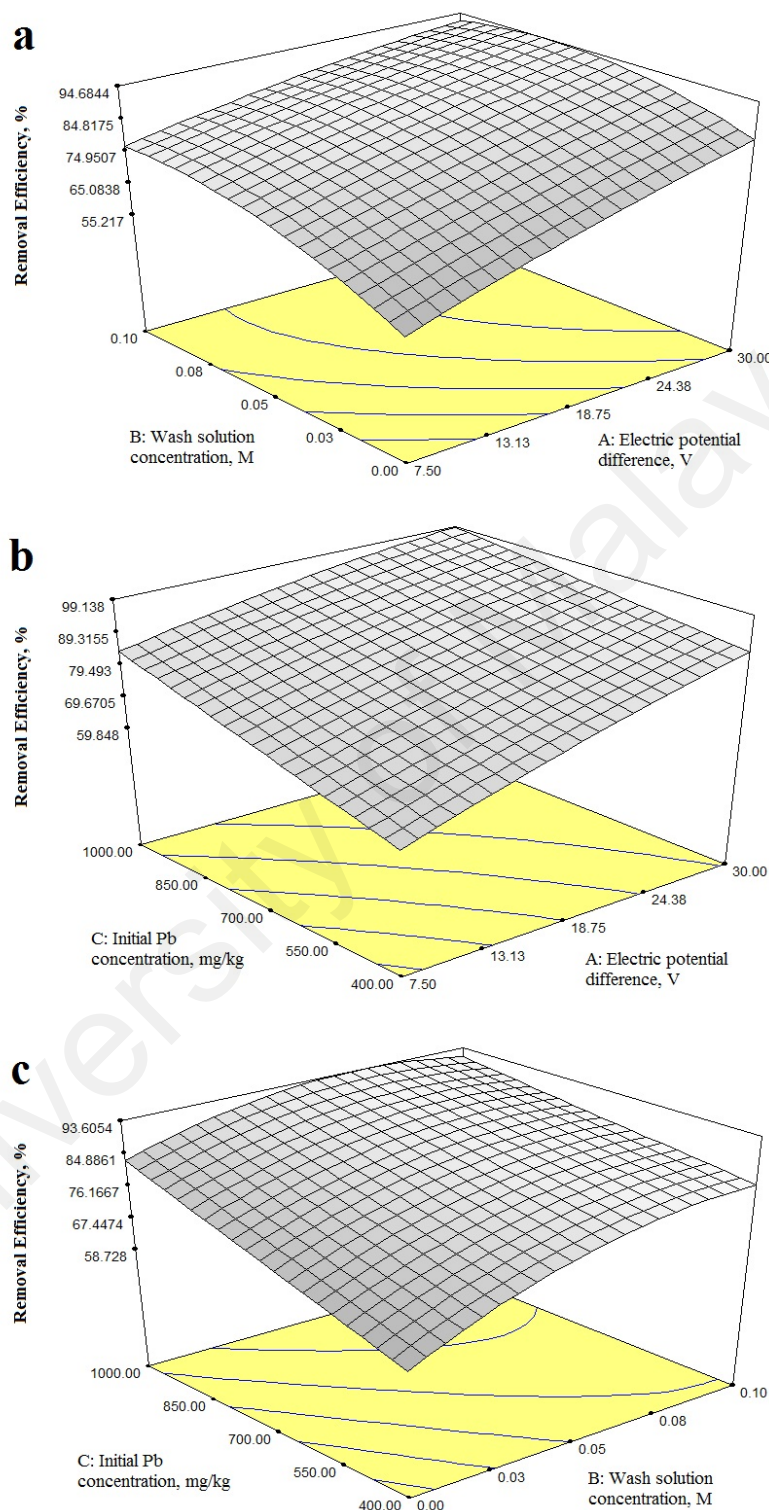
Figure 4.19: Interaction effect of parameters on Pb removal efficiency: a) electric potential difference and wash solution concentration (initial Pb concentration: 700 mg/kg); b) electric potential difference and initial Pb concentration (wash solution concentration: 0.0505 M); c) wash solution concentration and initial Pb concentration (electric potential difference: 18.75 V)

4.4.4.3 Effluent generation

Sub-section 4.4.4.2 concluded that high Pb removal efficiency could be achieved under high electric potential difference with high wash solution concentration. However, it should be noted that the generation of high electric field/current under this condition can induce higher electroosmosis, resulting in higher effluent generation. This is not favoured as it requires higher cost for spent wash solution treatment. Thus, a study on the effect of the parameters mentioned in Table 4.5 on effluent generated was conducted.

The experimental setup had been configured by adjusting the overflow level in the cathode chamber to ≈0.6 cm higher than that of anode chamber's such that a consistent volume of effluent that was mainly attributed to strong electroosmosis only can be observed. Even though the adjustment was expected to reduce effluent generation, Table 4.6 shows that significant high amount of effluent is still generated in Tests 3, 4, 9, 14 and 17. These tests shared similar conditions, which were: i) high electric potential difference of >18.75 V, and ii) high wash solution concentration of >0.0505 M. According to Helmholtz-Smoluchowski theory as shown in Equation (2.4), electroosmosis is directly proportional to electric field strength across the soil and the negativity of the zeta potential of the soil (Lee *et al.*, 2009; Asadi *et al.*, 2013). In the present study, electric field strength had more impact than soil zeta potential, considering that the range for soil pH in this study was less than one (2.66-3.35). Thus, the effect of soil zeta potential difference was relatively small. This is supported by the experimental results illustrated in Figure 4.20, showing effluent generation via electroosmosis is strongly proportional to the electric current density in the system whereby a current density of ≥ 0.7 mA/cm^2 generates significant amount of effluent.
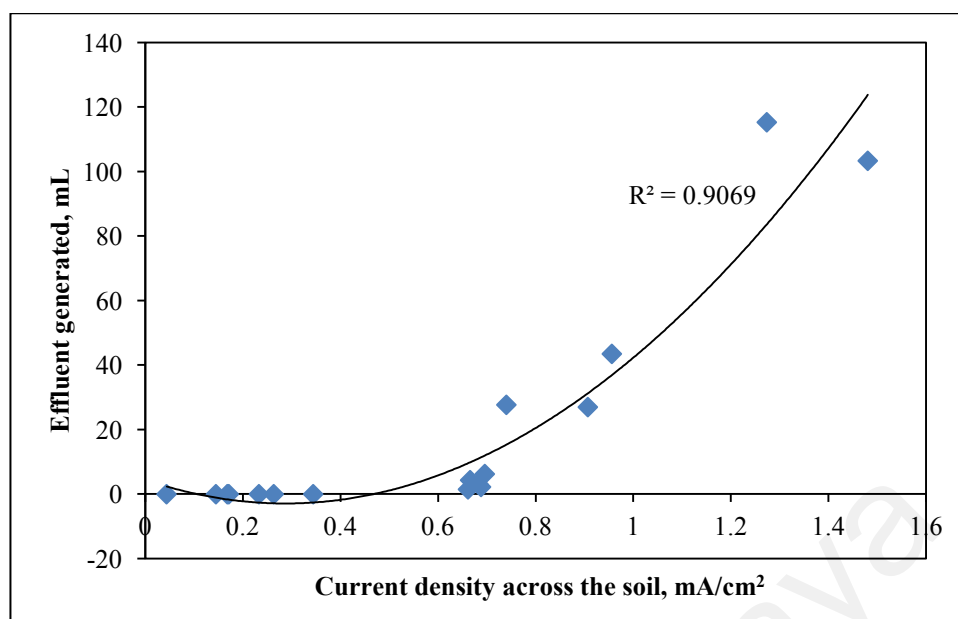
Figure 4.20: Relationship between effluent generated with electric current density

The response surface curves as shown in Figure 4.21 suggest that the increase in electric potential difference causes higher effluent generation. This is in line with the work of Zhou *et al*. (2004) which claimed that high electroosmosis was observed at high electric potential difference. However, the effect given by electric potential difference was also dependent on wash solution concentration and initial Pb concentration, as they governed the electric current in the system. Figure 4.21a shows that under low wash solution concentration of 0.001 M, insignificant amount of effluent was observed when electric potential difference was increased from 7.5 V to 30 V. This may be due to the relatively low electric current density (maximum at 0.34 mA/cm^2), which indicated high electrical resistance in the system. In contrast, higher wash solution concentration and initial Pb concentration were responsible in reducing soil electrical resistance, which enhanced the electric current. Thus, higher electroosmosis was obtained, especially at an electric potential difference of >18.75 V. This was also in line with the works of Yang and Long (1999) and Kim *et al*. (2005a) which reported that higher electroosmosis was achieved when the current density across the system was enhanced. Nevertheless, it is worth noting that the effects of wash solution and initial Pb concentrations are low

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unless high electrical driving force is applied, i.e. electric potential difference of ≥ 18.75 V, as shown in Figures 4.21a and 4.21b.
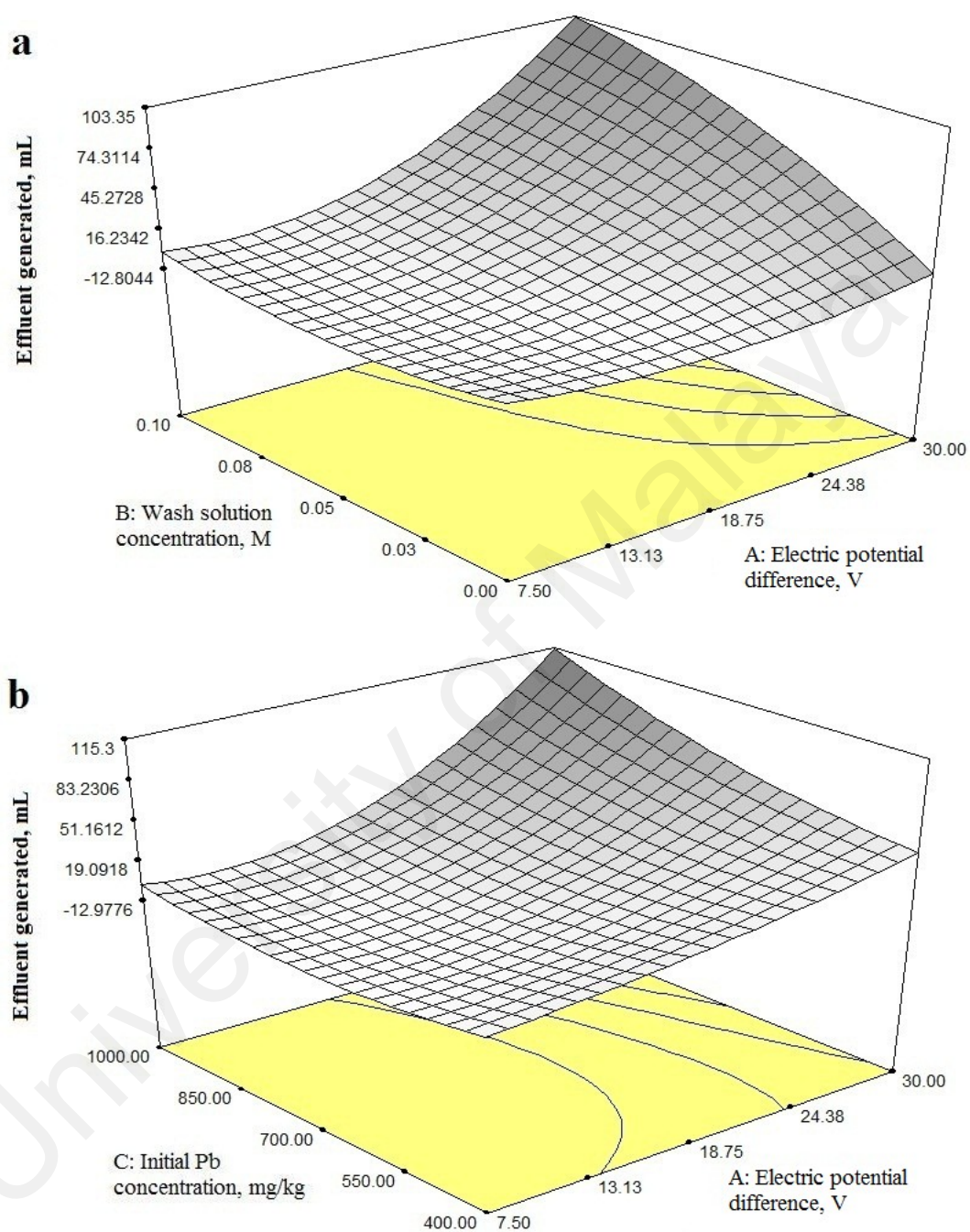
Figure 4.21: Interaction effect of parameters on effluent generation: a) electric potential difference and wash solution concentration (initial Pb concentration = 700 mg/kg); b) electric potential difference and initial Pb concentration (wash solution concentration = 0.0505 M)

4.4.4.4 Power consumption
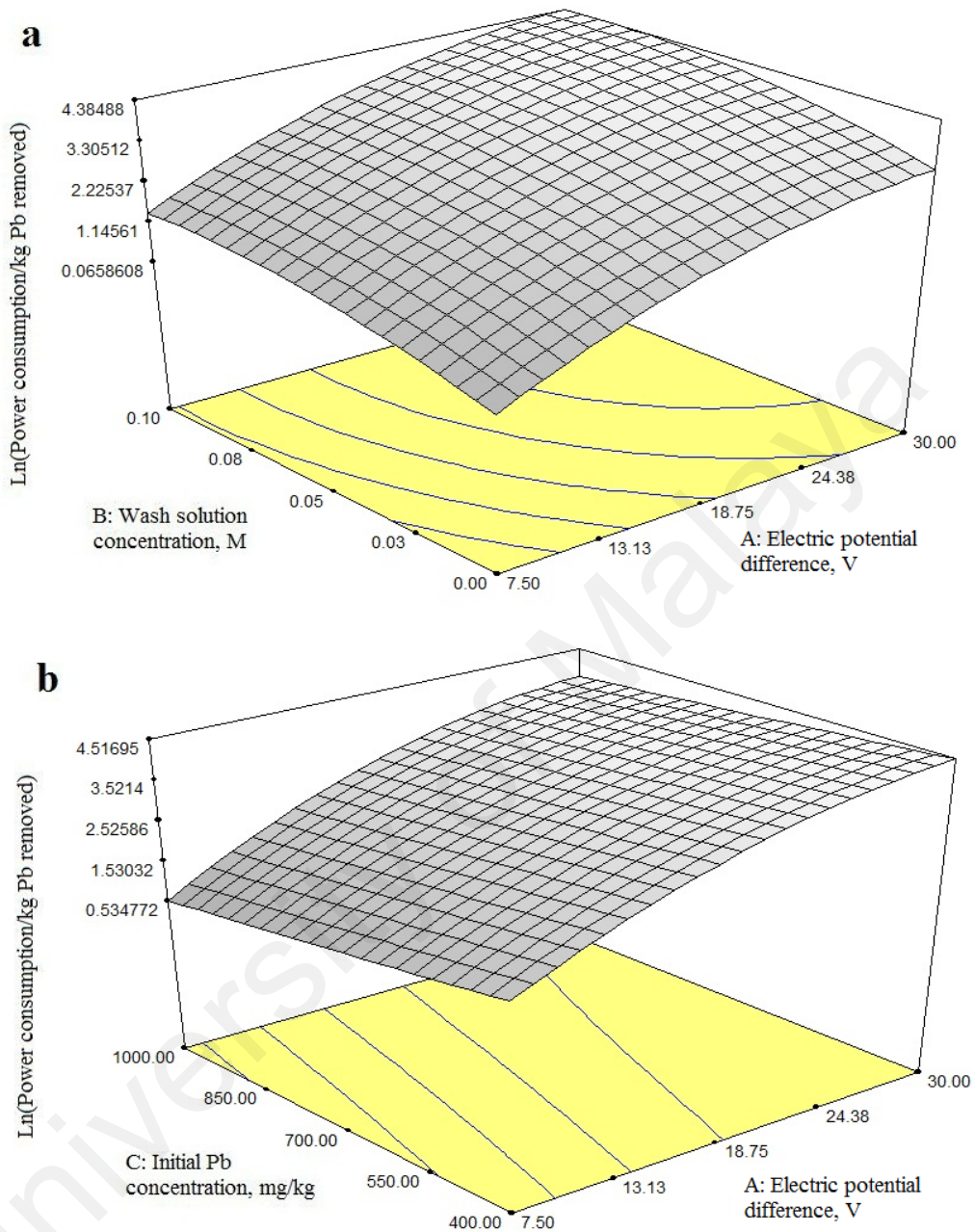
Figure 4.22: Interaction effect of parameters on power consumption: a) electric potential difference and wash solution concentration (initial Pb concentration: 700 mg/kg); b) electric potential difference and initial Pb concentration (wash solution concentration: 0.0505 M)

Power consumption was evaluated by the power consumed per kg Pb removed in a two-stage electrokinetic washing process, based on Equation (4.6). The ANOVA analysis suggests that the power consumption is an exponential function of the parameters studied, as shown in Equation (4.9). The response surface curves of ln (power consumption/kg Pb removed) versus the above-mentioned parameters are as

illustrated in Figure 4.22. The figure reveals that the use of higher electric potential difference and wash solution concentration increased the power consumption due to the presence of excessive current, as a result of higher electrical driving force and amount of free ions available via electrolysis and wash solution concentration. Excessive current not only enhances Pb transport towards the cathode chamber but also transports non-targeted ions such as H^+, Fe^{2+}, Fe^{3+}, Al^{3+} and other ions that are dissolved in the wash solution, which in turn consumes unnecessary electric power. Thus, the use of excessive electric potential difference and wash solution concentration to enhance removal efficiency is not an attractive option from the economic point of view. In contrast, the power consumption per kg Pb removed is found to be reduced when treating the soil that has higher initial Pb concentration, as shown in Figures 4.22b. A more effective Pb transport was achieved under this condition as the availability of Pb in the system was higher. Thus, it is suggested that two-stage electrokinetic washing is favoured for the soil that is highly contaminated.

4.4.4.5 Electric current density and pH in wash solution chambers and soil

Besides the properties mentioned above, other electrokinetic properties such as electric current density across the soil, the pH in wash solution chambers and soil were also investigated. The experiments showed that the current density in the system was stable during 24 h experiment. Therefore, the effect of operating parameters on the current density can be evaluated using "average current density". Figure 4.23a and 4.23b illustrate that the current density was proportional to the electric potential difference and wash solution concentration. The increase in electric potential difference from 7.5 V to 30 V and wash solution concentration from 0.001 M to 0.1 M increase the current density, when other parameters are held constant, as shown in Figure 4.23a and 4.23b. This followed normal electrokinetic process trend; according to Ohm's law,

electric potential difference is directly proportional to the electric current (Zhou *et al.*, 2004; Park *et al.*, 2009), which in turn increases ions' mobilities in the system (Reddy and Karri, 2006a). On the other hand, the use of higher wash solution concentration provided high amount of mobile ions in the system, which reduced the overall electrical resistance of the system. Thus, the current density was increased. In contrast, Figure 4.23c reveals that the effect of initial Pb concentration on current density is not as high as the other two. The effect of initial Pb concentration on the current density of the system was appreciable only when high electric potential difference and wash solution concentration were used.
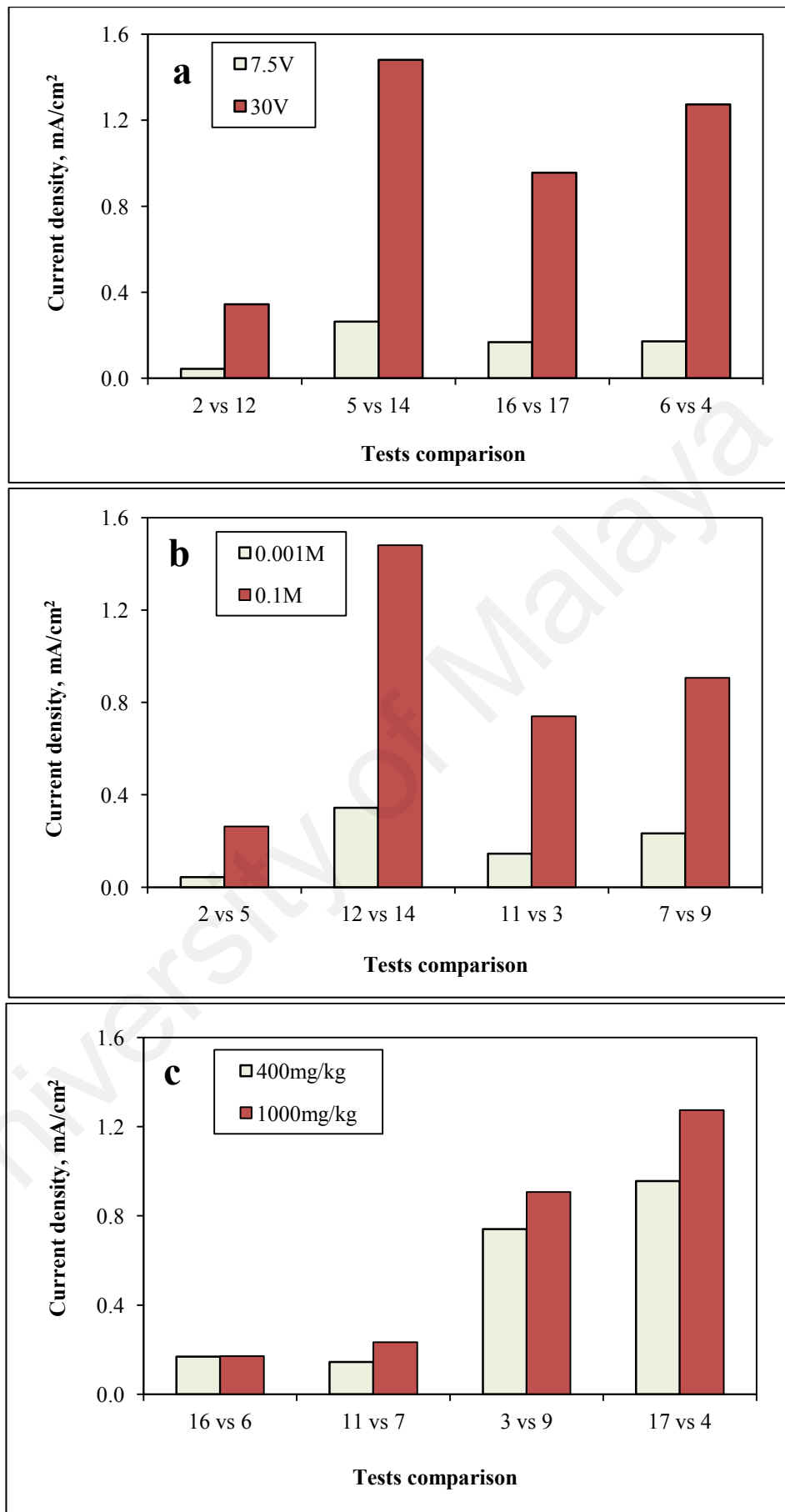
Figure 4.23: Average current density of the system at different operating conditions: a) electric potential difference; b) wash solution concentration; c) initial Pb concentration
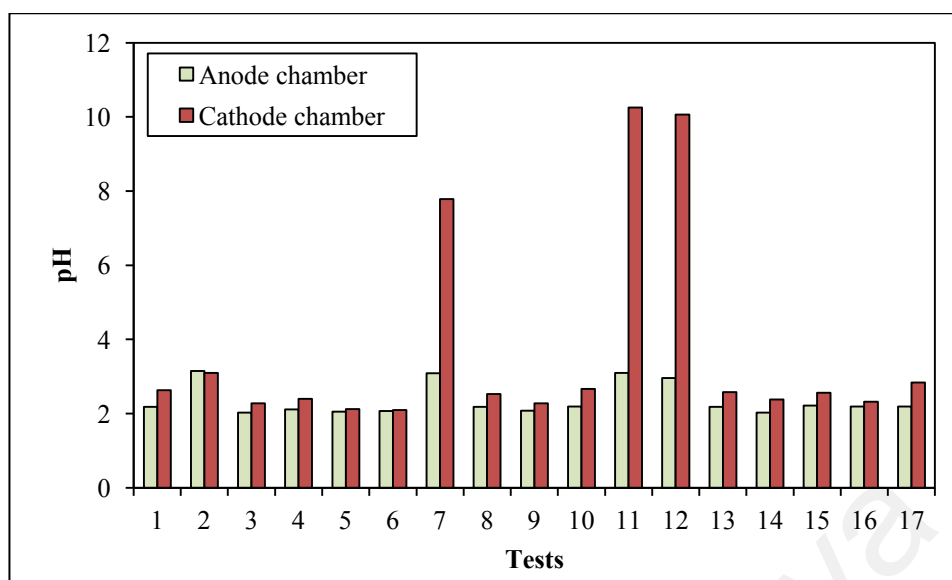
Figure 4.24: pH in anode and cathode chambers after 24 h experiments

Figure 4.24 shows that, in general, the pH in both anode and cathode chambers are low and stable throughout the experiments. As discussed in Sub-section 4.4.3.4, citric acid serves as buffer solution to prevent pH change in cathode chamber and this consequently eliminates base front from the cathode. However, it should be mentioned that high cathode chamber pH is observed in three cases, which are Tests 7, 11 and 12, as shown in Figure 4.24. These tests shared a similarity of low citric acid concentration (0.001 M) and high electric potential difference (>18.75 V). In these tests, the electrolysis, which generated high amount of OH^- ion outperformed H^+ available in the cathode chamber. Thus, the pH increased. For other cases, which utilised citric acid concentration of >0.0505 M, the pH in the cathode chamber only increased slightly to ≤3, indicating the ability of citric acid to maintain cathode chamber's pH.
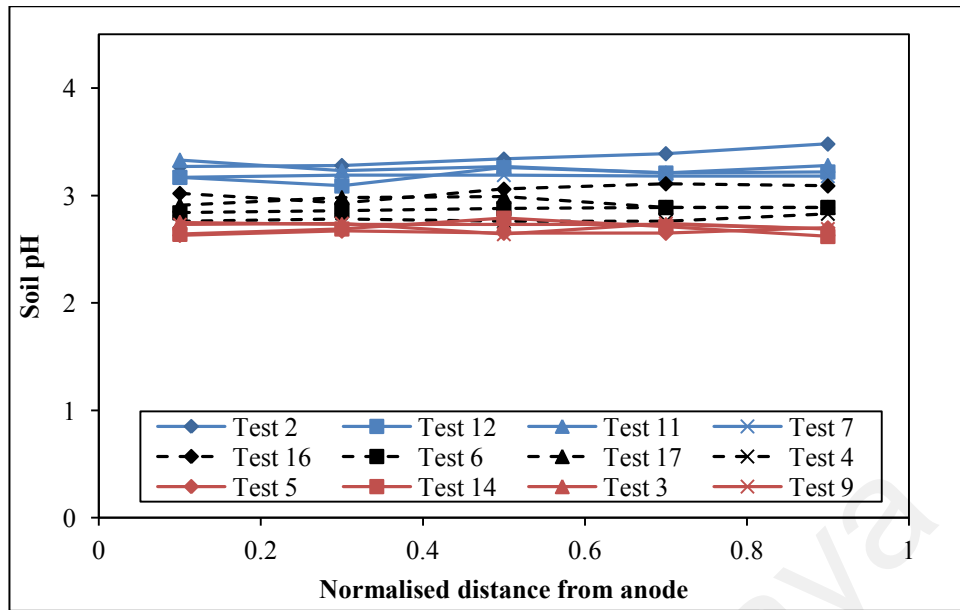
Figure 4.25: Soil pH at different soil sections after 24 h experiments (Wash solution concentration: blue: 0.001 M; black: 0.0505 M; red: 0.1 M)

Other than affecting the pH of wash solution chambers, the use of higher citric acid concentration from 0.001 M to 0.1 M also results in lower soil pH, as shown in Figure 4.25. The soil pH was generally stable throughout the soil sections for all tests without drastic pH jump. This was mainly due to the increase in soil acidity when citric acid was flushed through the soil, considering the soil had low acid buffering capacity. In contrast, electric potential difference and initial Pb concentration showed relatively less impact on the soil pH. The acid front from electrolysis and citric acid in the soil column served as buffer for preventing pH change. Considering H^+ electromigrated at a speed of ≈ 1.8 times than OH^- in the soil (Acar and Alshawabkeh, 1993; Acar *et al.*, 1995; Chung and Kang, 1999; Gioannis *et al.*, 2008; Park *et al.*, 2009; Kim *et al.*, 2011b) and H^+ buffer in the soil, the high pH generated in the cathode chamber in Tests 7, 11 and 12 was insufficient to create a strong base front to induce pH jump in the soil within the experimental duration.

4.4.4.6 Pb deposition efficiency
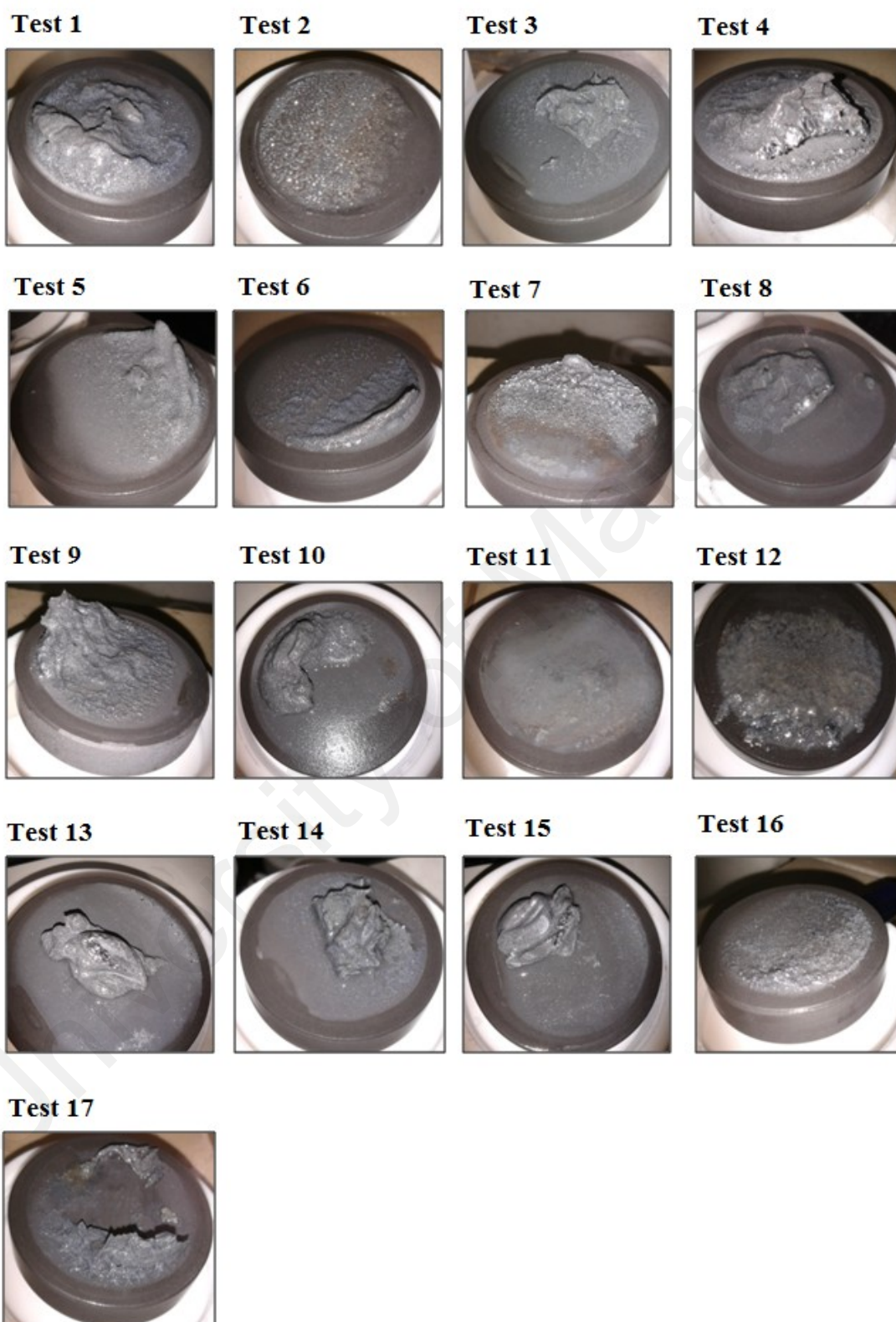
Figure 4.26: Physical appearance of deposit on cathode after the experiments
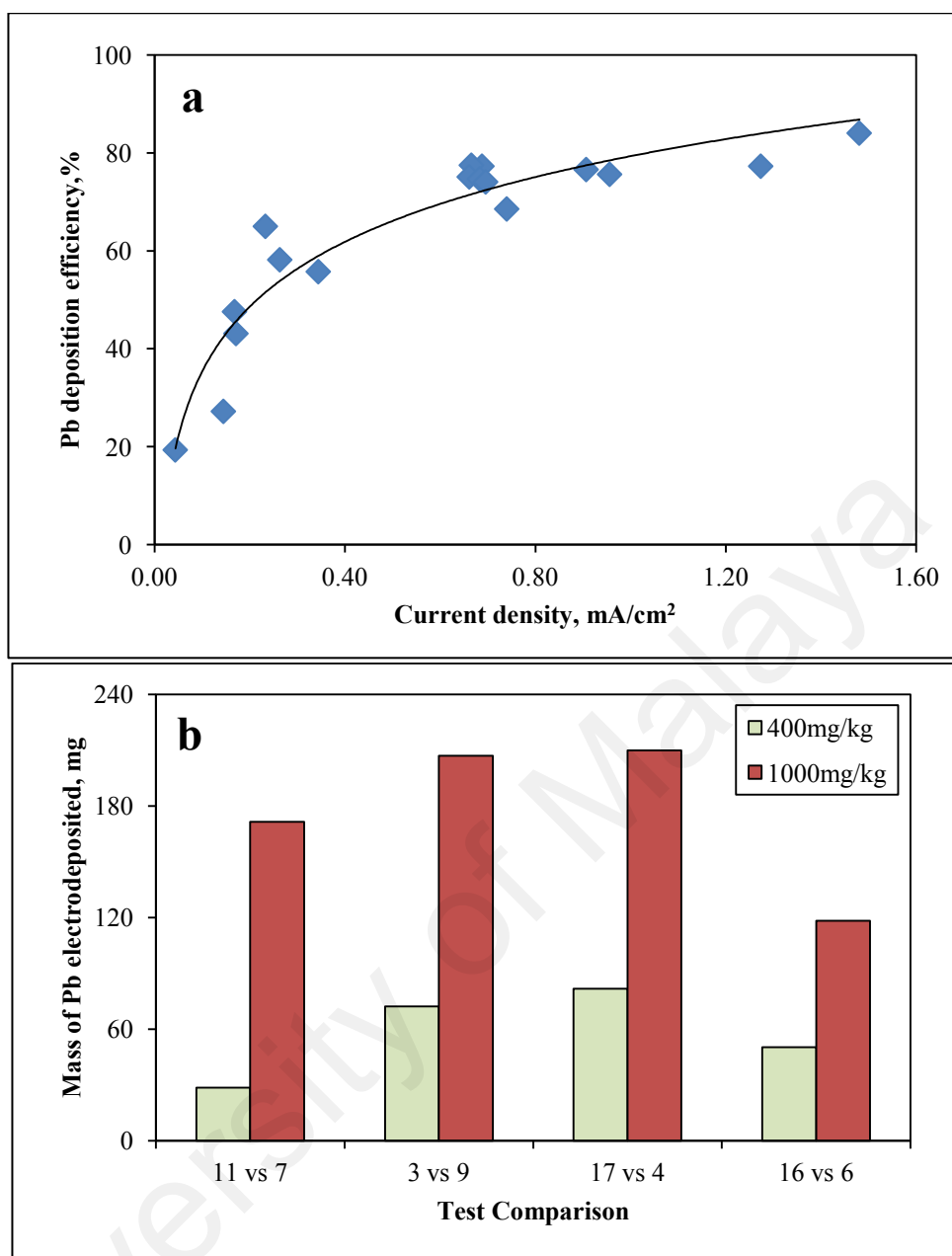
Figure 4.27: a) Deposition efficiency for Pb on the cathode at different current density; b) Mass of Pb electrodeposited at different initial Pb concentration (Wash solution: citric acid)

Figure 4.26 shows that Pb (grey solid) is recovered on the cathode during the experiments via electrodeposition. In general, it was found that the amount of Pb deposited was strongly dependent on the operating parameters studied. Figure 4.27a shows that the deposition efficiency is highly dependent on the current density across the system when citric acid is applied as the wash solution. This was in line with the Faraday 1st Law of Electrolysis that the mass of electrodeposited Pb during electrolysis is proportional to the quantity of electricity transferred at the electrode (Lou and Huang,

2007). Based on the discussion in Sub-section 4.4.4.5, the increase in electric potential difference and wash solution concentration which increased the current density of the system provided higher electrodeposition. Other than providing high electric current, the use of higher electric potential difference and wash solution concentration also improved Pb removal from soil and this could increase the availability of Pb in the cathode chamber for electrodeposition and thus, deposition efficiency. On the other hand, initial Pb concentration did not show a consistent trend in deposition efficiency, as the deposit on the cathode may affect the surface chemistry of the electrode and thus, the Pb electrodeposition rate. Nevertheless, the mass of electrodeposited Pb is found higher at higher initial Pb concentration, as shown in Figure 4.27b. This is mainly due to electrodeposition rate for a metal is higher when it has higher availability in the cathode chamber's solution (Senese, 2010).

4.4.4.7 Optimisation study

Sub-sections 4.4.4.2-4.4.4.4 highlight the fact that the increase in electric potential difference and wash solution concentration increase the removal efficiency. However, undesirable effluent generation and power consumption were also increased. Thus, an optimisation study was conducted on two-stage electrokinetic washing in order to determine the conditions to achieve optimum removal efficiency with negligible effluent generation at low power consumption. The optimisation study was conducted using Design Expert software 6.0.1 for treating 1000 mg/kg Pb contaminated soil. The criteria were set for: i) maximum removal efficiency; ii) minimum effluent generation, and iii) minimum power consumption.

The software suggests that a combination of 7.58 V and 0.057 M wash solution concentration can give an optimum removal efficiency of 84.58% at low power consumption (1.89 kWh/kg Pb removed) and ≈0 mL of effluent generation, with a criteria desirability of 0.887. An experimental work was conducted based on these conditions for validation purpose. As shown in Table 4.8, the experimental results are in close agreement with the predicted results whereby the removal efficiency of 84.14% is obtained, which is within 1% error. The power consumption under these conditions was 2.27 kWh/kg Pb removed and no effluent was detected during the experiment.

Table 4.8: Predicted and experimental results for removal efficiency, effluent generated, and power consumption under the optimum conditions

Set Parameters	Predicted Value	Experimental
Electric potential difference, V	7.58	7.58
Wash solution concentration, M	0.057	0.057
Responses	**Predicted Value**	**Experimental**
Effluent generated, mL	0.017	0
Removal efficiency, %	84.58	84.14
Power consumption, kWh/kg Pb removed	1.89	2.27

4.4.5 Performance of two-stage electrokinetic washing under optimum conditions

The performance of two-stage electrokinetic washing under optimum conditions as suggested in Table 4.8 was further evaluated for its electrokinetic properties, such as current density, pH and electrodeposition. In addition, a comparison study on the performance of two-stage electrokinetic washing and normal soil washing on Pb removal efficiency was also carried out. Based on the results obtained, a possible transport mechanism has been proposed.

4.4.5.1 Electrokinetic properties
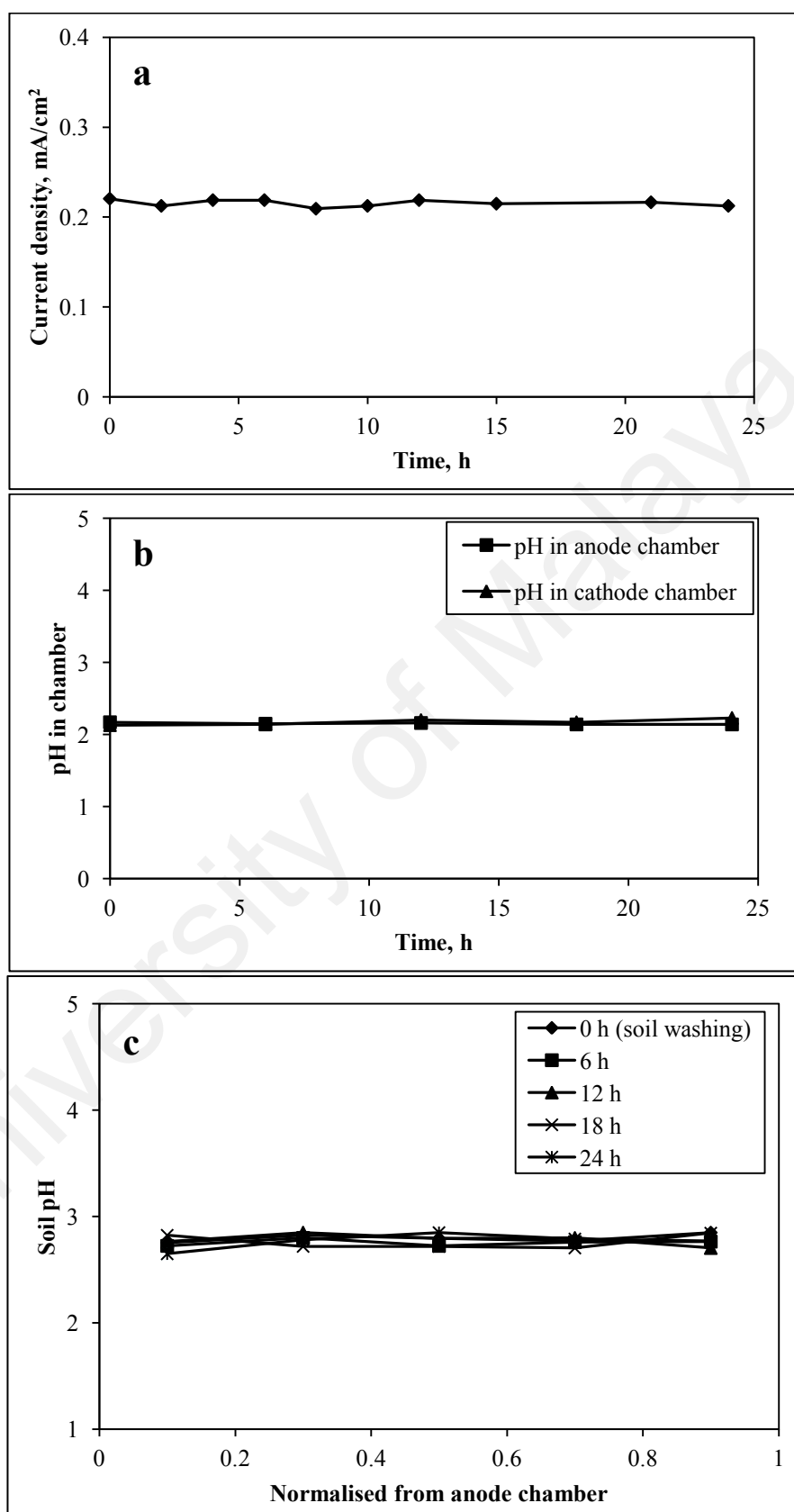
Figure 4.28: a) Change of current density with time during the experiment; b) Change of pH in wash solution chambers with time during the experiment; c) Change in soil pH during the experiment

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The electrokinetic properties were evaluated from the aspect of variation in current density and pH in both wash solution chambers and soil sections. Figure 4.28a shows that a stable current density on average of 0.22 mA/cm^2 is achieved under the optimum condition during the experimental duration of 24 h. The low electric current provided minimum changes in the pH in wash solution chambers as a result of low electrolysis rate. This is observed throughout the experiment, whereby the pH values in both anode and cathode chambers remain in the range of 2.1-2.2, regardless of experimental duration, as shown Figure 4.28b. A stable pH in the cathode chamber was mainly attributed to the use of 0.057 M citric acid, which served as buffer solution in the cathode chamber to depolarize cathode reaction and maintain the pH (Gioannis *et al.*, 2008; Murillo-Rivera *et al.*, 2010; Li *et al.*, 2012). Under low electrolysis rate, the amount of OH$^-$ generated was relatively lower than citric acid buffer in the cathode chamber in the 24 h experiment. Thus, base front was eliminated in this operating condition. This eventually caused a stable low soil pH of 2.8 on average without any significant pH gradient, regardless of experimental duration and soil location, as illustrated in Figure 4.28c.

4.4.5.2 Removal efficiency

Figure 4.29a illustrates the effect of time on the removal efficiency for two-stage electrokinetic washing under optimum conditions. The figure shows that, in general, the application of electrokinetic process after soil washing increases the removal efficiency up to ≈84% in 24 h in comparison to normal soil washing (0 h) at ≈68% without extra wash solution consumption. The enhancement achieved by the electrokinetic process is mainly attributed to the electromigration of Pb towards the cathode chamber, whereby the increase in the experimental duration resultant improved removal efficiency, as

shown in Figure 4.29a. On the other hand, the effect of electroosmosis was negligible as no effluent was generated at these operating conditions.
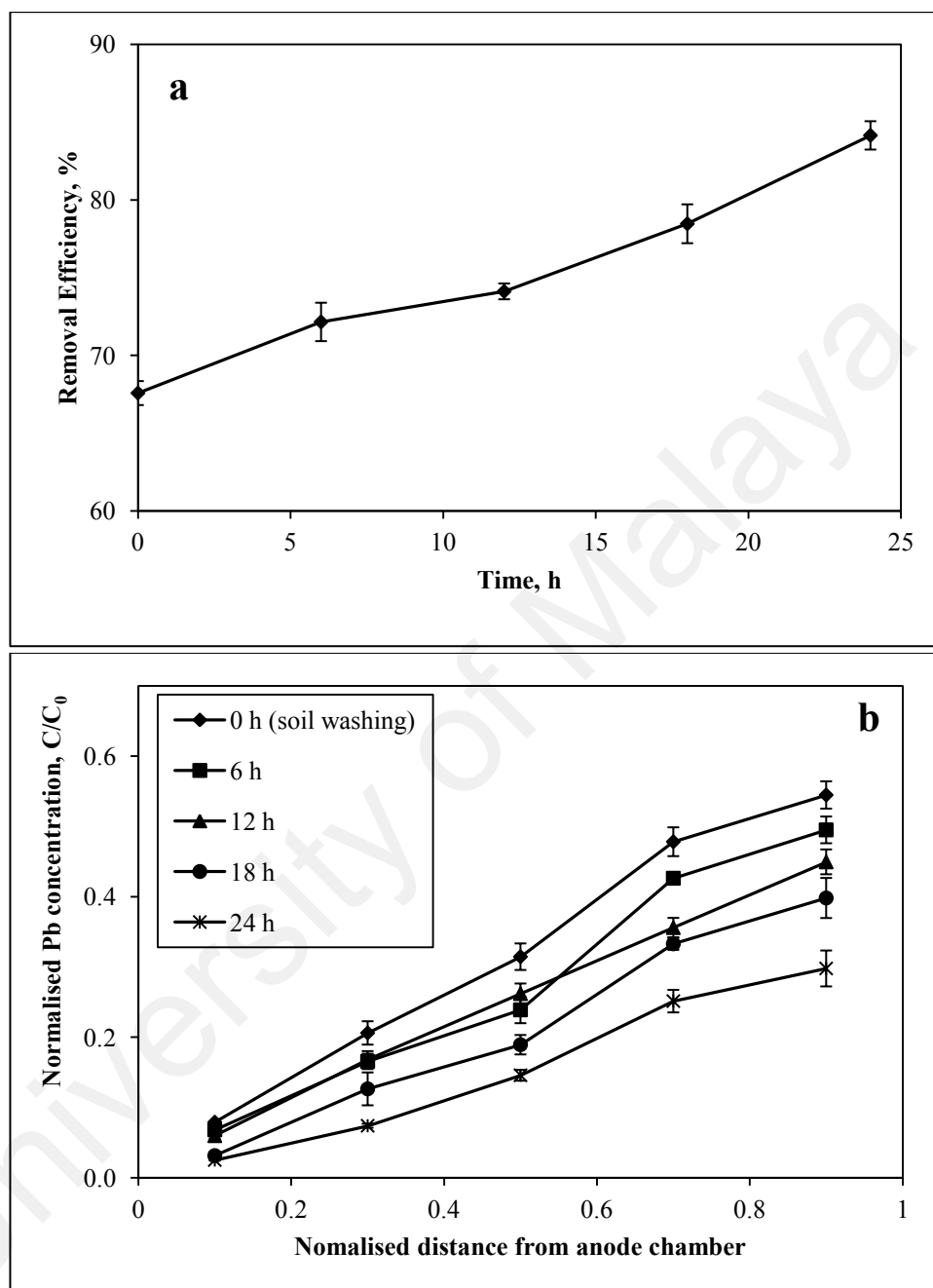
Figure 4.29: Effect of time on two-stage electrokinetic washing at 7.58 V and 0.057 M citric acid concentration: a) removal efficiency; b) normalised Pb concentration at different soil sections (Initial Pb concentration, 1000 mg/kg)

In relation to Pb distribution in the soil, Figure 4.29b shows that low normalised Pb concentration is detected at anode region whilst higher normalised Pb concentration is found at cathode region after initial soil washing (0 h) as the washing process flushed the desorbed Pb towards the cathode chamber. When electrokinetic process is further applied, the normalised concentration decreases with time, following a similar Pb distribution trend as in soil washing, as shown in Figure 4.29b. Thus, it can be suggested that electrokinetic process provided one way Pb electromigration towards the cathode chamber and the effect of counter migration as observed in EDTA case (Sub-section 4.4.3.1) was not found.

The above argument was strengthened via a general mathematical model. Based on the experimental results, three main assumptions were made:

i) the removal efficiency enhancement was mainly due to net one way electromigration towards the cathode chamber,

ii) the effect of diffusion was neglected, as ionic mobility of a charged species is normally much higher than the diffusion coefficient under electric field (Acar and Alshawabkeh, 1993; Reddy and Cameselle, 2009), and

iii) the change of electric potential difference across the soil with time is minimum at the experimental duration of 24 h.

Based on these assumptions, a general kinetic model for Pb electromigration in this study can be suggested as in Equation (4.10) (Acar and Alshawabkeh, 1993; Baraud et al., 1997), where $C_{Pb,soil}$ is the normalised Pb concentration in soil, v_{EM} is electromigration velocity, A is cross sectional area of the column, $D_{soil/sys}$ is other soil and system constants such as porosity, tortuosity, and distribution coefficient. By grouping the constants A, v_{EM}, and D_{soil} as a general kinetic constant k, Equation (4.10)

can be simplified as a first order kinetic model, as shown in Equation (4.11). A kinetic model that explains Pb concentration in the soil is obtained as Equation (4.12) after integrating the differential equation (4.11) from t=0 to t=t.

$$\frac{dC_{Pb,soil}}{dt} = -v_{EM} A D_{soil/sys} C_{Pb,soil} \tag{4.10}$$

$$\frac{dC_{Pb,soil}}{dt} = -k C_{Pb,soil} \tag{4.11}$$

$$C_{Pb,soil} = e^{\ln(C_{Pb,soil0}) - kt} \tag{4.12}$$
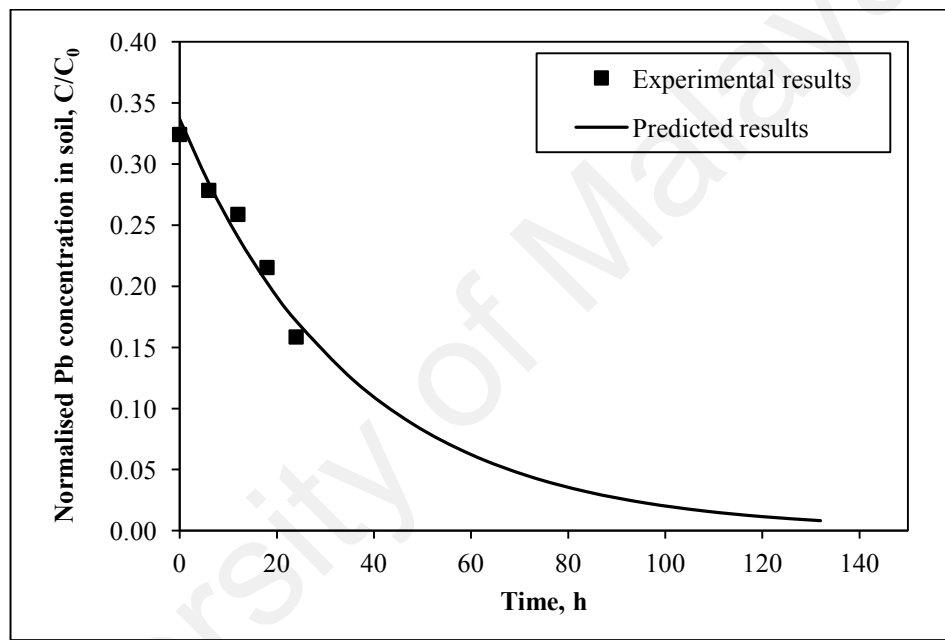
Figure 4.30: Average normalised Pb concentration in the soil at different treatment time during electrokinetic process stage

Figure 4.30 shows that the kinetic model expressed in Equation (4.12) explains the experimental results well, with an overall kinetic constant, k of 0.0281 h^{-1} and normalised Pb concentration after soil washing, $C_{Pb,soil0}$ of 0.34 when the process is conducted for 24 h. Hence, it is suggested that a net transport for Pb towards the cathode chamber is achieved in electrokinetic process via first order electromigration. In addition, it is also suggested that further increase in treatment time to 70 h may achieve an equilibrium removal efficiency of 95%, if other system conditions such as cathode chamber pH and current are maintained throughout the experiments.

4.4.5.3 Deposition efficiency
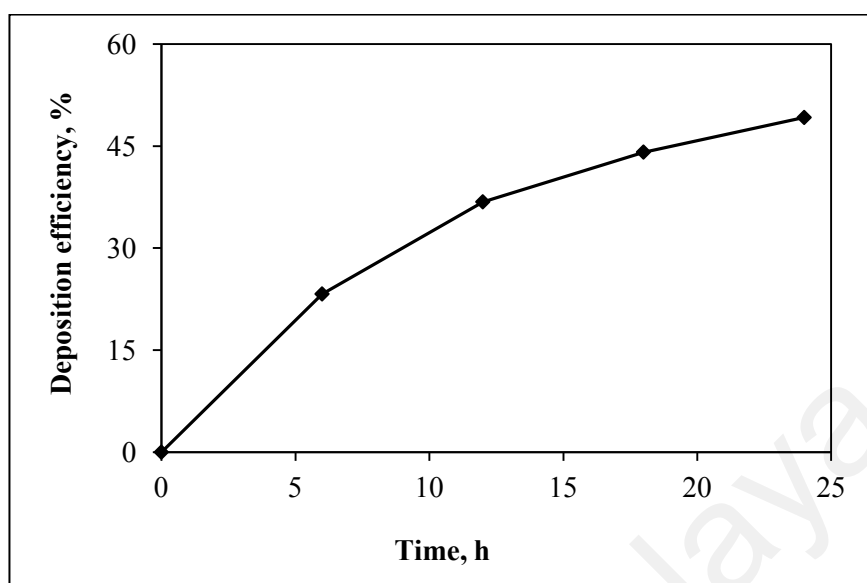
Figure 4.31: Deposition efficiency of Pb in cathode chamber at different experimental duration at optimum conditions.

Figure 4.31 shows that Pb electrodeposition efficiency on cathode increases with time. However, unlike the trend for removal efficiency, the deposition rate slowed down as the experiment progressed and eventually achieved 49% deposition efficiency in 24 h test. This could be due to the fact that electrodeposition reduced Pb concentration in the wash solution in the cathode chamber with respect to time. This in turn reduced Pb availability for maintaining the electrodeposition rate as it was one of the main factors that affect electrodeposition rate (Senese, 2010). Moreover, the thickening of Pb deposits on the cathode during the experiment may also influence the electrodeposition process by affecting uniformity of current distribution on the cathode surface (Lou and Huang, 2007).

4.4.5.4 Possible transport mechanisms
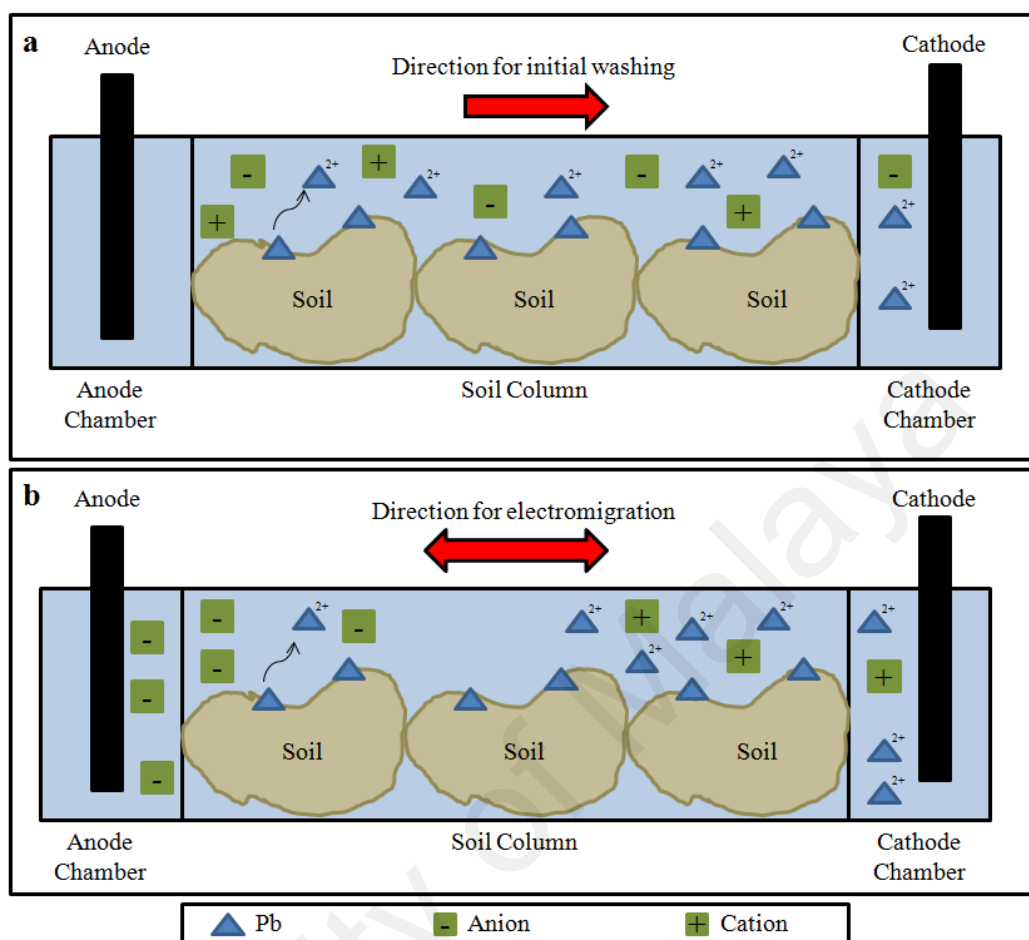
Figure 4.32: General transport mechanisms in a two-stage electrokinetic washing process: a) initial washing; b) electrokinetic process

Based on the experimental results, transport mechanisms for Pb in a two-stage electrokinetic washing process using citric acid can be suggested. Figure 4.32 illustrates a general mechanism involved in two-stage electrokinetic washing. In general, the transport mechanisms can be divided into two sections: i) Pb desorption via initial washing process, and ii) Pb transport via electrokinetic process. Figure 4.32a illustrates Pb desorption when citric acid is in contact with the soil surface. Some of the desorbed Pb ions are transported to the cathode chamber via wash solution during the fill up process. Then, application of electricity further transports the suspended ions in the soil column towards their respective chamber, as shown in Figure 4.32b.

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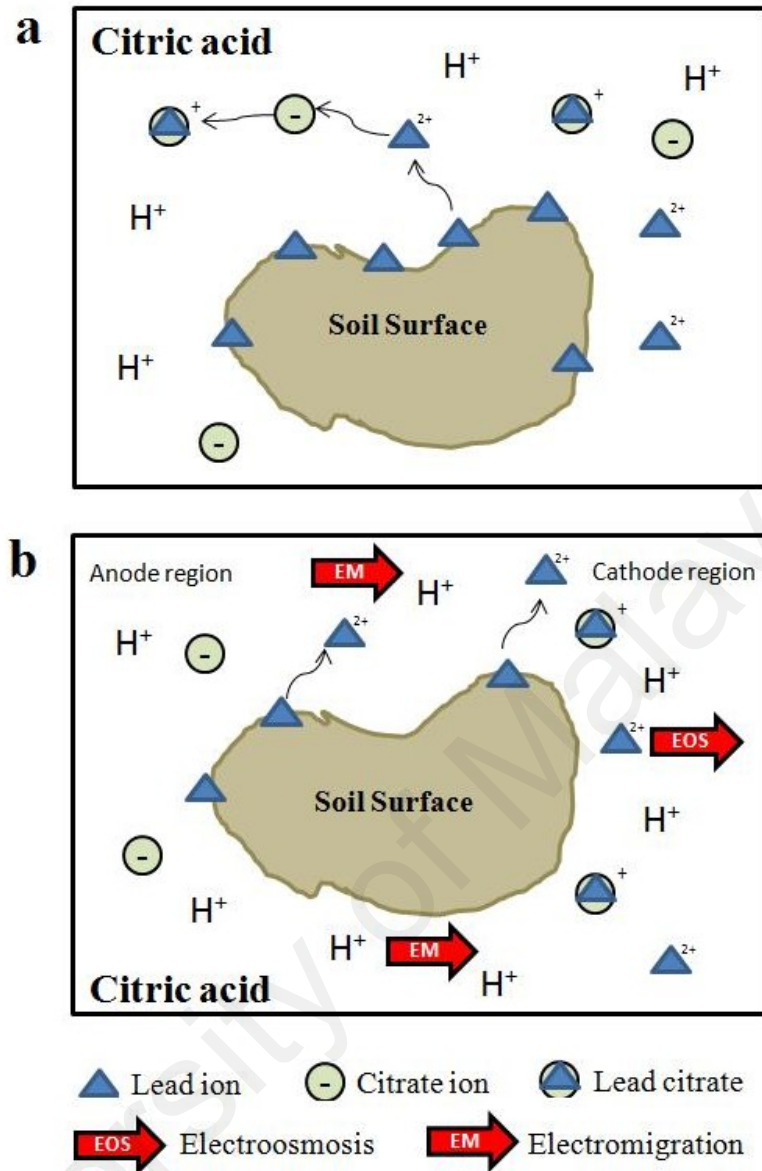
Figure 4.33: Schematic diagram for a) Pb desorption and b) Pb transport in two-stage electrokinetic washing when citric acid is applied as the wash solution

Figure 4.33 illustrates a) Pb desorption from a soil particle via soil washing, and b) Pb transport in electrokinetic process when citric acid is applied as the wash solution at the optimum condition in Sub-section 4.4.4.7. In general, Pb desorption process is pH dependent, in which low pH condition could give higher Pb desorption (Carlon *et al.*, 2004). Citric acid not only provides low pH condition for Pb desorption (Kim *et al.*, 2011b) but also acts as buffer solution for maintaining cathode chamber pH by nullifying OH$^-$ via dissociated H$^+$. Besides that, citric acid also causes detachment of

surface ions via its viscosity and possible Pb complexation with citrate anions (Li *et al.*, 2012). As shown in Figure 4.33a, Pb is desorbed from soil surface due to low pH condition. Then, the desorbed Pb could undergo two mechanisms: i) remain as Pb^{2+} ions, and ii) react with citrate ions to form water soluble complexes. The possible complexes formed are suggested to be mainly $PbH_2Citrate^+$, as the pH of the soil system is ≈ 2.8 for the case of optimum condition, while $PbH_2Citrate^+$ has higher stability constant (Niinae *et al.*, 2008). This was supported by Gu and Yeung (2011) in their work on Cd removal, whereby the major species in acidic condition (pH<3) were reportedly to be Cd^{2+} and $CdH_2Citrate^+$. Under this pH, the citrate ions in the system will be mostly in undissociated and $H_2Citrate^-$ forms, as the acid dissociation constant, pKa for citric acids are 3.13, 4.76, and 6.40 (Silva *et al.*, 2009), respectively, and the dissociations of citric acid at different pKa are as shown in Equations (4.13)-(4.15).

$$H_3Cit \Leftrightarrow H_2Cit^- + H^+ \qquad \text{pKa}_1: 3.13 \qquad (4.13)$$
$$H_2Cit^- \Leftrightarrow HCit^{2-} + H^+ \qquad \text{pKa}_2: 4.76 \qquad (4.14)$$
$$HCit^{2-} \Leftrightarrow Cit^{3-} + H^+ \qquad \text{pKa}_3: 6.40 \qquad (4.15)$$
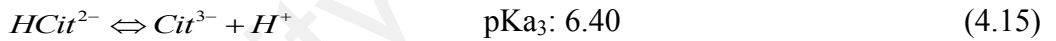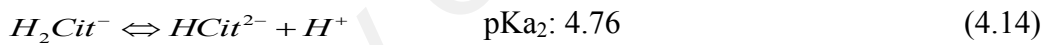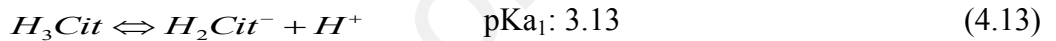
After the initial soil washing is completed, the use of electricity could provide electromigration as additional driving force to transport the desorbed Pb towards the cathode chamber, as illustrated in Figures 4.33b. One way Pb transport is achieved when citric acid is applied at low pH as Pb ions/complexes are in cationic forms and they are mainly electromigrated towards the cathode chamber. The electroosmosis is weak at the optimum parameters. However, it is worth noting that electroosmosis may also involve in Pb transport if it is significant, as discussed in Sub-section 4.4.3.2.

4.4.6 Summary and limitations

Table 4.9 shows that two-stage electrokinetic washing can enhance Pb removal efficiency from 68% to 84% without extra effluent generation at 0.057 M citric acid concentration and low magnitude electricity of 7.58 V (0.22 mA/cm^2). Enhanced removal of 16% could be achieved by this process in comparison to normal soil washing at similar low solution: soil ratio of <0.8 mL/g soil and operating condition. This proves that two-stage electrokinetic washing is effective in enhancing Pb removal efficiency at low amount of wash solution consumption in comparison to soil washing which often requires high solution: soil ratio for high removal efficiency, as discussed in Sub-section 2.2.1. It is worth noting that Pb has more affinity towards the soil in comparison to other divalent heavy metals (Turer and Genc, 2005; Kim *et al.*, 2005b; Violante *et al.*, 2007; Giannis *et al.*, 2009; Giannis *et al.*, 2012). Hence, based on the present study, it is suggested that two-stage electrokinetic washing is generally suitable for removal of divalent heavy metal cations that are mainly bound with the soil in the exchangeable, carbonate bounded and Fe-Mn oxides bounded forms.

Table 4.9: Comparison between the performance of two-stage electrokinetic washing and normal soil washing under optimum operating parameters

Method	Electric potential difference, V	Citric acid concentration, M	Removal Efficiency, %	Solution: soil concentration, mL/g
Soil washing	-	0.057	68	<0.8: 1
Two-stage electrokinetic washing	7.58	0.057	84	<0.8: 1

In spite of enhanced Pb removal efficiency, it is to be noted that there are several limitations for the present setup. As it involves initial soil washing, this configuration is only applicable to the soil that has higher hydraulic permeability, considering soil washing is normally poor for clayey soil (Kim *et al.*, 2012c). Besides that, electrokinetic process is also limited by the degree of solubilisation of the contaminants, as reported

by Acar *et al*. (1995) and Shenbagavali and Mahimairaja (2010). Two-stage electrokinetic washing is applicable if and only if the wash solution used can dissolve the contaminants and form uniformly charged (either in cationic only or anionic only) compounds for major contaminants for electromigration. It is worth noting that the performance of wash solution strongly affects the feasibility of two-stage electrokinetic washing from the aspects of removal efficiency, treatment time and electromigration direction. Thus, an evaluation of wash solution on the contaminant removal must be conducted before the application of this process.

4.5 Application of electrokinetic process as soil pretreatment method

4.5.1 Introduction

Electrokinetic process can transport dissolved heavy metals in saturated soil via electromigration even in the absence of pore flow (Acar *et al.*, 1995). This suggests that electrokinetic process can be utilised as soil pretreatment method to concentrate the heavy metals into smaller soil volume. The volume reduction of contaminated soil can in turn reduce the chemical costs when further remediation methods such as stabilisation and solidification (SS) is applied as the amount of chemical solution needed and waste produced are lower.

In this study, application of electrokinetic process as soil pretreatment method in migrating and concentrating heavy metals was investigated using a simple design. Unlike two-stage electrokinetic washing, there was no wash solution chamber for flushing in this setup. Instead, the electrode was in direct contact with the soil, as shown in Figure 3.3. The soil was saturated with the wash solution via sprinkling from the top of the soil, as proposed by Finzgar *et al.* (2006). Then, electrokinetic process was initiated by the application of low magnitude direct current through the electrodes for heavy metals migration. The details for the experimental setup and procedure were discussed in Sub-sections 3.2.2 & 3.3.5, respectively

The remediation study was investigated for two types of Pb contaminated soil, which were: i) single contaminated soil, and ii) co-contaminated soil. The effects of different types of wash solutions on electrokientic properties and Pb migration were evaluated. In addition, the feasibility of approaching electrode techniques in enhancing Pb migration using reduced power consumption was also investigated.

4.5.2 Approaching electrode assisted electrokinetic process

Approaching electrode is a technique in electrokinetic process. The term approaching electrode can be defined as the switching of either anode or cathode towards the other electrode from time to time with the purpose of reducing the distance between the electrodes and the migration path. In general, two types of approaching electrodes have been studied, namely: i) approaching anode (Shen *et al.*, 2007; Li *et al.*, 2012; Zhang *et al.*, 2014), and ii) approaching cathode (Shen *et al.*, 2009; Zhou *et al.*, 2014). The schematic diagrams for these configurations are as shown in Figures 4.34a and 4.34b.

The use of approaching electrode has been investigated to remove both cationic and anionic contaminants such as Cd (Shen *et al.*, 2007), Hg (Shen *et al.*, 2009), Cr (Li *et al.*, 2012), Pb (Zhang *et al.*, 2014) and fluorine (Zhou *et al.*, 2014). It is noteworthy that the selection of approaching electrode is dependent on the types of contaminants to be removed, whereby approaching anode is mainly applied for cation contaminants whilst approaching cathode for anions. In general, the removal enhancement caused by approaching electrodes is mainly due to progressive soil conditioning, as approaching anode and cathode are reported to provide progressive soil acidification (Shen *et al.*, 2007; Li *et al.*, 2012; Zhang *et al.*, 2014) and alkalisation (Shen *et al.*, 2009; Zhou *et al.*, 2014), respectively, for enhancing the desorption/migration conditions and preventing focusing effect of the contaminants in the soil. Besides that, electric current can also be enhanced by approaching electrode via reduction in migration distance (Shen *et al.*, 2007; Shen *et al.*, 2009; Li *et al.*, 2012; Zhou *et al.*, 2014). This could provide more intense electric field for electromigration in the soil and thus increase the removal efficiency. In addition, approaching electrode is also claimed to reduce the power consumption of the system by 16-44% (Shen *et al.*, 2007; Shen *et al.*, 2009; Zhou *et al.*, 2014), as far less electrical energy is wasted in the cleaned soil (Shen *et al.*, 2009). In

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this study, the feasibility of approaching electrode in improving Pb electromigration in single and co-contaminated soils as well as the power consumption was investigated.
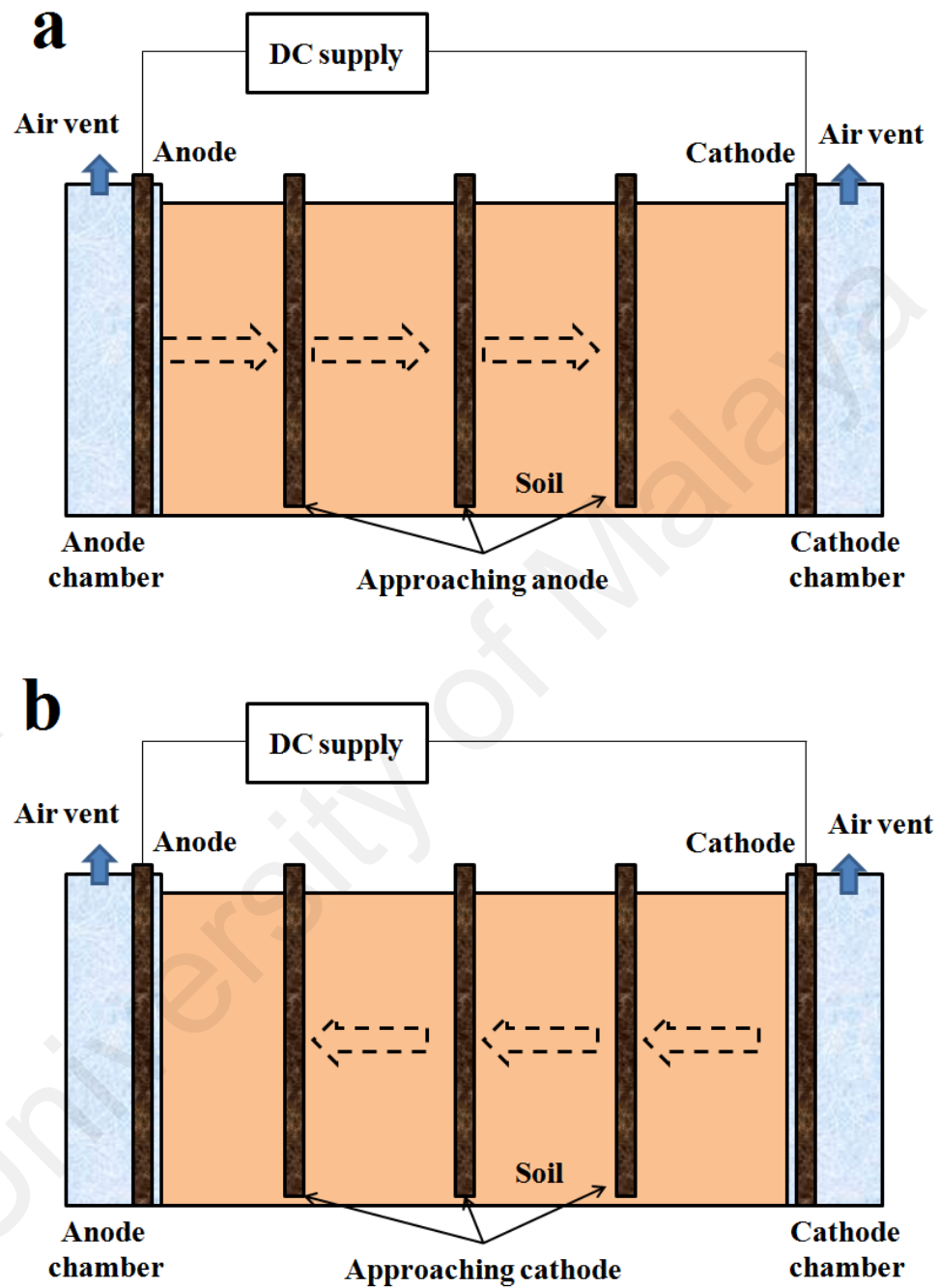
Figure 4.34: Schematic diagram for a) approaching anode, and b) approaching cathode (Shen *et al.*, 2007; Shen *et al.*, 2009)

4.5.3 Application of electrokinetic process in treating single contaminated soil

Technical feasibility of an electrokinetic process in treating Pb contaminated soil was investigated. The ability of the electrokinetic process to concentrate Pb into smaller soil volume via electromigration was evaluated using three wetting agents, namely i) 0.01 M $NaNO_3$, ii) 0.1 M citric acid, and iii) 0.1 M EDTA solution as they showed promising Pb desorption efficiency, as reported in Section 4.3. In contrast, HNO_3 was not utilised as the wetting agent in this study as it could corrode the graphite electrodes, as discussed in Sub-section 4.4.3.3.

4.5.3.1 Effect of wetting agents on electric current and soil pH

The variation in electric current and soil pH under different wetting agents are as illustrated in Figures 4.35a and 4.35b, respectively. Figure 4.35a shows that 0.1 M EDTA yields highest electric current, followed by 0.1 M citric acid and 0.01 M $NaNO_3$. This was perhaps due to the fact that EDTA produced more mobile ions in the system as it underwent multiple dissociations at solution pH of ≈8-9 in comparison to citric acid and $NaNO_3$, which only dissociated partially at low pH and was in low concentration, respectively. Moreover, considering the relatively high availability of other metal ions such as Fe and Al in the soil, EDTA, as a non-selective metal chelating agent could also provide dissolution of metal-oxides and subsequently the formation of water soluble metal-EDTA complexes via ligand exchange reaction (Komárek *et al.*, 2007) besides the targeted contaminants, as observed in the work of Kim *et al.* (2011b). These increased the number of mobile ions in the soil system and thus, highest electric current was observed in 0.1 M EDTA test. The electric current was found to reduce steadily throughout the experiments for all types of wetting agents studied. This was mainly due to the loss of free ions and ionic strength in the system during the experiments and the

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increase in resistance polarisation in the soil as they accumulated at their respective electrodes due to electromigration (Saichek and Reddy, 2003; Shen *et al.*, 2007; Shen *et al.*, 2009; Shrestha *et al.*, 2009; Giannis *et al.*, 2012; Li *et al.*, 2012; Zhang *et al.*, 2014). As wash solution/electrolyte chambers were absent for continuous supply of wetting agent, the amount of mobile ions decreased with time due to electromigration. Thus, the electric current across the soil decreased.
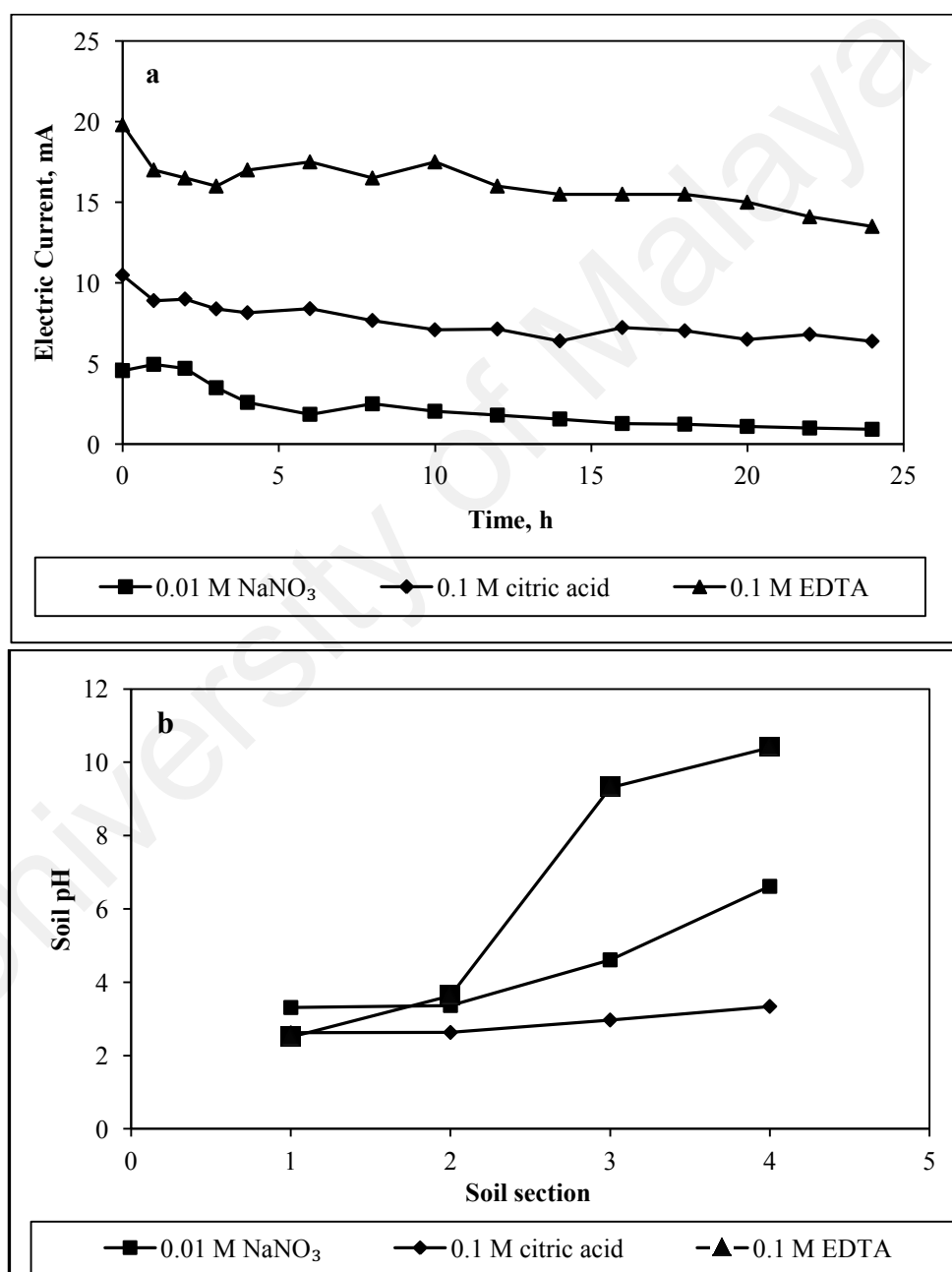
Figure 4.35: Effect of wetting agents on: a) electric current, and b) soil pH at different soil sections

The use of different types of wetting agents is found to show different soil pH development, as shown in Figure 4.35b. The soil is divided into four equivalent sections after the experiments, which are Soil Section 1 (S1), Soil Section 2 (S2), Soil Section 3 (S3) and Soil Section 4 (S4), as labelled in Figure 3.3. Among the soil sections, S1 and S2 are denoted as the anode region while S3 and S4 were denoted as the cathode region. In general, low pH was found in anode region S1 and high pH was observed in cathode region S4 as a result of electrolysis on the electrode, as shown in Equations (2.1) and (2.2). However, the pH gradient between both regions was dependent on the types of wetting agents. Figure 4.35b reveals that the use of 0.1 M EDTA shows a high pH gradient of 7.89. This could be attributed to high initial solution pH of 8-9, which increased the soil pH, especially at the cathode region. In addition, high pH gradient was also caused by high electric current generated in this test. This phenomenon enhanced the electrolysis at both anode and cathode (Tsai $et\ al.$, 2010) for H^+ and OH^- generation, respectively. Thus, a high pH gradient was observed. This argument was also applicable for 0.01 M $NaNO_3$ test, which had lower electric current in comparison to 0.1 M EDTA test. In this test, a lower pH gradient of 3.31 is observed, as shown in Figure 4.35b, as a result of lower electrolysis rate. However, in addition to the electric current, the nature of wetting agent may also have significant impact on the soil pH. As shown in Figure 4.35b, 0.1 M citric acid creates an acidic soil environment with a pH gradient of less than one even though it records higher electric current than 0.01 M $NaNO_3$ test. This was mainly attributed to the characteristic of citric acid which not only dissociated and provided additional H^+ for soil acidification but also served as a buffer solution to prevent pH change in the cathode region (Kim $et\ al.$, 2011b). Thus, a drastic pH change, especially in S3-S4 region was not observed in the present study which utilised an experimental duration of 24 h.

4.5.3.2 Effect of wetting agents on Pb migration
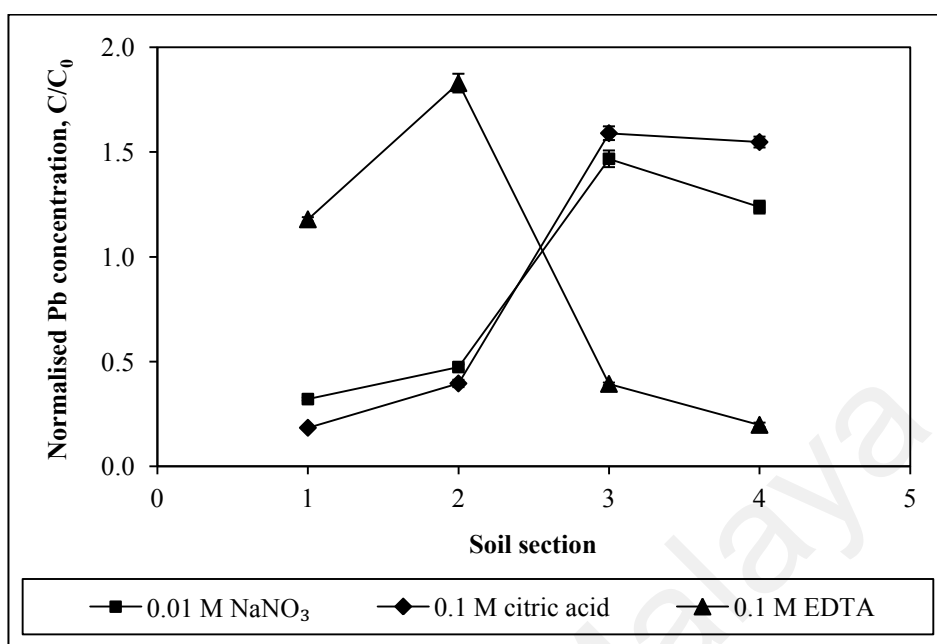
Figure 4.36: Normalised Pb concentration at different soil sections after the experiments

The electromigration trend of Pb in the soil under different types of wetting agents is as shown in Figure 4.36. In general, it was found that the electrokinetic process had the potential to provide volume reduction in contaminated soil as the Pb concentration in ≈50% of the soil sections was reduced to below the threshold concentration of 400 mg/kg (normalised concentration = 0.54) set up by Department of Environment Malaysia (DoE-Malaysia, 2009) via electromigration. In term of Pb migration, it was found that the use of 0.01 M $NaNO_3$ and 0.1 M citric acid provided Pb electromigration from anode region towards cathode region, and the latter generally provided better Pb migration than 0.01 M $NaNO_3$, as the normalised Pb concentrations in S1 and S2 were lower. The experimental evidence supported the fact that citric acid dissociated to provide additional H^+ for soil acidification in all soil sections. Low pH environment provided favourable condition for Pb desorption (Yang *et al.*, 2006). Thus, better Pb mobility and electromigration was achieved. In contrast, $NaNO_3$ only served as an electrolyte for conducting electricity and initiating electrolysis in the system. Its inability to buffer OH^- generated during electrolysis caused relatively high pH at S3-S4

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region than citric acid test, as shown in Figure 4.35b. High pH region may be the main cause for cessation of Pb electromigration and accumulation in S3 region. In this test, the pH at S3 is 4.61, which was reported to favour Pb adsorption (Chaari *et al.*, 2008; Mohapatra *et al.*, 2009). Moreover, a pH of higher than 6 at S4, which can cause Pb hydrolysis into $Pb(OH)_2$ precipitate or even $Pb(OH)_3^-$ (Niu *et al.*, 2013) also served as another reason for Pb accumulation in S3 for 0.01 M $NaNO_3$ test.

On the other hand, 0.1 M EDTA showed a different migration trend. Figure 4.36 depicts that lower Pb concentration is recorded at the cathode region whilst higher Pb concentration is observed in anode region, with an accumulation of Pb at normalised concentration of 1.83 in S2 region. The different trend could be mainly due to the nature of the wetting agent used. In this test, the desorption process was mainly attributed to complex formation between Pb and EDTA, considering Pb mobility was poor at high pH condition (Niu *et al.*, 2013). EDTA could be attached to Pb up to six sites, which helped in desorbing Pb effectively from the soil surface (Zhang *et al.*, 2014). As the complexes formed were in negatively charged, the complexes electromigrated towards anode when electricity was applied (Amrate *et al.*, 2005; Niinae *et al.*, 2008; Alcántara *et al.*, 2012; Zhang *et al.*, 2014). However, Figure 4.36 also shows that Pb significantly accumulated in the S2 region. This trend was also observed in the work of Alcantara *et al.* (2012) whereby Pb accumulated in the middle soil section when EDTA was applied as the wash solution in electrokinetic process. This could be attributed to low soil pH of 2.5-3.6 in S1-S2 region, as shown in Figure 4.35b. Low pH condition was not conducive for EDTA as it was generally less soluble at low pH condition for complex formation (Allen and Hsien, 1993, as cited in Alcántara *et al.*, 2012). In addition, the negatively charged Pb-EDTA complex may also be adsorbed on the soil surface (Reddy *et al.*, 2010), especially at low pH condition. These mechanisms may contribute to the lower Pb electromigration, causing Pb accumulation at low pH S2 region.

4.5.3.3 Effect of approaching electrode on electric current and soil pH
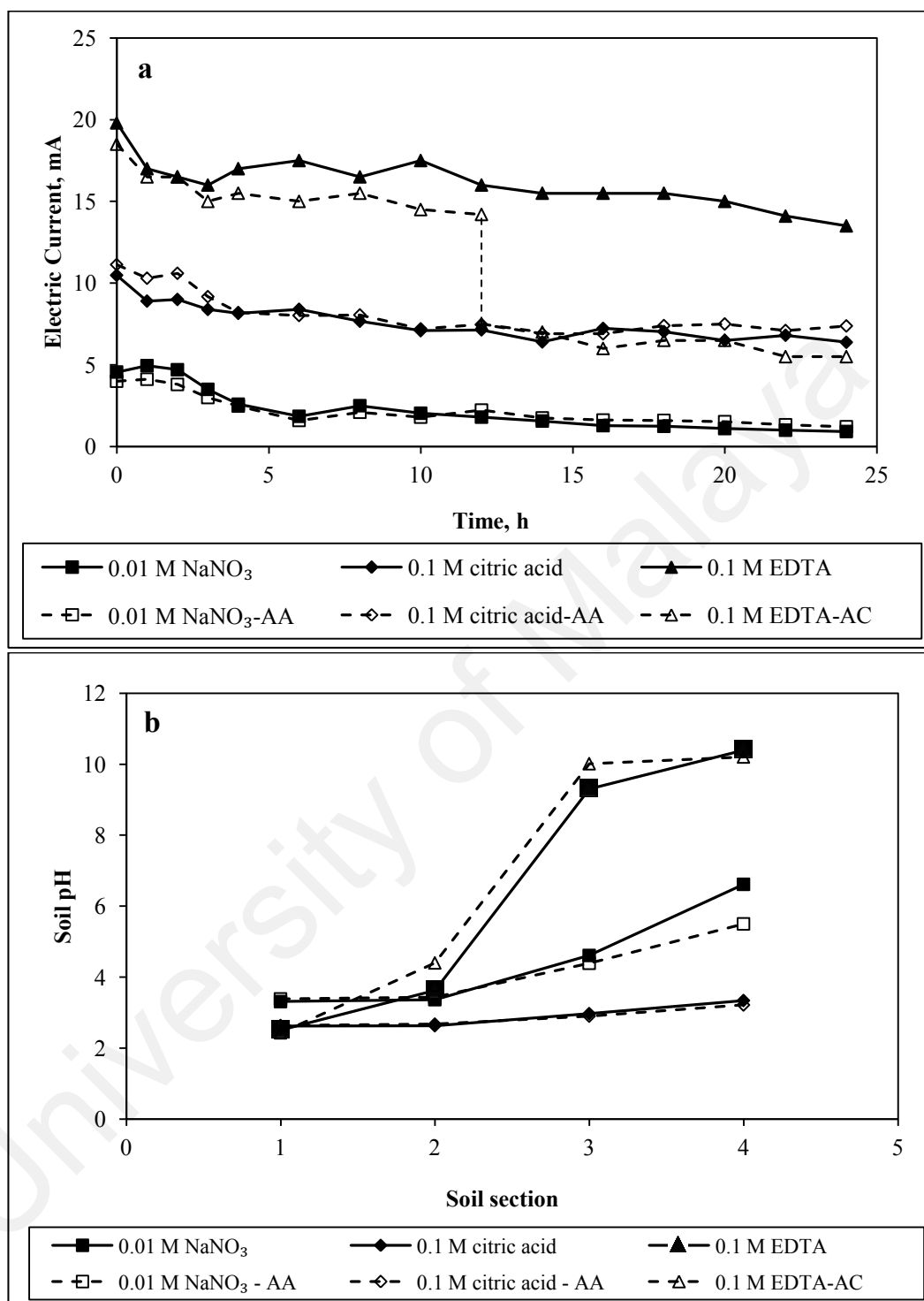
Figure 4.37: Effect of approaching electrode technique on: a) electric current across the soil, and b) soil pH in electrokinetic process under different types of wetting agents (AA: approaching anode; AC: approaching cathode)

The ability of approaching electrode in enhancing system performance was investigated by switching one of the electrode pairs (anode or cathode) to the middle electrodes (Figure 3.3) at 12th hour of the experiments while maintaining a voltage gradient of 1 V/cm by adjusting the electric potential difference from 7.5 V to 3.75 V. Approaching anode was used for 0.01 M $NaNO_3$ and 0.1 M citric acid tests as Pb migration headed towards cathode. On the other hand, approaching cathode was applied for 0.1 M EDTA test, considering Pb electromigration towards anode was dominant.

Figure 4.37a illustrates that the use of approaching anode does not affect the electric current across the soil significantly when 0.01 M $NaNO_3$ and 0.1 M citric acid are applied as the wetting agents. This observation was different from other approaching anode studies which reported that the electric current was enhanced (Shen *et al.*, 2007; Li *et al.*, 2012). Unlike other studies, this could be due to the fact that the present system was operated in a close system without continuous supply of wetting agent/electrolyte from wash solution chambers. As majority of mobile ions were accumulated in S3-S4 region, the reduction in migration distance did not enhance ions mobility significantly and thus the current enhancement was less significant. The reduction in migration distance also did not enhance electric current for EDTA test. Instead, the electric current is reduced from 14.2 mA to 7.5 mA when the cathode is switched to the middle electrodes, as shown in Figure 4.37a. This trend was also observed in the work of Zhang *et al.* (2014) in which the electric current obtained by approaching anode technique was lower than fixed electrode tests. This could be attributed to several reasons. Firstly, the present study was conducted in a closed system which did not have any wash solution chamber for continuous supply of wetting agent. Considering there was significant amount of ions present in S3-S4 regions, such as OH^- and EDTA complexes, the switching of cathode into the middle soil section (S2) after 12th hour experiment may reduce the amount of mobile ions available under the electric

field, as the ions in S3-S4 were no longer involved in electrokinetic process. In addition, the reduction in electric current may also be attributed to the nature of EDTA and Pb-EDTA complexes, which had lower mobility at low pH S1-S2 region (Amrate *et al.*, 2005; Alcántara *et al.*, 2012), as discussed in Sub-section 4.5.3.2. This suggested that the amount of free mobile ions in this region was low. Thus, the electric current was reduced.

The use of approaching electrode technique in electrokinetic process had a strong bearing on the soil pH. Figure 4.37b shows that approaching anode provides progressive acidification for S3-S4 region in 0.01 M $NaNO_3$ test. As the anode was switched to the middle electrodes, H^+ was produced in the S2-S3 region. This shortened the migration distance for H^+ transport towards S4 region and improved the acid front, considering the electromigration speed of H^+ is about 1.8 times faster than OH^- (Acar and Alshawabkeh, 1993; Acar *et al.*, 1995; Chung and Kang, 1999; Gioannis *et al.*, 2008; Park *et al.*, 2009; Kim *et al.*, 2011b). Thus, high pH region was compressed. This observation was also in line with the study carried out by Li *et al*. (2012). On the other hand, Figure 4.37b reveals that progressive soil acidification is not significant in 0.1 M citric acid test as low soil pH was already achieved by the amount of H^+ supplied by citric acid.

In contrast, the application of approaching cathode was found to provide progressive soil alkalisation. As shown in Figure 4.37b, soil pH in S2 and S3 are slightly higher when approaching cathode is adopted in 0.1 M EDTA test even though the electric current was reduced. This was also in line with the work of Shen *et al*. (2009) and Zhou *et al*. (2014) which reported that the use of approaching cathode increased soil pH via progressive soil alkalisation. The electrode switching into the middle electrode not only reduced the acid front towards S2-S3 but also induced electrolysis in S2 for

providing more OH⁻ to nullify the H⁺ available in S2 region and thus the soil pH was increased.

4.5.3.4 Effect of approaching electrode on Pb migration
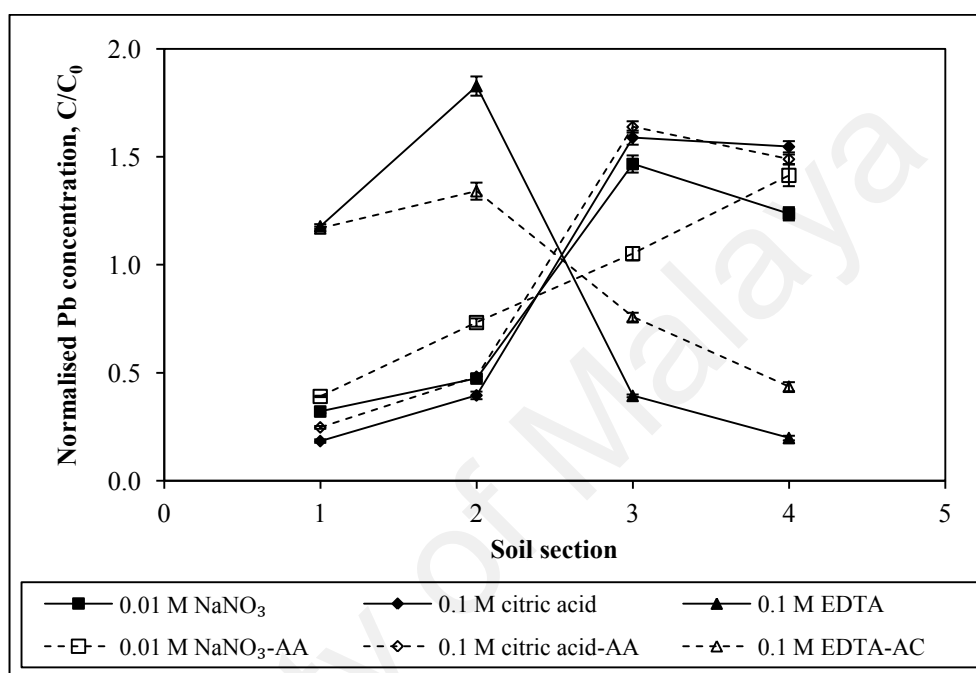
Figure 4.38: Normalised Pb concentration at different soil sections after the experiments for both fixed electrode tests and approaching electrode tests (AA: approaching anode; AC: approaching cathode)

Figure 4.38 illustrates the distribution of Pb at different soil sections between fixed electrode tests and approaching electrode tests. For approaching anode tests, the results showed that 0.01 M NaNO₃ provided a steady transport of Pb from anode to cathode, without accumulation of Pb in S3 region. The reduction in soil pH in cathode region provided weaker Pb adsorption on soil surface (Yang *et al.*, 2006), which improved Pb mobility for electromigration. Thus, higher normalised Pb concentration at 1.41 was observed in S4 in comparison to fixed anode test of 1.24. This was also in line with the work of Li *et al.* (2012) who claimed that Cr focusing effect was reduced via better soil acidification when approaching anode technique was applied. However, the shift of anode at the 12ᵗʰ hour during the experiment causes lower Pb migration in S1-S2

region as higher normalised Pb concentration is detected, as illustrated in Figure 4.38. This could be due to incomplete Pb electromigration during electrode switching when 0.01 M $NaNO_3$ was used as the wetting agent. The lack of electrical force to maintain Pb electromigration in S1-S2 regions after anode switching was suggested to be the main cause for higher Pb concentration in S1-S2 region.

In contrast, the use of approaching anode does not affect Pb electromigration trend significantly under citric acid test, as shown in Figure 4.38. A highly acidic condition established by citric acid provided high Pb desorption and mobility in comparison to $NaNO_3$. Thus, Pb electromigration rate was higher and majority of Pb migrated to S3-S4 region before anode switching. Nevertheless, as discussed above, normalised Pb concentration in S1-S2 is slightly increased by 0.06-0.09 (47-65 mg/kg), as shown in Figure 4.38, resultant from anode switching.

On the other hand, approaching cathode showed different Pb migration trend in 0.1 M EDTA test. Unlike the work of Shen *et al*. (2009) and Zhou *et al*. (2014), Figure 4.38 reveals that approaching cathode does not enhance Pb electromigration as Pb concentration remained high in S3-S4 region. This was mainly due to incomplete Pb electromigration in this region, as a result of the absence of electric field after cathode switching. Besides that, Figure 4.38 also shows that there is insignificant enhancement in Pb electromigration in S1-S2 region when approaching cathode is applied in 0.1 M EDTA test. Pb accumulation was still observed in S2 region. This could be attributed to the soil pH in this region favoured for Pb-EDTA adsorption as the pH was still low at 4.4 even though alkalisation occurred. In addition, a lowering in electric current after the switching (Figure 4.37a) also suggested that low amount of mobile ions were available in S1-S2 regions, as discussed in Sub-section 4.5.3.3. The low Pb-EDTA mobility at low pH condition was perhaps the main reason for insignificant enhancement in Pb migration in S1-S2 region during approaching cathode tests.

4.5.3.5 Removal efficiency and power consumption
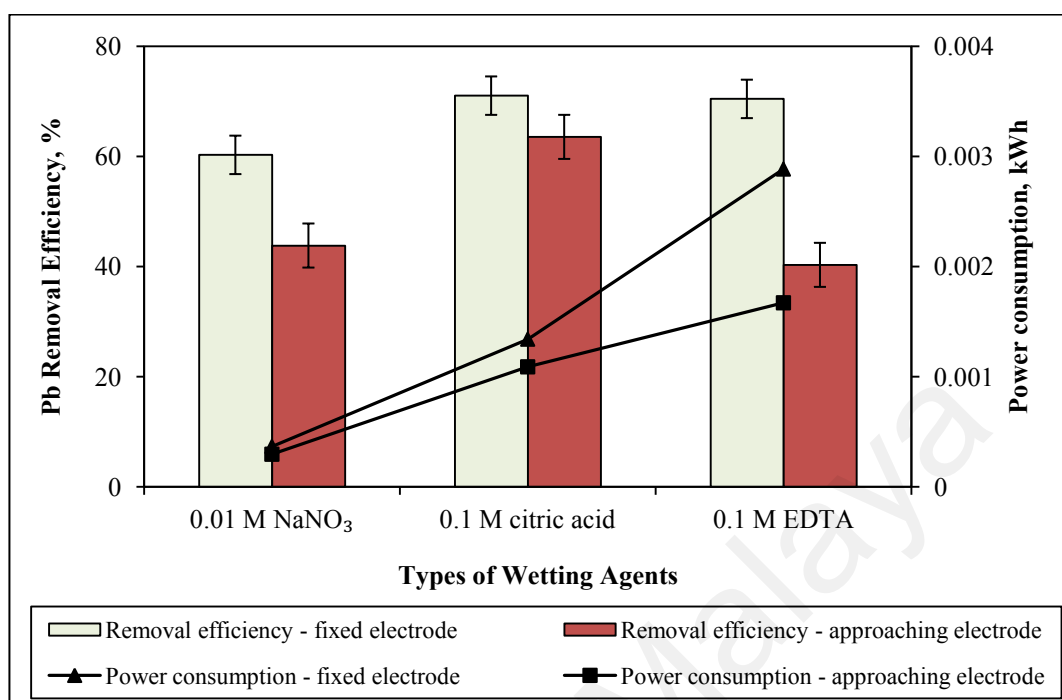
Figure 4.39: Removal efficiency in the pretreated region and power consumption of the system under different types of wetting agents

Sub-sections 4.5.3.2 set forth electrokinetic process as an effective method in reducing contaminated soil volume via concentrating Pb into smaller soil volume. Figure 4.36 shows that, in general, a contaminated soil volume reduction of 50% could be achieved in this study for all types of wetting agents, as Pb concentration of less than the threshold concentration of 400 mg/kg (normalised concentration: 0.54) (DoE-Malaysia, 2009) is detected in either S1-S2 ($NaNO_3$ and citric acid) or S3-S4 region (EDTA). Pb removal efficiency in these regions is illustrated in Figure 4.39. The results showed that high removal efficiency in the range of 60% to 71% was achieved, in a sequence of 0.1 M citric acid $\approx$ 0.1 M EDTA > 0.01 M $NaNO_3$. On the other hand, the power consumption, which was calculated based on Equation (4.16), was in the sequence of 0.1 M EDTA > 0.1 M citric acid > 0.01 M $NaNO_3$. This suggested that high power consumption did not always yield high Pb electromigration. Instead, a proper wetting agent which could desorb Pb effectively was more important in governing the removal efficiency.

$$\text{Power Consumption, kWh} = \int_0^t VI \cdot dt \qquad (4.16)$$

On the other hand, Figure 4.39 also reveals that the use of approaching electrode did not enhance the removal efficiency in this study. As shown in Figure 4.39, the application of approaching electrode reduces the power consumption by 18% to 42%. This was attributed to the reduction in the applied voltage from 7.5 V to 3.75 V for maintaining the voltage gradient at 1V/cm, as the migration distance is reduced after electrode switching. However, this also reduces the removal efficiency by 7% to 30%. Approaching electrodes did not enhance overall Pb migration and contaminated soil volume reduction in 0.01 M NaNO$_3$ and 0.1 M EDTA tests. Instead, soil volume reduction decreased from 50% to 25%, as Pb concentration of >400 mg/kg (normalised concentration >0.54) was detected in S2 and S3 for 0.01 M NaNO$_3$ and 0.1 M EDTA tests, respectively. Nevertheless, Figures 4.38 and 4.39 also show that the use of approaching anode technique demonstrates advantageous in 0.1 M citric acid test through reducing the power consumption by 18.75% while maintaining 50% soil volume reduction, with a slight decrease in removal efficiency in S1-S2 region from 71% to 64%.

4.5.3.6 Summary of remediation of single contaminated soil

The study revealed that Pb ion migrated and concentrated to a smaller soil volume under electrokinetic process with the aid of wetting agent. In this study, citric acid showed better Pb migration than NaNO$_3$ as it provided better soil acidification for Pb desorption while preventing Pb adsorption/ precipitation in cathode region. In contrast, EDTA was not suitable as a wetting agent for Pb eletromigration in this study due to its poor mobility at low pH S1-S2 section. Introduction of approaching anode and

cathode enhanced soil acidification and alkalisation, respectively. However, using the present set up, they did not enhance Pb migration significantly, especially for 0.1 M EDTA tests. Nevertheless, this technique could reduce power wastage by 18.75% while maintaining efficient Pb migration and 50% soil volume reduction when citric acid was used as the wetting agent.

4.5.4 Application of electrokinetic process in treating co-contaminated soil

Sub-section 4.5.3 proves that electrokinetic process can be successfully applied as soil pretreatment method for concentrating Pb into smaller soil volume for the soil that was mainly contaminated by Pb. In order to further justify the feasibility of electrokinetic process in contaminated soil volume reduction, another study was conducted for treating a co-contaminated soil which consisted of 402.2 mg/kg Pb (cation contaminant) and 797.9 mg/kg Cr(VI) (anion contaminant) using similar equipment setup. Through this study, the effect of different types of contaminants with different charge on the effectiveness of electrokinetic process in electromigration and contaminated soil volume reduction could be evaluated.

4.5.4.1 Effect of wetting agents on electric current and soil pH

Figures 4.40a and 4.40b record the electric current passed through the soil during the experiments and final soil pH at different soil sections, respectively. In general, it is found that the magnitude of electric current is in a sequence of 0.1 M EDTA > 0.1 M citric acid > 0.01 M $NaNO_3$, as shown in Figure 4.40a. This trend is similar to single contaminated soil study, as discussed in Sub-section 4.5.3.1. However, it was worth noting that the initial electric current generated was higher in this study than single contaminated soil as the number of moles of mobile ions in the co-

contaminated soil (≈400 mg/kg Pb and ≈800 mg/kg Cr) was higher. In addition, the electric current for 0.01 M $NaNO_3$ test is found to increase from 11.2 mA to 18.0 mA at the first 3 h of the experiment, as shown in Figure 4.40a. This was mainly due to the increase in concentration for mobile ions as a result of electrolysis and desorption/solubilisation of Pb and Cr. As the experiments progressed, the electric current decreased even at constant voltage gradient, regardless of wetting agent used. This was also observed in the works of other researchers; it could be attributed to the increase in resistance polarisation in the soil and loss of ionic strength in the system, as a result of the electromigration of mobile ions towards their respective electrodes (Saichek and Reddy, 2003; Shen et al., 2007; Shen et al., 2009; Shrestha et al., 2009; Colacicco et al., 2010; Giannis et al., 2012; Zhang et al., 2014).

Figure 4.40b illustrates soil pH at different soil sections after the experiments. It was found that, in general, low pH of 2.45-3.05 was observed in S1 whilst high pH of 9.98-10.04 was observed in S4 region. When $NaNO_3$ is utilised as the wetting agent, a stable pH increment from 3.05 to 10.02 is observed, as shown in Figure 4.40b. This is a normal trend for electrokinetic process as electrolysis occurs at both anode and cathode which produce H^+ and OH^-, respectively (Acar and Alshawabkeh, 1993), as discussed in Sub-section 4.5.3.1. As the migration speed of H^+ is about 1.8 times faster than OH^- migration (Acar and Alshawabkeh, 1993; Acar et al., 1995; Chung and Kang, 1999; Gioannis et al., 2008; Park et al., 2009; Kim et al., 2011b), a pH gradient is observed in the S3 region. In contrast, when 0.1 M citric acid is used, the soil is at low pH in S1-S3 whilst S4 shows a much higher pH at 9.98, as shown in Figure 4.40b. Citric acid generally acidified the soil and served as buffer solution for preventing pH change. Thus, the only high pH region observed after the experiment was S4, which had undergone electrolysis via the cathode (Acar and Alshawabkeh, 1993). For 0.1 M EDTA test, high overall soil pH was obtained. Figure 4.40b depicts that a soil pH of 6.81 was achieved

in S2 region and a pH of >10 was obtained for S3-S4 regions whilst the only low pH region was in S1 at 2.45. High overall pH was mainly due to the pH of EDTA solution, which was around 8-9. The presence of OH^- in the wetting agent was responsible for increasing the soil pH before electrokinetic process was applied. This eventually caused higher soil pH in S2-S4 region in comparison to the tests that used 0.01 M $NaNO_3$ and 0.1 M citric acid.
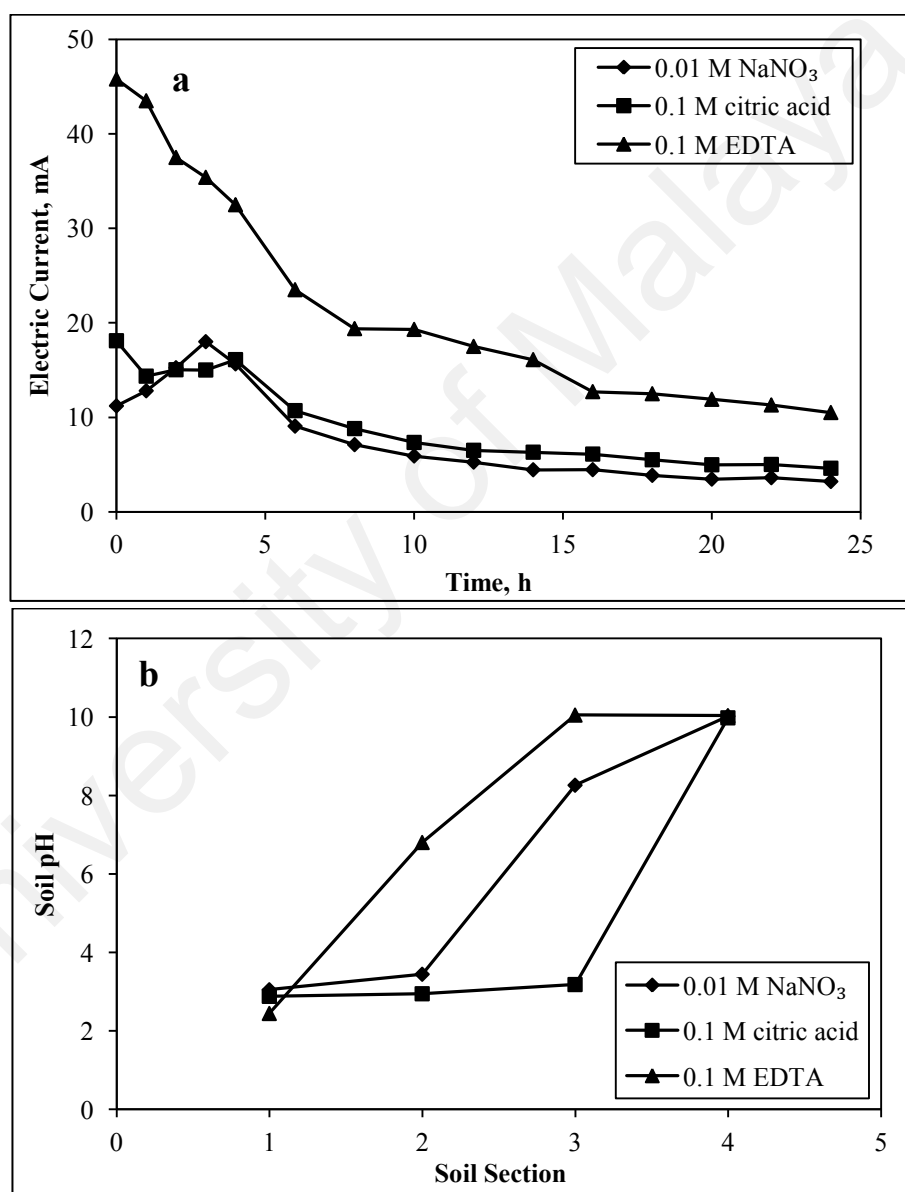
Figure 4.40: a) Electric current across the soil, b) soil pH at different soil sections after the experiments

It was worth noting that higher pH gradient was observed in these tests in comparison to the single contaminated soil (Sub-section 4.5.3.1). This was mainly due to the difference in nature of soils manifested after spiking with different types of heavy metals. A higher electric current generated in these tests (Figure 4.40a) enhanced the electrolysis process (Tsai *et al.*, 2010). The higher rate in increment of H^+ and OH^- concentrations at both regions for co-contaminated soil study eventually caused a sharper pH gradient in the soil. Besides that, a higher initial soil pH for co-contaminated soil ($\approx$6) than single contaminated soil ($\approx$4) after spiking could be responsible for higher pH in cathode region. This suggested that the acid buffering capacity for the co-contaminated soil was higher than that of single contaminated soil. The amount of H^+ provided by the wetting agent in co-contaminated soil was inadequate to maintain low pH condition as in single contaminated soil.

4.5.4.2 Effect of wetting agents on Pb migration
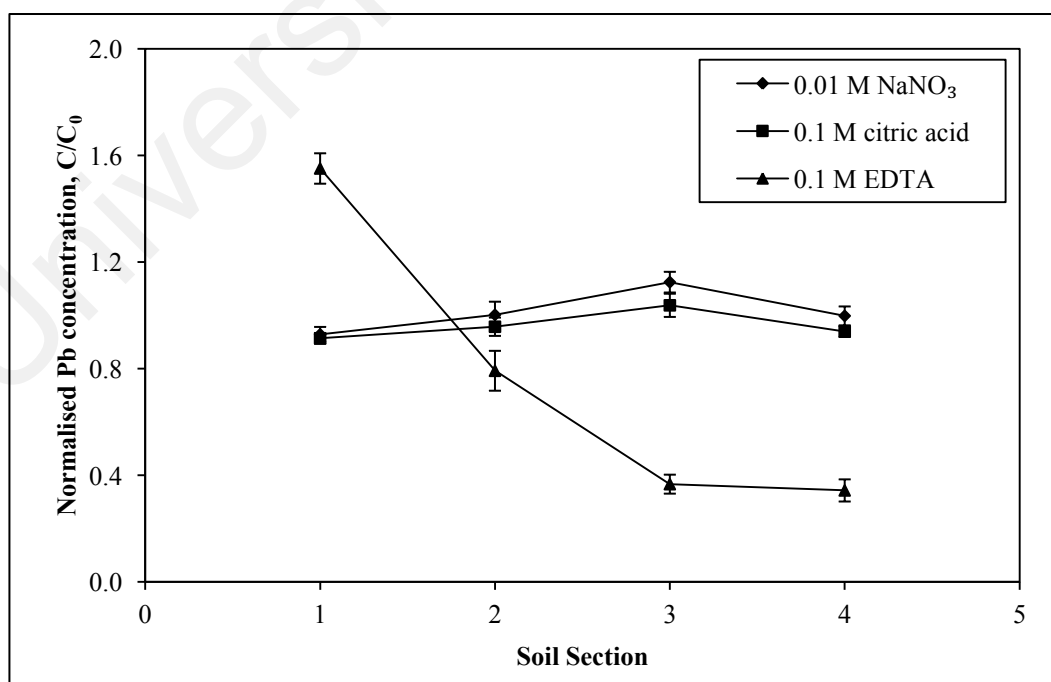
Figure 4.41: Normalised Pb concentration at different soil sections after the experiments

Figure 4.41 illustrates the distribution of normalised Pb concentration at different soil sections after the experiments. The results revealed that different migration trends were observed for Pb when different types of wetting agents were used. The figure illustrates that, in general, significant Pb migration is only observed when 0.1 M EDTA is applied as the wetting agent whilst 0.01 M $NaNO_3$ and 0.1 M citric acid provides poor migration, even though these tests have significant electric current. For $NaNO_3$ and citric acid tests, minor migration of Pb was observed from both S1 and S4. The Pb is accumulated in S3 region with enrichment factor of 1.04-1.12 while other regions show normalized concentration of 0.9-1, as shown in Figure 4.41. The migration trend was contradictory to the work reported in Sub-section 4.5.3.2. This was mainly due to the difference in Pb species in Pb/Cr co-contaminated soil. In the presence of excessive Cr, the main Pb species in the co-contaminated soil was $PbCrO_4$, as a result of precipitation reaction between $Pb(NO_3)_2$ and $K_2Cr_2O_7$ during soil spiking (Madan and Prakash, 1987). $PbCrO_4$ generally had very low solubility in water (Eagleson, 1994) and they dissolve partially in acidic and basic media for electromigration, as shown in Equations (4.17) and (4.18), respectively (BUTE, n.d.). The low overall mobility for $PbCrO_4$ in these wetting agents could be the main reason for poor electromigration. This observation was also reported by Jensen *et al*. (2007) and Zhang *et al*. (2012) on the electromigration of $PbCrO_4$ using $NaNO_3$ and deionized water, respectively. Besides that, the enrichment of Cr in S1-S2 region during electromigration could also slowed down Pb migration towards the cathode via possible formation of water insoluble $PbCrO_4$ (Zhang *et al.*, 2012) during the contact. Moreover, the pH jump in S3-S4 region (Figure 4.40b) which favoured Pb adsorption and $Pb(OH)_2$ precipitation (Chaari *et al.*, 2008; Mohapatra *et al.*, 2009; Niu *et al.*, 2013) may also contributed to Pb accumulation in S3 region, as discussed in Sub-section 4.5.3.2.

$$2PbCrO_4 + 2H^+ \Leftrightarrow 2Pb^{2+} + Cr_2O_7^{2-} + H_2O \qquad\qquad (4.17)$$

$$PbCrO_4 + 4OH^- \Leftrightarrow \left[Pb(OH)_4 \right]^{2-} + CrO_4^{2-} \qquad\qquad (4.18)$$
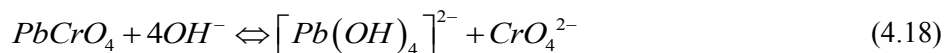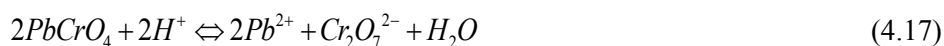
In contrast, Figure 4.41 shows that the use of 0.1 M EDTA provides Pb migration towards S1 (anode region), even though it had relatively lower concentration than Cr. This was mainly due to the effect of high pH EDTA solution which not only dissolved $PbCrO_4$ (Koshi and Iwasaki, 1983; Madan and Prakash, 1987; Tuli and R.L. Madan, 1999; Trishna Knowledge Systems, 2012) but also served as chelating agent for water soluble Pb-EDTA complexes formation (Niinae *et al.*, 2008; Zhang *et al.*, 2014). As the complexes formed are anionic, Pb electromigrates towards S1 under the electric field and accumulates with an enrichment factor of 1.55, as shown in Figure 4.41. Unlike the migration in single contaminated soil, Pb accumulation was not observed in S2 region. This was plausibly due to relatively high soil pH in S2 region (6.81 vs 3.63) which improved the stability of both EDTA and Pb-EDTA complex while minimizing the adsorption process, as discussed in Sub-section 4.5.3.2. In addition, Pb concentration in S3-S4 region also reduced to 0.34-0.37 of its initial concentration.

4.5.4.3 Effect of wetting agents on Cr migration

Figure 4.42 depicts the normalised Cr concentration at different soil sections using different types of wetting agents. It was found that the migration trend was generally different from Pb whereby Cr migration from S4 to S1 regions was achieved in all types of wetting agents. In this study, majority of Cr was more mobile than Pb as they were initially in hexavalent form after spiking and they were mainly adsorbed on the soil surface rather than in water insoluble form. The results, as shown in Figure 4.42, suggest that the migration follows the sequence of 0.1 M EDTA > 0.01 M $NaNO_3$ > 0.1 M citric acid. This trend is also observed from the physical appearance of the soil after

the experiment, as shown in Figure 4.43 where the yellow and purple textures in the figure indicate high concentration of Cr ions and Cr(III)-EDTA (Hedrick, 1965), respectively, in the soil region. A stronger yellow texture in 0.01 M NaNO$_3$ test (Figure 4.43a) and purple texture in 0.1 M EDTA test (Figure 4.43c) in S1 region indicate Cr is electromigrated and concentrated in S1 region whilst a mild yellow texture in S1-S3 region, as shown in Figure 4.43b, shows poor Cr migration in 0.1 M citric acid test.
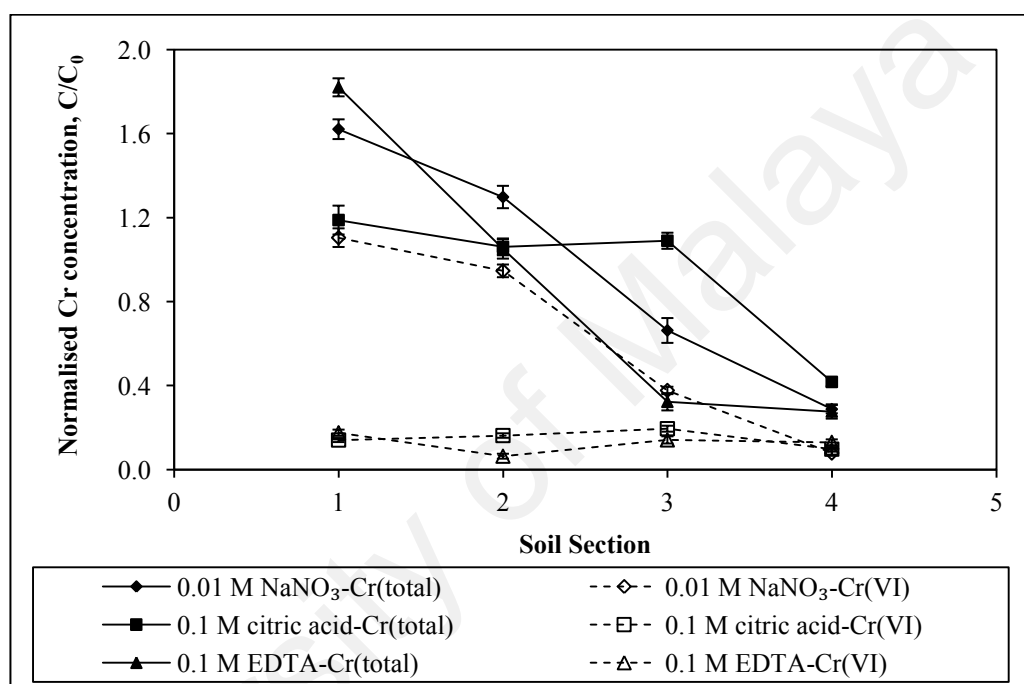
Figure 4.42: Normalised Cr concentration at different soil sections after the experiments

Figure 4.42 shows that unlike Pb, a smooth migration from S4 to S1 is observed for both 0.01 M NaNO$_3$ and 0.1 M EDTA even though the former does not enhance Cr solubility in aqueous phase. This could be mainly due to the higher mobility for Cr(VI) than PbCrO$_4$ in this study. Among the wetting agents, EDTA provided lower Cr concentration in S3-S4 region, which could be attributed to higher current for electromigration and relatively high soil pH provided by 0.1 M EDTA, which favoured Cr(VI) desorption (Hu *et al.*, 2005; Reddy, 2013; Troy, 2013). In addition, EDTA also showed higher Cr migration in S2 region as it could enhance Cr(VI) desorption via

relatively higher soil pH provided in S2 region. Moreover, it can complex with H^+ ions or adsorbed on the soil surface, releasing Cr(VI) from the soil (Saeedi *et al.*, 2013). EDTA also served as a chelating agent for the formation of Cr(III)-EDTA anionic complexes (Jung *et al.*, 1997; Cao *et al.*, 2011; Saeedi *et al.*, 2013), which ensured one way electromigration towards S1. This migration trend was also in line with the work of Reddy and Chinthamreddy (2004) and Saeedi *et al*. (2013). In contrast, Cr migration slows down at low pH S1-S2 region when 0.01 M $NaNO_3$ is applied, as shown in Figure 4.42. Low soil pH condition provided more positively charged binding sites for the adsorption of negatively charged Cr(VI) compounds such as $Cr_2O_7^{2-}$ and CrO_4^{2-} (Hawley *et al.*, 2005). This was also in line with the works of Hu *et al.* (2005) and Troy (2013) which reported that acidic condition favoured Cr(VI) adsorption on the soil surface's iron oxides. This in turn reduced the desorption process and Cr(VI) mobility in S1-S2 region and thus the electromigration was slowed down. In addition, low pH condition may also cause Cr(VI) reduction into Cr(III), especially in the presence of iron species as electron donor (Huang *et al.*, 1995; Hawley *et al.*, 2005; Weng and Tsai, 2009; Barrera-Díaz *et al.*, 2012). These conditions were achieved in S1-S2 region in this test, as the soil had significant amount of iron content (3719 mg/kg). The formation of positively charged Cr(III) species and the inability of $NaNO_3$ to form anionic complexes with Cr(III) may lead to transport of Cr(III) towards the cathode region (S4) via electromigration. Consequently, the net electromigration rate for Cr towards anode in S1-S2 region decreased.
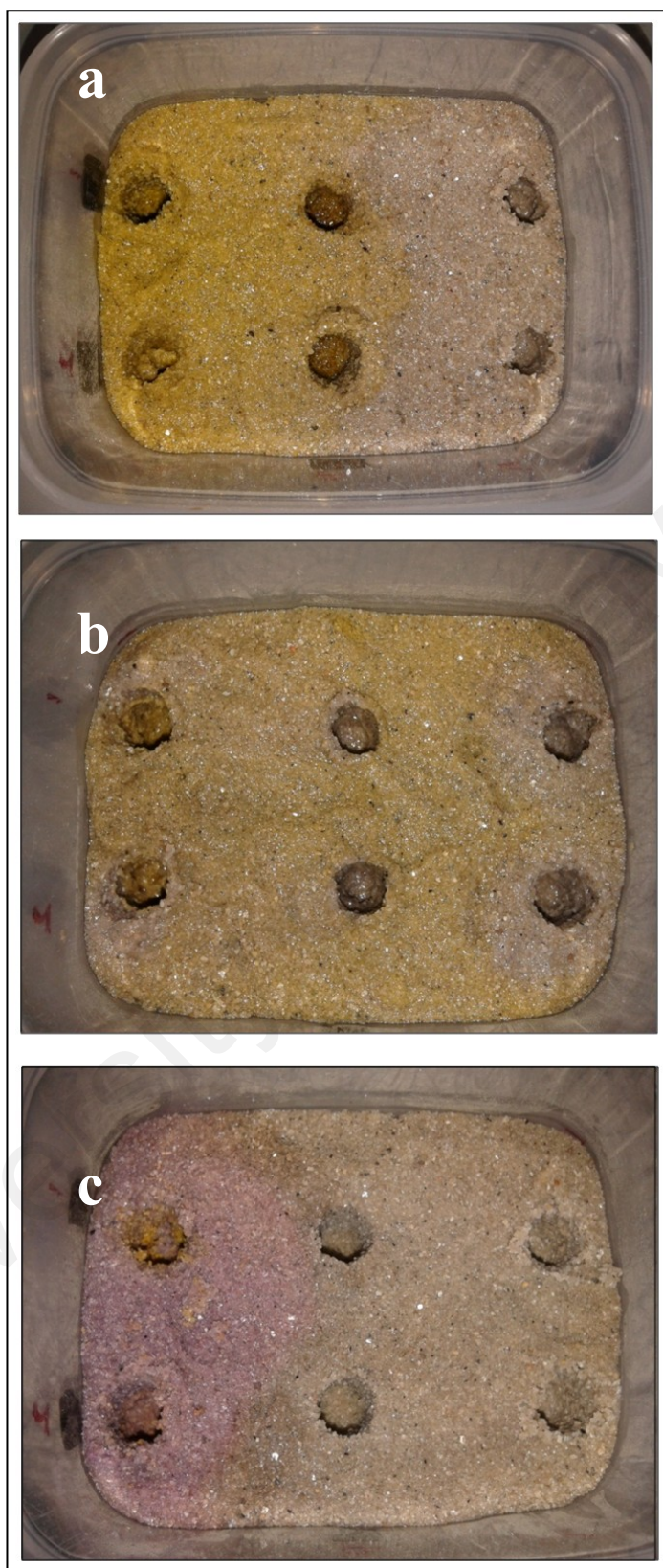
Figure 4.43: Physical observation of soil after the experiments under: a) 0.01 M NaNO$_3$; b) 0.1 M citric acid; c) 0.1 M EDTA (Left section: anode region (S1); Right section: cathode region (S4))

For the case of 0.1 M citric acid, Figures 4.42 and 4.43b show that significant Cr migration takes place only in S4 region whilst S1-S3 region shows weak migration. The migration in S4 was mainly attributed to high pH condition that favoured Cr(VI) desorption (Hu *et al.*, 2005; Troy, 2013). In addition, citric acid was also reported to cause Cr(VI) reduction into Cr(III) (Meichtry *et al.*, 2007), which could further form negatively charged complexes with citrate ion at a pH of >9 (Cao *et al.*, 2011). Thus, Cr migrated away from S4. However, as S1-S3 was in low pH, the migration declined. Low soil pH condition not only favoured Cr(VI) adsorption (Hu *et al.*, 2005; Troy, 2013) but also Cr(VI) reduction (Barrera-Díaz *et al.*, 2012), especially in the presence of citric acid (Meichtry *et al.*, 2007). This is observed in the present study, as shown in Figure 4.42, where most of the Cr ion in the soil is in the form of Cr(III). Moreover, the formation of Cr(III)-citrate complex in the presence of citric acid could be another reason for poor Cr electromigration in S1-S3. As majority of Cr(III)-citrate complexes formed were in neutral or positive charged (Cao *et al.*, 2011) at the resulted pH condition, it may have halted Cr electromigration towards S1. Furthermore, Cr(III)-citrate is also reported to show high affinity towards adsorption on soil at low pH condition (Cao *et al.*, 2011) and this could reduce the migration in S1-S3 region.

4.5.4.4 Effect of approaching electrode on electric current and soil pH

The results as shown in Figures 4.41 reveal that Pb is generally immobilized in the co-contaminated soil when 0.01 M NaNO$_3$ and 0.1 M citric acid are applied as wetting agents. On the other hand, 0.1 M EDTA provides one way electromigration for both Pb and Cr from S4 to S1 region, as shown in Figures 4.41 and 4.42. Thus, the feasibility of approaching electrode in enhancing Pb and Cr migration was evaluated for 0.1 M EDTA test only as it showed positive electromigration for both Pb and Cr in

comparison to the other two. As the electromigration headed towards the anode, approaching cathode was applied.
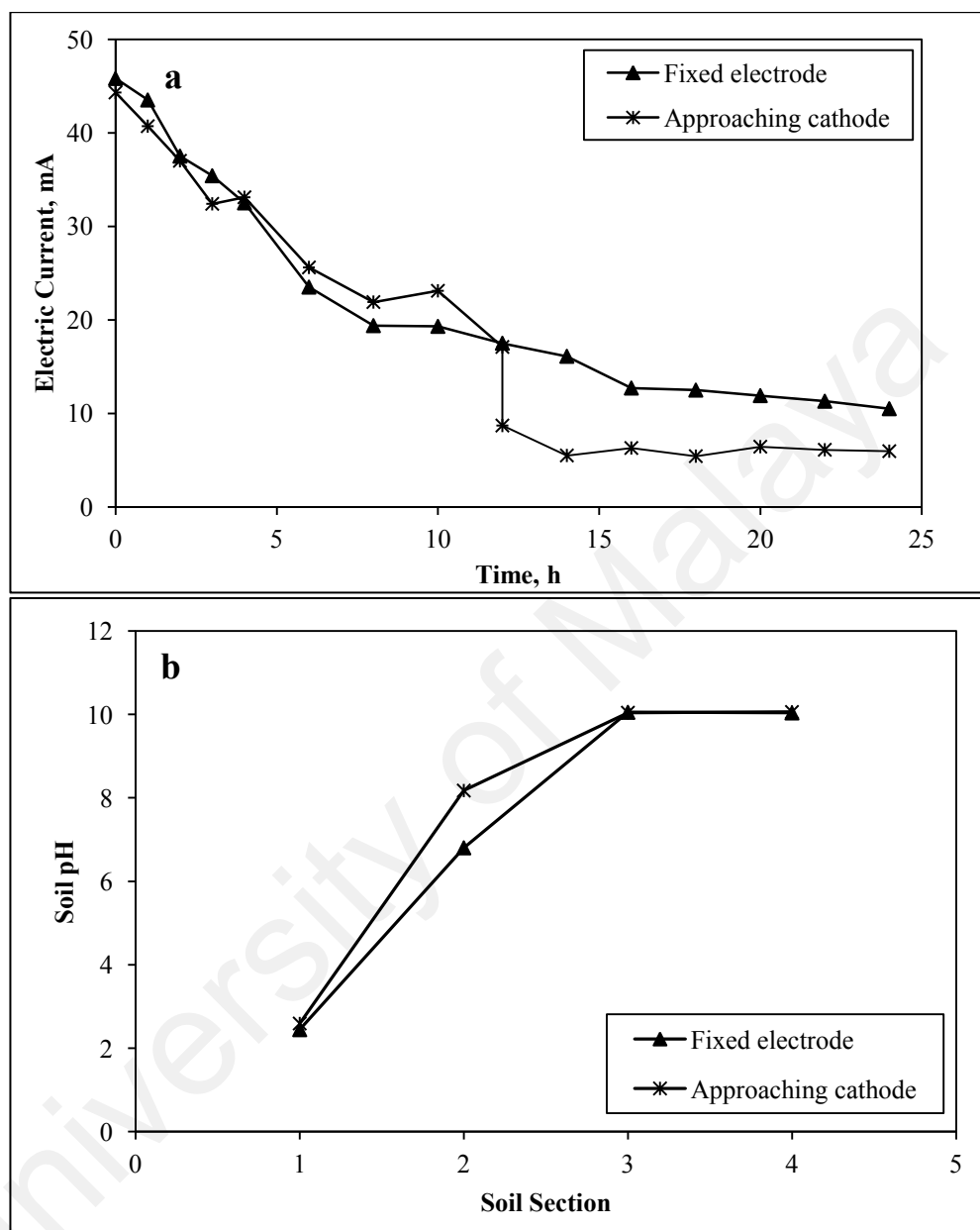
Figure 4.44: Electrokinetic properties for fixed electrode test and approaching cathode test using 0.1 M EDTA as wetting agent: a) electric current across the soil; b) soil pH at different soil sections

Figure 4.44a shows that, unlike the works of Shen *et al*. (2009) and Zhou *et al*. (2014) which reported that approaching cathode enhanced electric current in the remediation process, the electric current generated is found to decrease from 17.1 mA to 8.7 mA when the cathodes are switched to the middle electrodes at 12th hour. The results follow similar trend as the single contaminated soil, as shown in Figure 4.37a.

This could be mainly due to the present experimental setup, which was a closed system in which the wash solution chamber was absent for continuous supply of wetting agent/ions into the system. The switching of electrode at 12th hour of the experiment reduced the amount of mobile ions available under the electric field, as the ions in S3-S4 were no longer involved in electrokinetic process, as discussed in Sub-section 4.5.3.3. Thus, the electric current was reduced. Nevertheless, it is worth noting that despite the current reduction in approaching cathode test, Figure 4.44b depicts that soil pH in S2 increases from 6.81 to 8.18, indicating progressive soil alkalisation. Progressive alkalisation was also observed in the works of Shen *et al.* (2009), Zhou *et al.* (2014) and the treatment for single contaminated soil in the present work (Sub-section 4.5.3.3). This could be attributed to the OH^- production in S2 region for nullifying the available H^+ in S2 and reduction in OH^- migration distance for better base front after the cathode was switched to the middle of the soil.

4.5.4.5 Effect of approaching electrode on Pb and Cr migrations

Figure 4.45a illustrates that, in general, the improvement in Pb migration from S2 to S1 via approaching cathode is insignificant under the present experimental conditions. Unlike the work of Shen *et al.* (2009), the increment in soil pH in the S2 region as well as the reduction in migration distance did not show significant improvement in Pb migration. In comparison with other publications which reported that approaching electrode enhanced the electromigration and removal efficiency (Shen *et al.*, 2007; Shen *et al.*, 2009; Li *et al.*, 2012; Zhang *et al.*, 2014; Zhou *et al.*, 2014), electromigration for Pb-EDTA was not enhanced in the present study as majority of Pb ions had already electromigrated close to the anode (S1 region). Thus, the mobility was not significantly enhanced when electrode distance was reduced. Moreover, possible

adsorption of negatively charged Pb-EDTA complexes on the soil (Reddy *et al.*, 2010) in low pH S1 region may be another reason for poor electromigration enhancement. Furthermore, Figure 4.45a also depicts that the switching process results in higher Pb concentration in S3-S4 region in comparison to fixed electrode test. This is in line with the observation for single contaminated soil, as shown in Figure 4.38, as the absence of electric field in S3-S4 region after cathode switching may cause incomplete Pb-EDTA migration in this region, as discussed in Sub-section 4.5.3.4. However, it was worth noting that the increase in normalised Pb concentration in S3-S4 region in approaching cathode test was relatively low for co-contaminated soil (0.36 to 0.43) in comparison to single contaminated soil (0.30 to 0.60). This can be mainly attributed to higher soil pH achieved in S2 region in co-contaminated soil for better Pb-EDTA complex electomigration in comparison to single contaminated soil, which tended to accumulate in low pH S2 region and reduced Pb electromigration.

Similar observation is also made for Cr, as shown in Figure 4.45b. The use of approaching cathode did not enhance Cr accumulation in S1 region significantly. Instead, it showed higher Cr concentration in S3-S4 region as a result of incomplete Cr migration due to cathode switching. Thus, it was suggested that the present soil pretreatment set-up and experimental condition is not appropriate for approaching cathode techniques to enhance electromigrations of Pb and Cr. Nevertheless, it is suggested that the effect of approaching cathode on heavy metals migration could be more significant when larger size of soil sandbox is used, whereby the distance between anode and cathode is longer so that multiple electrode switching can be used, as reported by Shen *et al*. (2009).
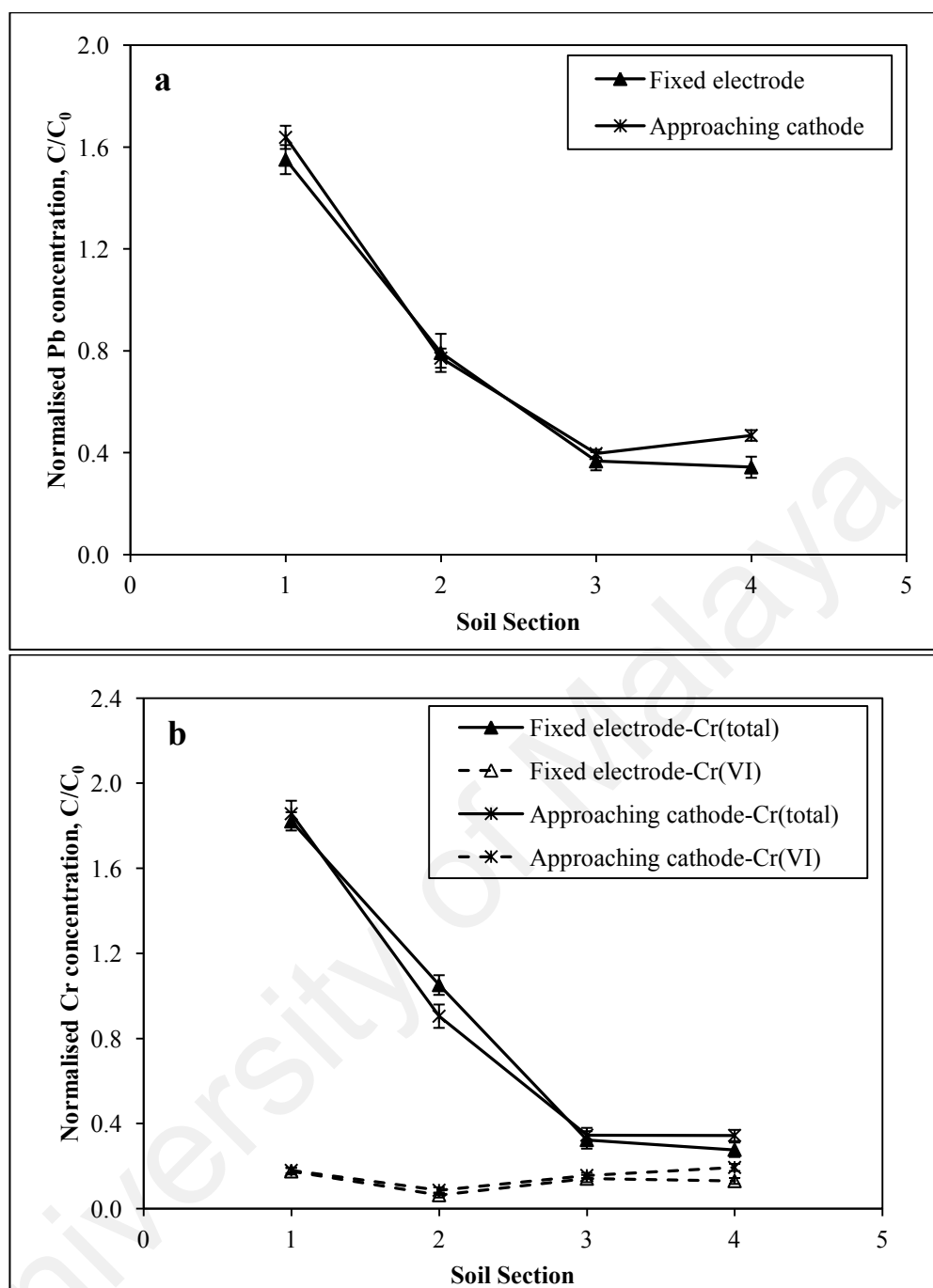
Figure 4.45: Normalised concentration for a) Pb, and b) Cr after the experiments at different soil sections under fixed electrode and approaching electrode tests using 0.1 M EDTA as the wetting agent

4.5.4.6 Removal efficiency and power consumption
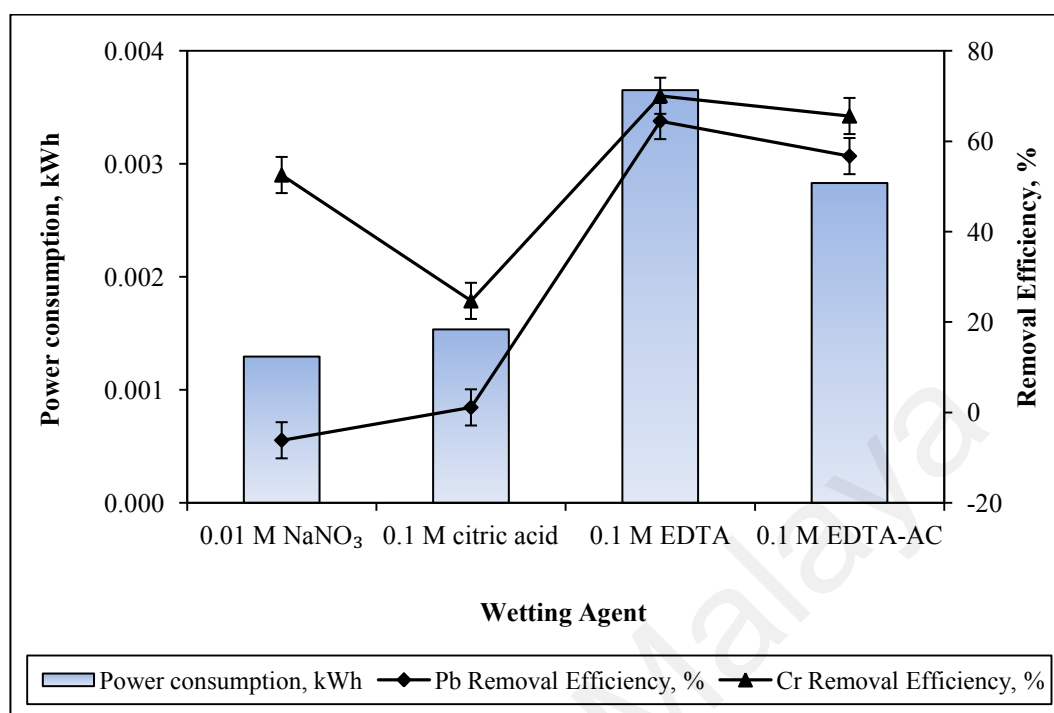
Figure 4.46: Power consumption and removal efficiency in pretreated soil regions (S3-S4) under different types of wetting agents (AC: approaching cathode)

As shown in Figures 4.41 and 4.42, electrokinetic process concentrates Pb and Cr into S1 and S2 regions when EDTA is applied as the wetting agent. This generally provided soil pretreatment and contaminated soil volume reduction indirectly in S3-S4 region as the concentrations of Pb and Cr were reduced. Therefore, Pb and Cr removal was achieved in these regions. Figure 4.46 reveals that electrokinetic process yields high removal efficiency for both Pb and Cr at 64-70% in S3-S4 regions via electromigration when 0.1 M EDTA is used as the wetting agent in comparison to the other two. On the other hand, 0.01 M $NaNO_3$ and 0.1 M citric acid showed poor Pb removal efficiency in S3-S4 at -6% and 1%, respectively. This was particularly true for Pb due to poor mobility of $PbCrO_4$ for electromigration. Moreover, the removal efficiency for Cr in S3-S4 regions using these agents is also found to be relatively lower than 0.1 M EDTA, as shown in Figure 4.46.

The power consumption for electrokinetic soil pretreatment process was calculated based on Equation (4.16). Despite 0.1 M EDTA showing higher removal efficiency for Pb and Cr, Figure 4.46 shows that 0.1 M EDTA causes an electric power consumption of ≈2.8 and ≈2.4 times higher than 0.01 M $NaNO_3$ and 0.1 M citric acid tests, respectively. As an effort to improve Pb/Cr electromigrations at lower power consumption, the study on approaching cathode using 0.1 M EDTA revealed that enhancement of electromigrations in S1-S2 region was not achievable using the present setup. Nevertheless, a high saving in power consumption of 22.5% from $3.65x10^{-3}$ kWh to $2.83x10^{-3}$ kWh was obtained with a minor decrease in removal efficiency for both Pb and Cr by 4% to 8%.

4.5.4.7 Summary of remediation of co-contaminated soil

The study revealed that electrokinetic process can electromigrate and concentrate heavy metals into smaller soil volume even for the metal ions carrying different charges, as long as suitable wetting agent was used. In this study, EDTA emerged as the best wetting agent among the three. It not only provided high pH condition for enhancing Cr(VI) desorption but also performed as a chelant for negatively charged water soluble complexes formation for sparingly soluble Pb and Cr(III). Unlike the test for single contaminated soil, EDTA did not show Pb and Cr accumulation in the S2 region as a result of relatively high initial soil pH for co-contaminated soil. In contrast, $NaNO_3$ and citric acid showed poorer performance, particularly in providing Pb mobility for electromigration. From the aspect of approaching electrode technique, the use of approaching cathode in 0.1 M EDTA test provided better soil alkalisation in S2 region. However, this did not enhance the electromigration significantly for both Pb and Cr in S1-S2 region. Nevertheless, this

technique could save 22.5% of power consumption while maintaining efficient migration in S3-S4 when EDTA was used as wetting agent.

4.5.5 Summary

The study reveals that electrokinetic process is effective in electromigrating and concentrating Pb into smaller soil volume. This generally serves as a good choice as soil pretreatment method before the application of other remediation techniques such as stabilisation and solidification as the volume of contaminated soil can be reduced. The present study showed that this technique was in potential to reduce the contaminated soil volume for both single Pb contaminated soil and Pb/Cr co-contaminated soil. The performance of electrokinetic process was highly dependent on the types of wetting agents used, the nature of contaminants, and the soil condition. As discussed in Sub-sections 4.5.3.2, citric acid emerged as the best wetting agent in providing high Pb electromigration in single contaminated soil, in which the Pb was mainly adsorbed/ bounded on the iron/mineral oxides in the soil. However, citric acid showed poor Pb electromigration in co-contaminated soil which mainly consisted of water insoluble $PbCrO_4$, as discussed in Sub-section 4.5.4.2. Instead, EDTA emerged as a superior wetting agent in providing one way electromigration for both Pb and Cr towards the anode region in co-contaminated soil study.

The application of approaching electrodes in this study did not enhance electromigration for Pb and Cr significantly for both contaminated soils. Nevertheless, this technique reduced the power consumption for electrokinetic process while it only slightly reduced the removal efficiency in the pretreated soil sections when suitable wetting agent was used, as discussed in Sub-sections 4.5.3.5 and 4.5.4.6. Power wastage on the pretreated soil sections could be prevented by using approaching electrode.

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CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

This chapter summarises the findings on the technical feasibility study of the incorporation of electrokinetic process with other soil remediation methods based on the research objectives established. This chapter also proposes recommendations on future works.

5.1 Conclusions

The suitability of electrokinetic process to incorporate with other soil remediation methods was investigated from two angles: i) to enhance removal efficiency in soil washing at low chemical solution consumption, and ii) to serve as soil pretreatment method to concentrate heavy metals into smaller soil volume such that chemical usage for further remediation could be reduced.

5.1.1 Application of two-stage electrokinetic washing

Electrokinetic process had been incorporated with soil washing as a two-stage electrokinetic washing for remediating Pb contaminated soil in this study. Two-stage electrokinetic washing is a novel soil remediation technique in which the soil washing and electrokinetic process were operated at two different stages in a single equipment. This process consists of: i) initial soil washing to provide desorption condition to the soil, and ii) electrokinetic process to transport the desorbed Pb away from the soil. Soil washing was initiated by filling up anode chamber while the cathode chamber was left empty. Due to the hydraulic gradient difference between the chambers, the wash solution entered the soil column and provided Pb desorption. The transport of wash solution into cathode chamber provided early Pb removal until the cathode chamber was

fully filled up. Once the soil washing process was completed, electrokinetic process was induced as the second driving force for transporting the desorbed Pb in the soil towards the cathode chamber in the absence of hydraulic flow.

The study on the removal of Pb from high iron content sandy soil was initiated by screening the chemical agents via shake flask desorption tests. Based on the tests, 0.1 M HNO_3, 0.1 M citric acid and 0.01 M EDTA solution were used for two-stage electrokinetic washing as they not only showed high Pb removal efficiency but also had negligible undesirable effects such as odour and possible release of harmful gas during electrokinetic washing compared to H_2SO_4, HCl and acetic acid.

The feasibility of two-stage electrokinetic washing in remediating 1000mg/kg Pb contaminated soil was investigated using 0.01 M $NaNO_3$, 0.1 M HNO_3, 0.1 M citric acid as well as 0.01 M EDTA as the wash solutions at a constant electric potential difference of 15 V for 24 h. The study revealed that two-stage electrokinetic washing could enhance Pb removal efficiency by 4.98-20.45% in comparison to normal soil washing via electromigration and electroosmosis. As for the wash solution, it was found that the removal efficiency followed a trend of 0.1 M HNO_3 > 0.1 M citric acid > 0.1 M $NaNO_3$ > 0.01 M EDTA. The removal efficiency was found higher when the wash solution provided low soil pH condition and high current density. This could be attributed to the fact that low soil pH condition enhanced Pb desorption while high electric current improved Pb electromigration rate after soil washing.

Among the wash solutions, it was suggested that $NaNO_3$ was unsuitable as it induced high degree of electroosmosis. High generation of effluent at 492.9mL ($\approx$5.6 pore volume) was contradictory to the objective of two-stage electrokinetic washing. EDTA solution was also screened out as it only showed low removal efficiency enhancement of 7.84%, as a result of unfavorable counter-migration of Pb-EDTA in the

two-stage electrokinetic washing. In contrast, the acidic based agents 0.1 M HNO_3 and 0.1 M citric acid achieved >90% removal efficiency. However, 0.1 M HNO_3 not only caused high amount of effluent generation (288.5 mL) with high electric power consumption but also fluctuation in cathode chamber's pH and corrosion of graphite anode, making the system unstable. Among the wash solutions, 0.1 M citric acid emerged as the best wash solution in this study as it not only yielded high removal efficiency enhancement by 20.45% in comparison to soil washing (from 70.39% to 90.84%) at relatively low effluent generation (65.9 mL) and power consumption in comparison to $NaNO_3$, HNO_3, and EDTA, but also maintained a stable system conditions for the electrodes and the pH values in wash solution chambers.

The effect of operating conditions such as electric potential difference, wash solution concentration and initial Pb concentration was further investigated using citric acid as the wash solution. The process was evaluated from the aspects of i) Pb removal efficiency, ii) effluent generation, and iii) power consumption such that the feasibility of two-stage electrokinetic washing in enhancing Pb removal efficiency while minimising effluent generation and power consumption could be justified. The results revealed that the increase in electric potential difference and wash solution concentration enhanced the removal efficiency and the interaction between these two parameters was significantly positive. Low pH and high current density were the most important criteria in the removal process. However, unfavourable high effluent generation and power consumption were also observed under these conditions. The optimisation study showed that optimum removal efficiency of 84.14% with negligible extra effluent generation and low power consumption of 2.27 kWh/kg Pb removed could be achieved under 7.58 V and 0.057 M citric acid concentration. The optimisation study proved that two-stage electrokinetic washing process was capable in enhancing the soil remediation efficiency by ≈16% in comparison to normal soil washing (84% vs 68%) under similar low

solution: soil ratio of <0.8 mL: 1 g and operating conditions. In addition, this process also provided *in situ* Pb recovery as solid in cathode chamber by electrodepositing 49% of Pb from the system at the optimum condition. Based on the experimental results, it can be recommended that the incorporation of electrokinetic process into soil washing could enhance Pb removal via one way electromigration to cathode chamber at low wash solution consumption when a proper wash solution was used.

5.1.2 Application of electrokinetic soil pretreatment process

Application of electrokinetic process as soil pretreatment method to reduce contaminated soil volume via concentrating Pb into smaller soil section by electromigration was investigated for two types of contaminated soils, namely i) single Pb contaminated soil, and ii) Pb and Cr co-contaminated soil. The wetting agents investigated in this study were 0.01 M $NaNO_3$, 0.1 M citric acid and 0.1 M EDTA solution.

In general, it was observed that there was variation in the transport of Pb under different types of soils/contaminant species. For single contaminated soil, a potential contaminated soil volume reduction of ≈50% was achieved for all wetting agents studied. Electrokinetic process provided good electromigration for Pb, which was mainly adsorbed/ bounded on the iron/mineral oxides. The migration trend was highly dependent on the types of wetting agent used, with a sequence of 0.1 M citric acid > 0.1 M EDTA > 0.01 M $NaNO_3$. For $NaNO_3$ and citric acid, Pb electromigrated towards cathode; the main mechanism for this process could be attributed to Pb^{2+} desorption at low soil pH condition, which was generated by either acid front (electrolysis) or the wetting agent (citric acid). On the other hand, the use of 0.1 M EDTA provided Pb electromigration towards anode region as a result of the formation of negatively charged

water soluble Pb-EDTA complexes. It was worth noting that electromigration process was highly influenced by the soil pH. For $NaNO_3$, the increase in soil pH in S3-S4 caused cessation in Pb electromigration and accumulation of Pb in S3 was detected. On the other hand, Pb accumulated in low pH S2 region with a normalised concentration of 1.83 in EDTA test due to attenuation of Pb-EDTA electromigration, as a result of instability of EDTA and adsorption of Pb-EDTA on soil surface at low pH condition.

On the other hand, contaminated soil volume reduction for co-contaminated soil was only observed when 0.1 M EDTA solution was used as the wetting agent. $NaNO_3$ and citric acid showed poor Pb electromigration, as the Pb species in the co-contaminated soil was primarily water insoluble $PbCrO_4$. In this study, low pH condition generated by acid front and citric acid did not enhance Pb dissolution into ions significantly. In addition, low pH condition also slowed down Cr electromigration towards the anode region, especially in citric acid test. In contrast, EDTA solution emerged as a better wetting agent for this soil due to its high pH for Cr desorption and its chelating ability for water soluble Pb-EDTA and Cr(III)-EDTA complexes formation. One way electromigration towards anode was achieved for both Pb and Cr as the complexes formed were negatively charged, and this favoured soil volume reduction. The study proved that electrokinetic process is a technically feasible soil pretreatment method as it has the potential to reduce soil volume to about 50% of its initial amount in the present setup for both ions as well as both types of soils via electromigration when proper wetting agent was used, which was highly dependent on the properties of contaminants and soils.

The approaching electrode technique was further applied to improve electromigration via progressive soil conditioning. However, the results obtained were contradicted other publications as the use of approaching electrode did not enhance Pb electromigration significantly. Nevertheless, the study suggested that approaching

electrodes reduced the power consumption for electrokinetic process. For single contaminated soil, approaching anode reduced power consumption by 18.75% while maintaining Pb electromigration when 0.1 M citric acid was applied as the wetting agent. On the other hand, the application of approaching cathode in co-contaminated soil using 0.1 M EDTA also showed a reduction in power consumption by 22.5%. This suggested that power wastage on the pretreated soil sections could be prevented using the approaching electrode technique. However, it was worth noting that the use of approaching electrodes caused a slight reduction in the removal efficiency for Pb and Cr in the pretreated regions (7-8% for single Pb contaminated soil and 4-8% for Pb/Cr co-contaminated soil), as a result of the absence of electrical driving force in these regions after electrode switching.

5.2 Recommendations for future studies

The study reveals that two-stage electrokinetic washing provides enhanced performance in Pb removal from iron rich sandy soil in Malaysia in comparison to normal soil washing at similar low wash solution: soil ratio in a laboratory scale set-up. However, it is to be noted that the current set-up restricts data collection, especially for continuous checking of heavy metal concentration in the soil. There is a need for further investigation on the feasibility of this process on heavy metal removal at a larger scale such that the kinetics and detailed transport mechanisms can be evaluated more effectively. The current small scale design and closed column is not suitable for soil sampling at different time interval as the sampling may cause drastic variation in the results.

For electrokinetic soil pretreatment process, a larger equipment is proposed to be utilised in future works instead of current small scale sandbox so that the effect of approaching electrode in electrokinetic process can be investigated more effectively. In addition to that, studies from the viewpoint of other hardware such as the materials, shapes and number of electrodes used, the arrangement as well as the distance between the electrodes in the soil are proposed as future works for evaluating/maximizing the effectiveness and uniformity of electric field/current. This is important for the improvement of the electromigration of heavy metals in the soil, especially when the process is applied at a larger scale such that the ability of electrokinetic process as soil pretreatment method in reducing contaminated soil volume can be enhanced at minimum power consumption.

Moreover, the feasibility studies on the applications of two-stage electrokinetic washing and electrokinetic soil pretreatment process in treating other types of soils, in particular, heavy metals contaminated sites, is urgently required. It should also be noted that the wash solutions/wetting agents used in the present study are conventional chemical agents, which are frequently used for soil remediation. However, these solutions are normally less environmental benign (e.g. HNO_3, EDTA) and often cause damage to the soil after the remediation process. Thus, there is an urgent need to study the feasibility of other types of chemicals that are least harmful such as ionic liquids, deep eutectic solvents and natural surfactants as the wash solution/ wetting agent in the two-stage electrokinetic washing as well as electrokinetic soil pretreatment process.

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LIST OF PUBLICATIONS AND PAPER PRESENTED

Article

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Ng, Y. S., Sen Gupta, B., & Hashim, M.A. (2016). Remediation of Pb/Cr co-contaminated soil using electrokinetic process and approaching electrode technique, *Environmental Science and Pollution Research 23(1)*, 546-555.

Conference Proceeding

Ng, Y.S., Hashim, M.A., & Sen Gupta, B. (2014). "Effects of Wetting Agents and Approaching Anode on Lead Migration in Electrokinetic Soil Remediation". In T. Gong (Ed). *International Proceeding of Chemical, Biological & Environmental Engineering: Chemical Engineering and Applications V*: *Proceeding of the 5ᵗʰ International Conference on Chemical Engineering and Applications*, *Taipei* (pp. 44-48). Singapore, IACSIT Press.

Stability and performance enhancements of Electrokinetic-Fenton soil remediation

Y. S. Ng · B. Sen Gupta · M. A. Hashim

Abstract Electrokinetic process is a potential in situ soil remediation process which transports the contaminants via electromigration and electroosmosis. For organic compounds contaminated soil, Fenton's reagent is utilized as a flushing agent in electrokinetic process (Electrokinetic-Fenton) so that removal of organic contaminants could be achieved by in situ oxidation/destruction. However, this process is not applied widely in industries as the stability issue for Fenton's reagent is the main drawback. The aim of this mini review is to summarize the developments of Electrokinetic-Fenton process on enhancing the stability of Fenton's reagent and process efficiency in past decades. Generally, the enhancements are conducted via four paths: (1) chemical stabilization to delay H_2O_2 decomposition, (2) increase of oxidant availability by monitoring injection method for Fenton's reagent, (3) electrodes operation and iron catalysts and (4) operating conditions such as voltage gradient, electrolytes and H_2O_2 concentration. In addition, the types of soils and contaminants are also showing significant effect as the soil with low acid buffering capacity, adequate iron concentration, low organic matter content and low aromatic ring organic contaminants generally gives better efficiency.

1 Introduction

Electrokinetic soil treatment is a remediation process that operates under a low direct current gradient in soil, as opposed to a hydraulic pressure gradient, which promotes the migration of water and various contaminants under coulombic forces (Shenbagavalli and Mahimairaja 2010). This process produces an electrical gradient that acts as a driving force for the transport of various pollutants in soil, which makes it suitable for both saturated and unsaturated soil (Acar et al. 1995; Yang and Liu 2001; Shenbagavalli and Mahimairaja 2010; Tsai et al. 2010). The main feature of the electrokinetic process is in situ soil contaminant removal, and it may be considered as a preferable treatment option compared to some conventional ex situ treatment processes, such as solidification/stabilization and soil washing. Electrokinetic soil treatment has been studied for the removal of a wide range of contaminants, such as heavy metals, phenols,

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Contents lists available at ScienceDirect

Electrochimica Acta

Performance Evaluation of Two-Stage Electrokinetic Washing as Soil Remediation Method for Lead Removal using Different Wash Solutions

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ABSTRACT

The study explores the application of a two-stage electrokinetic washing system on remediation of lead (Pb) contaminated soil. The process involved an initial soil washing, followed by an electrokinetic process. The use of electrokinetic process in soil washing not only provided additional driving force for transporting the desorbed Pb away from the soil but also reduced the high usage of wash solution. In this study, the effect of $NaNO_3$, HNO_3, citric acid and EDTA as wash solutions on two-stage electrokinetic washing system were evaluated. The results revealed that a two-stage electrokinetic washing process enhanced Pb removal efficiency by 2.52-9.08% and 4.98-20.45% in comparison to a normal electrokinetic process and normal washing process, respectively. Low pH and adequate current were the most important criteria in the removal process as they provided superior desorption and transport properties. The effect of chelating by EDTA was less dominant as it delayed the removal process by forming a transport loop in anode region between Pb ion and complexes. HNO_3 was not suitable as wash solution in electrokinetic washing in spite of offering highest removal efficiency as it caused pH fluctuation in the cathode chamber, corroded graphite anode and showed high power consumption. In contrast, citric acid not only yielded high Pb removal efficiency with low power consumption but also maintained a low soil: solution ratio of 1 g: <1 mL, stable pH and electrode integrity. Possible transport mechanisms for Pb under each wash solution are also discussed in this work.

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1. Introduction

Lead (Pb) has been identified as one of the top six toxic threats in the world [1] as it can cause acute and chronic illnesses by damaging central and peripheral nervous systems, cardiovascular and reproductive systems as well as gastrointestinal and urinary tracts when it is inhaled and ingested [2,3]. As a result of its extensive use, humans are exposed to Pb via several pathways. One of the pathways is soil contamination. Pb concentration as high as 751.98-138,000 mg/kg was reported in shooting range soil, dumpsite for lead-acid battery as well as manufacturing and mining regions over the world [1,4–6]. Therefore, a proper treatment must be conducted for these soils.

According to Dermont et al. [7], soil washing is one of the *ex situ* remediation methods for treating Pb and heavy metals contaminated soil especially for higher permeability soil that has lower silt and clay content [8]. There has been several studies on the treatment of Pb contaminated soil using different washing agents such as surfactants [9] acids [10] and chelating agents [11–13] and positive results have been reported. However, it is worth noting that one of the disadvantages of soil washing is the occurrence of spent chemicals in the wash solution and this increases the cost for treatment [7]. Moreover, a high ratio for soil: solution in the system of 1 g:3.33-20 mL [9,11,12] is another disadvantage for soil washing as the amount of spent wash solution to be treated is large.

In contrast, electrokinetic soil remediation could reduce the amount of wash solution needed in remediating heavy metals contaminated soil. Electrokinetic process is a potential soil treatment method that uses electricity as the driving force for ion transport. The induction of low intensity direct current through the soil augments the transport of water and contaminants via two major mechanisms, namely electromigration for ion transport and electroosmosis for pore water/neutral compounds transport [14–16]. Electromigration transports the desorbed heavy metals in the wash

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Effects of operating parameters on the performance of washing–electrokinetic two stage process as soil remediation method for lead removal

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ARTICLE INFO

ABSTRACT

The application of washing–electrokinetic two stage process on remediation of lead (Pb) contaminated soil was investigated. The process consisted of an initial soil washing, followed by an electrokinetic process. The use of electrokinetic process in soil washing could provide additional driving force for transporting the desorbed Pb away from the soil even in the absence of pore flow. Thus, high usage of wash solution may be mitigated. In this study, the effect of operating conditions such as electric potential difference, wash solution concentration and initial Pb concentration on the feasibility of washing–electrokinetic two stage process on Pb removal was investigated using response surface methodology based on Box–Behnken design. The wash solution used was citric acid and three main aspects were examined, namely: (i) removal efficiency, (ii) effluent generated, and (iii) power consumption. The results revealed that the increase in electric potential difference and wash solution concentration generally enhanced Pb removal efficiency and the interactions of these parameters were significantly positive. However, undesirable high effluent generation and power consumption were also caused by these increments. Optimisation study revealed that 84.14% removal efficiency with zero effluent generation and a power consumption of 2.27 kW h/kg Pb removed could be achieved at 7.58 V and 0.057 M citric acid concentration. In comparison with normal soil washing, washing–electrokinetic two stage process showed an enhancement in removal efficiency by ≈16% via electromigration under optimum conditions using similar solution: soil ratio of <0.8 mL:1 g soil. The study reveals that incorporation of electrokinetic process in soil washing is feasible as it not only enhances Pb removal efficiency at minimum wash solution usage with respect to normal soil washing, but also provides in situ Pb recovery in cathode chamber via electrodeposition.

1. Introduction

Lead (Pb) is a highly toxic substance to living organisms. Its ability to bio-accumulate often causes acute and chronic illnesses which damage human body systems when it is inhaled and ingested [1,2]. Pb has been extensively used as a raw material in manufacturing processes such as ammunition, batteries, bearings, plumbing, ceramic glazes, weights, caulks, dyes, pigments and pesticides [2,3]. In order to support huge demand for Pb in the world, global Pb production as high as 10,654,000 tonnes was reported in 2012. As a result of its huge production and usage, humans can be easily exposed to Pb via variety pathways. Soil contamination is one of the pathways for Pb exposure especially from industrial lands with the activities like battery manufacturing, gould casing, scrap Pb handling [4] as well as Pb smelting and mining [1,2]. High Pb concentration in the range of 751.98–138,000 mg/kg was reported in the soil from these industries [3,5–8]. Thus, a proper treatment to these soils is necessary.

Soil washing has been reported as one of the effective soil remediation methods for removing Pb and heavy metals [9]. However, it is worth noting that soil washing requires high amount of wash solution for effective treatment. A high solution: soil ratio of 3.33–20 mL:1 g [10–12] shows the disadvantage of applying soil washing as the amount of spent wash solution that requires post treatment is large. In contrast, electrokinetic process could reduce the amount of wash solution needed in soil remediation.

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Performance evaluation of natural iron-rich sandy soil as a low-cost adsorbent for removal of lead from water

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ABSTRACT

Technical feasibility of natural iron-rich sandy soil as a low-cost adsorbent for removal of lead from water was investigated. The soil, which had an iron content of 3,719 mg/kg, was collected from Hulu Langat, Malaysia, and was used for adsorption studies without any surface modification through chemical treatment. The effects of pH, solution: soil ratio and initial lead concentration on the adsorption efficiency were studied using response surface methodology based on Box–Behnken experimental design. The results showed that pH of the solution had the highest impact on the adsorption efficiency whereby adsorption efficiency of 97% could be achieved at pH 3.5–5. The experimental data were also checked for compliance with different kinetic models and adsorption isotherms. The adsorption process was found to be rapid monolayer chemisorption with adsorption capacity of 0.9–1.0 mg/g, as it fitted Langmuir isotherm and followed pseudo-second-order kinetic model.

Keywords: Natural iron-rich sandy soil; Lead; Adsorption; Adsorption kinetics; Adsorption isotherm

1. Introduction

Lead is reported as a highly toxic material whereby the maximum allowable concentration in water is 0.1 ppm for standard A (effluent that is discharged upstream of a water supply intake) and 0.5 ppm for standard B (effluent that is discharged downstream of a water supply intake) in Malaysia [1]. Lead often contaminates water bodies as well as soil environment via different sources such as fertilisers, pesticides, metal mining, milling and smelting processes [2,3]. Inhalation and ingestion of lead can cause poisoning and even death to human as it accumulates in the organs. Lead can cause serious health effects such as loss of memory/brain damage, nausea, insomnia, anorexia and weakness of joints. Moreover, it may also inhibit the synthesis of haemoglobin, causing dysfunction on kidneys, joints and systems such as reproductive system, cardiovascular system, central

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Remediation of Pb/Cr co-contaminated soil using electrokinetic process and approaching electrode technique

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Abstract Electrokinetic process has emerged as an important tool for remediating heavy metal-contaminated soil. The process can concentrate heavy metals into smaller soil volume even in the absence of hydraulic flow. This makes it an attractive soil pre-treatment method before other remediation techniques are applied such that the chemical consumption in the latter stage can be reduced. The present study evaluates the feasibility of electrokinetic process in concentrating lead (Pb) and chromium (Cr) in a co-contaminated soil using different types of wetting agents, namely 0.01 M $NaNO_3$, 0.1 M citric acid and 0.1 M EDTA. The data obtained showed that $NaNO_3$ and citric acid resulted in poor Pb electromigration in this study. As for Cr migration, these agents were also found to give lower electromigration rate especially at low pH region as a result of Cr(VI) adsorption and possible reduction into Cr(III). In contrast, EDTA emerged as the best wetting agent in this study as it formed water-soluble anionic complexes with both Pb and Cr. This provided effective one-way electromigration towards the anode for both ions, and they were accumulated into smaller soil volume with an enrichment ratio of 1.55–1.82. A further study on the application of approaching cathode in EDTA test showed that soil alkalisation was achieved, but this did not provide significant enhancement on electromigration for Pb and Cr. Nevertheless, the power consumption for electrokinetic process was decreased by 22.5 %.

Introduction

Electrokinetic process is a potential soil remediation method. This process is carried out by the introduction of low magnitude direct current across the soil via electrodes that are in contact with the soil. During the process, electrolysis occurs in both anode and cathode chambers, and H^+ and OH^- are generated, respectively. The potential difference between the electrodes causes the contaminants/ions in the soil to migrate towards their respective chambers via two mechanisms, namely (i) electromigration for ions transport and (ii) electroosmosis for neutral compound transport (Acar and Alshawabkeh 1993; Acar et al. 1995). Among these mechanisms, electromigration not only transports charged ions in the soil but also transports H^+ and OH^- generated from electrolysis through the soil. As the migration speed of H^+ is about 1.8 times faster than of OH^- (Acar and Alshawabkeh 1993; Acar et al. 1995; Kim et al. 2011), soil acidification may occur, and this generally enhances heavy metals desorption from the soil. It makes electrokinetic process an effective method in remediating heavy metals polluted soil.

Electromigration is generally free from limitations of hydraulic gradient and pore flow (Acar et al. 1995). Thus, electrokinetic process can concentrate heavy metals into a smaller soil volume even in the absence of hydraulic flow. This ability provides an attractive soil pre-treatment option before other remediation methods are applied such that the reduction in

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Effects of Wetting Agents and Approaching Anode on Lead Migration in Electrokinetic Soil Remediation

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Abstract. Approaching anode is one of the enhancement techniques in electrokinetic soil remediation. This technique is reported to give promising migration for heavy metals under shorter treatment time and at lower cost in comparison to normal fixed anode system. In the present study, the effectiveness of fixed anode and approaching anode techniques in electrokinetic soil remediation for lead migration under different types of wetting agents (0.01M $NaNO_3$ and 0.1M citric acid) was investigated. The study showed that the use of citric acid enhanced lead migration in comparison to $NaNO_3$. For $NaNO_3$ tests, lead was found to accumulate in the middle of soil section due to high soil pH, which favoured lead adsorption and precipitation. Approaching anode reduced this effect by compressed high soil pH region and enhanced lead migration at cathode region. The approaching anode only showed technical advantages when $NaNO_3$ was used whereas the enhancement in citric acid test was insignificant. Nevertheless, this technique reduced electricity usage by 18-20% for both wetting agents.

Keywords: Lead, electrokinetic soil remediation, wetting agent, approaching anode

1. Introduction

McCartor and Becker [1] and Wuana and Okieimen [2] reported that lead (Pb) has been extensively used in manufacturing processes such as ammunition, batteries, plumbing, dyes, pigments and pesticides and this causes potential environmental pollution and human exposure. Soil contamination is one of the pathways for Pb exposure to humans especially from Pb smelting and mining areas [2], [3] as well as from industrial land used for battery and scrap Pb handlings [4]. As Pb is highly toxic and can cause health hazard to living organisms, a proper treatment to these soils is required.

Electrokinetic process is a soil remediation method which uses electricity as driving force for contaminant transport in the soil. This process is initiated by applying low magnitude direct current from the electrodes injected into the soil. During electrokinetic process, electrolysis occurs in both anode and cathode chambers which produce H^+ and OH^-, respectively. Due to the potential difference between the electrodes, H^+ and OH^- transport to the respective electrode, and these are named as acid front and base front. These mechanisms create two transport forces in the soil: i) electromigration for ions transport, and ii) electroosmosis for water/neutral compounds transport [5], [6]. The forces are responsible for contaminants removal from the soil, whereby the contaminants are concentrated in the electrolyte chambers or enriched in a smaller soil volume. To date, electrokinetic process has been proven as successful method in treating Pb contaminated soil using different types of desorption/flushing agents to enhance Pb mobility via better desorption condition [7], [8] or forming stable water soluble complexes [7]-[12].

However, it is worth noting that the lengthy remediation time and additional cost in power consumption in using electrokinetic process often restricts its wide application [13]-[15]. Besides that, simultaneous acid and base fronts create a region where H^+ and OH^- meet and this causes accumulation/focusing of heavy

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APPENDICES

APPENDIX A: Chemicals used in the analytical study

Acetic acid, HOAc

Ammonium acetate, NH_4OAc

Ammonium chloride, NH_4Cl

Ammonium hydroxide, NH_4OH

Ammonium Oxalate, $(NH_4)_2C_2O_4$

Bromocresol green-methyl red mixed indicator

Dipotassium phosphate, K_2HPO_4

Hydrochloric acid, HCl

Hydrogen peroxide, H_2O_2

Hydroxylamine hydrochloride, $NH_2OH.HCl$

Isopropyl alcohol, C_3H_7OH

Magnesium chloride, $MgCl_2$

Magnesium oxide, MgO

Monopotassium phosphate, KH_2PO_4

Nitric acid, HNO_3

Perboric acid, H_3BO_4

Silver nitrate, $AgNO_3$

Sodium acetate, NaOAc

Sodium carbonate, Na_2CO_3

Sodium chloride, NaCl

Sodium hydroxide, NaOH

Sulfuric acid, H_2SO_4

APPENDIX B: Procedures for soil characterisation study

Appendix B1: Procedure for cation exchange capacity (CEC) determination in soil

Cation exchange capacity (CEC) for the soil sample was determined using ammonium acetate method.

i) 3 g of air-dried soil sample was placed in a 250 mL Erlenmeyer flask. 100 mL of 1 N NH_4OAc (pH 7.0) solution was added into the flask. The flask was shaked thoroughly by hand and the mixture was allowed to stand overnight (cover the flask mouth with parafilm).

ii) The soil was filtered with light suction using a Buchner funnel and filter paper into a clean Buchner flask (25 mL at a time).

iii) The soil was filtered with additional 100 mL of 1 N NH_4OAc (pH 7.0). Check for Ca^{2+}: The vacuum was closed and funnel was lifted out of the flask. Three drops of filtrate was transferred into a test tube. Three drops of 1 N NH_4Cl, three drops of 1:1 NH_4OH, and three drops of 10% ammonium oxalate were added. No precipitate indicates the completion of filtering.

iv) The soil was filtered with light suction using 200 mL 1 N NH_4Cl, followed by 100 mL 0.25 N NH_4Cl.

v) The soil was washed with 150-200 mL of isopropyl alcohol (25 mL at a time). Check for Cl^-: Funnel was removed as in step 3, 10 drops of filtrate and 10 drops of 0.1N $AgNO_3$ was mixed into a clean test tube. A precipitate (AgCl) indicates the presence of chloride. When the chloride is no longer present, the collection flask was emptied and cleaned.

vi) The soil was further filtered with 300 mL of 10% NaCl in 5-6 portions. The filtrate was saved for CEC analysis.

Microkjeldahl Distillation of Ammonium for CEC Experiment

i) Rheostat to the heater was turned on and the water was allowed to boil

ii) Steam distillation apparatus was prepared by opening the lower stopcock on the steam-bypass assembly and closing the upper stopcock, which connected to the distillation head. These should be the positions of these stopcocks while the water heats.

iii) 5 mL of H_3BO_3 indicator solution was added into 100 mL beaker marked for 40 mL, and the beaker was positioned under the condenser of the distillation apparatus so that the up of the condenser is in contact with the side of the beaker.

iv) Kjedahl flasks which contained 20 mL NaCl filtrate and a spoon of MgO was attached to the distillation apparatus. The funnel was sealed with the peg stopper, and distillation was commenced immediately by opening the upper stopcock on the steam-bypass assembly and closing the lower stopcock.

v) When the volume of distillation reached 40 mL, the tip of the condenser was rinsed and the distillation was stopped.

vi)   10 drops of bromocresol green-methyl red mixed indicator was added and NH_4^+-N content in the distillate was determined by titration using 0.001 N H_2SO_4. At the end point, the colour changed from green to a faint pink.

CEC was calculated based on the equation as shown below:

CEC (meq/100g soil) = V x 0.001 N x 300 mL/20 mL x 100 g/m_s

Where:
V = volume of 0.001 N H_2SO_4 spent for titration in mL
m_s = weight of the soil sample used, g

Appendix B2: Procedures for specific gravity determination in soil

ASTM D 854 was used to determine the specific gravity for the soil sample.

i) The weight of empty clean and dry pycnometer was recorded, W_p.

ii) 10 g of dried soil sample was placed in a pycnometer. The weight of the dry soil and pycnometer was recorded, W_{sp}.

iii) Distilled water was filled to about 50-75% of the pycnometer. The sample was soaked for 10 minutes.

iv) Partial vacuum was applied for 10 minutes to remove the entrapped air.

v) The vacuum was stopped and the pycnometer was removed from the vacuum line.

vi) The pycnometer was filled with distilled water to the mark. The exterior surface of the pycnometer was cleaned with a clean and dry cloth. The weight of the pycnometer and contents, W_b was recorded.

vii) The pycnometer was emptied and cleaned. The, distilled water was filled to the mark. The exterior surface of the pycnometer was cleaned with a dry and clean cloth. The weight of the pycnometer and distilled water, W_a was recorded.

Specific gravity for the soil was calculated using the equation as shown below:

$$\text{Specific Gravity, } Gs = \frac{W_0}{W_0 + (W_a - W_b)}$$

where W_0 is the weight of dry soil sample, $W_{sp} - W_p$

Appendix B3: Procedures for organic matter determination in soil

Soil organic matter was estimated using Loss of Weight on Ignition Method (LOI).

    i.   A crucible was weighed to 3 decimal places (W1).

   ii.   A mass of 5-10 g of dried and ground soil sample was weighed into crucible.

  iii.   The crucible with soil samples was dried and heated for 2 h at 150 ^{o}C.

  iv.   The crucible with samples was removed and weighed to 3 decimal places (W2).

   v.   The crucible with samples was further heated at 360 ^{o}C for 2 h (After temperature reaches 360 ^{o}C).

  vi.   The crucible and samples was removed and was cooled to 150 ^{o}C.

 vii.   The sample was weighed to 3 decimal places (W3).

Loss of weight on ignition (LOI) was determined using the equation as shown below:

LOI % (OM) = [(W2-W3)/(W2-W1)] x 100

Appendix B4: Procedures for Tessier's method

The study on Pb speciation after the adsorption was conducted using Tessier's method. The general steps involved in this method are as summarized in Figure B4.1. The detailed procedures are elaborated by Tessier et al. (1979), Gworek and Mocek (2003) and Venkateswaran et al. (2007).
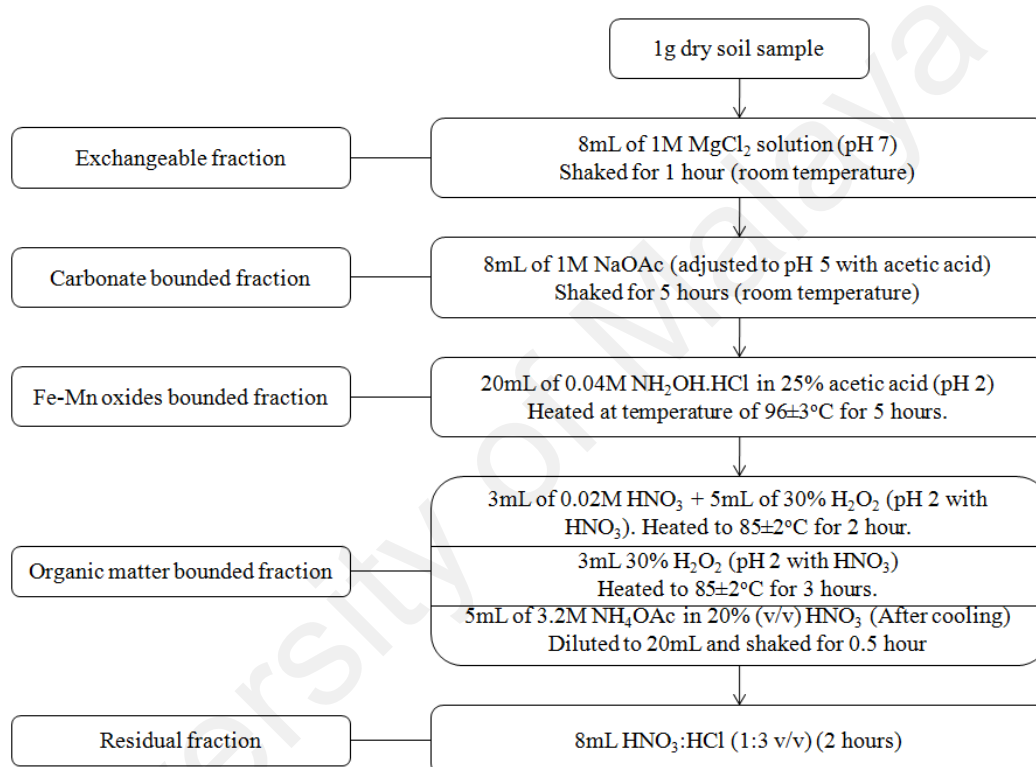
Figure B4.1: Schematic procedure for Pb speciation study using Tessier's Method

Appendix B5: Procedures for soil voidage

The voidage in the soil column in two-stage electrokinetic washing after soil packing was calculated based on the following equation:

$$\text{Soil voidage} = \frac{A - B}{A}$$

where:

A = Volume of the column, $\frac{\pi}{4}\left(D_{column}\right)^2 L_{column}$, and

B = Volume occupied by soil particles, $\dfrac{\text{Mass of soil used}}{\text{Density of the soil particle}}$

APPENDIX C: ANOVA for effluent generation and power consumption

Appendix C1: ANOVA for effluent generation

Source	Sum of Squares	DF	Mean Square	F value	Prob > F	
Model	20853.96	11	1895.81	666.81	< 0.0001	significant
A	6304.36	1	6304.36	2217.42	< 0.0001	
B	748.02	1	748.02	263.10	< 0.0001	
C	0.12	1	0.12	0.04	0.8438	
A^2	2465.09	1	2465.09	867.04	< 0.0001	
B^2	14.08	1	14.08	4.95	0.0766	
C^2	609.73	1	609.73	214.46	< 0.0001	
AB	2670.31	1	2670.31	939.22	< 0.0001	
AC	1288.81	1	1288.81	453.31	< 0.0001	
A^2B	295.85	1	295.85	104.06	0.0002	
A^2C	657.03	1	657.03	231.10	< 0.0001	
AB^2	384.34	1	384.34	135.18	< 0.0001	
Residual	14.22	5	2.84			
Lack of Fit	0.12	1	0.12	0.04	0.8612	not significant
Pure Error	14.09	4	3.52			
Cor Total	20868.17	16				
Std. Dev.	1.69		R-Squared	0.9993		
Mean	19.66		Adj R-Squared	0.9978		
C.V.	8.58		Pred R-Squared			
PRESS			Adeq Precision	81.51		

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Appendix C2: ANOVA for power consumption

Source	Sum of Squares	DF	Mean Square	F value	Prob > F	
Model	25.478	9	2.831	2958.52	< 0.0001	significant
A	18.050	1	18.050	18863.82	< 0.0001	
B	3.372	1	3.372	3524.30	< 0.0001	
C	0.710	1	0.710	741.87	< 0.0001	
A^2	1.553	1	1.553	1623.47	< 0.0001	
B^2	0.650	1	0.650	678.93	< 0.0001	
C^2	0.002	1	0.002	1.99	0.2015	
AB	0.002	1	0.002	2.39	0.1663	
AC	0.067	1	0.067	69.87	< 0.0001	
A^2C	0.009	1	0.009	9.59	0.0174	
Residual	0.007	7	0.001			
Lack of Fit	0.004	3	0.0011	1.88	0.2734	not significant
Pure Error	0.003	4	0.001			
Cor Total	25.485	16				

Std. Dev.	0.03	R-Squared	0.9997	
Mean	2.78	Adj R-Squared	0.9994	
C.V.	1.11	Pred R-Squared	0.9973	
PRESS	0.07	Adeq Precision	187.61	