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Evaluating the Effect of the Approaching Electrode on Migration of Zn and Cr Ions using Electro- Kinetic Technique in Contaminated Soil

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By

Zeina Thamer Jawad

(B.SC. Environment Engineering, 2014)

Supervised by

Prof. Dr. Amal Hamza Khalil

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جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل
كلية الهندسة
قسم الهندسة البيئية

تقييم تأثير اقتراب القطب الكهربي على انتقال أيونات الزنك والكروم باستخدام تقنية الحركية الكهربية في التربة الملوثة

رسالة

مقدمة الى مجلس كلية الهندسة في جامعة بابل كجزء من متطلبات نيل درجة

ماجستير في علوم الهندسة البيئية

من قبل

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(بكالوريوس هندسة بيئية ، ٢٠١٤)

اشراف

أ.د. آمال حمزة خليل

جمادى الثاني ،١٤٤٤ كانون الثاني ، ٢٠٢٣

Dedication

This letter is dedicated to the Creator, God Almighty, the Prophet Muhammad, may God's prayers and peace be upon him, and my beloved father, my dear mother, my husband Zaid, my brothers, sisters, and my two sons Zuha and Muhammad

ZEINA

2023

بسم الله الرحمن الرحيم

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ

صدق الله العلي العظيم

(سورة المجادلة/ الآية ١١)

Supervisors Certification

I certify that this thesis entitled **" Evaluating the Effect of the Approaching Electrode on Migration of Zn and Cr Ions using Electro- Kinetic Technique in Contaminated Soil"** presented by **zeina thamer jawad,** was prepared under our supervision in the Environmental Engineering Department, University of Babylon, in Partial Fulfillment of the requirements for the Degree of Master in Environmental Engineering.

Signature:

Prof. Dr. Amal Hamza Khalil

Supervisor

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Signature:

Name:

Title: Head of Environmental Engineering Department

Address: University of Babylon

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Abstract

The aim of this thesis is to determine how the electrode approach affects the electrokinetic technique's ability on transportation of zinc and chromium through contaminated soil using double fixed anode technique, approaching of two anode technique and approaching of one cathode technique. As well as verify the use of various purging solutions such as acetic acid (AA) and ammonium citrate (AC), to remove zinc and chromium from sandy loam soils. Fourteen different experiments (Series 1, Series 2, Series 3, Series 4, and Series 5) were performed on soil contamination with zinc and chromium at a concentration of 850 and 220 mg/kg, respectively. In all experiments conducted in this study, a continuous electrical current was applied between the electrodes in fixed anode technique 1.5 V/cm during 100 hours for series -1 and series-2, whereas in series-3 and series-4 carried out with approached anode technique. While, series-5 was applied with approached cathode technique.

In the experiment, when distilled water (DW) used as anolyte and catholyte solution for both fixed anode and approached anode, the findings showed that the average Zinc reduction efficiency was still rather low, approaching 23.16% and 28%, respectively, for the Zinc experiments. In the Chromium experiments, it was found that the removal percentages for the fixed anode and approached anode respectively, were 18.3% and 24.23%. On the other hand, utilizing a solution like 1M (AA) enhances the average removal efficiency; for example, using 1M AA in the fixed anode technique to remove zinc results in a removal efficiency of 42.71%, while at approach anode technique (using 1M AA) the removal efficiency rises to 63.103%.

In series (4) with chromium, when used 1M AA for both the fixed anode and approached anode, the removal efficiencies increase from 39.02% to 46.25%, respectively. On the other hand, it has been observed that the average removal efficiency of zinc was decreased with the fixed anode and approached anode techniques, to 26.322% and 27.79%, respectively, in each of the chromium and zinc studies while employing a different solution (1M AC).

The removal effectiveness of the fixed anode and approached anode for the chromium experiments, however, was equivalent to 29% and 44%, respectively. The final studies employing a cathode approach technique to remove both zinc and chromium using ammonium citrate solution (AC 1M), resulted in removal rates of 38.97% and 46.95%, respectively.

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Abbreviations

AA:	Acetic Acid.
AAs:	Approaching anodes.
ACs:	Approaching cathode.
AAS:	Atomic Absorption Spectrophotometer.
AC:	Ammonium Citrate.
CEC:	Cation Exchange Capacity.
CEM:	Cation Exchange Membrane.
DC:	Direct Current.
DW:	Distilled Water.
EC:	Electrical Conductivity.
EDS:	Energy Dispersive X-Ray Spectroscopy.
SEM	The scanning electron microscope.
EM	Electro Migration.
EK:	Electro kinetic Experiment.
EO:	Electro Osmotic.
EOF:	Electro Osmotic Flow.
FAs:	Fixed Anodes.
M:	Molarity.
MSW:	Municipal Solid Waste.
NRC:	North Refineries Company.
OMC:	Optimum Moisture Content.
pH:	Hydrogen ion concentration.
PS:	Purging solution.

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CHAPTER ONE
INTRODUCTION

1.1 General view

One of the major Environmental issues that concerned humanity is the contamination of soil by heavy metals. Heavy metals find its way to the soil through various sources such as geogenic origin, and anthropogenic sources like consumption of fossil fuel, discharge of industrial and domestic wastewater, agricultural leachate, mining and smelting processes. Heavy metals, which have the major influence on human, are Lead (Pb), Chromium (Cr), Cadmium (Cd), Mercury (Hg), Zinc (Zn), Selenium (Se) and Arsenic (As). Another source of soil contamination by heavy metals comes from air such as emissions from fuel combustion, waste piles which produce gases containing As, Cd and Pb, as well as burning of tires and lubricant which is the main source of Zn, Cd and Pb because of emitting aerosol as cited by (Bakshi et al., 2018)

Heavy metals are not biodegradable, persistent and accumulated in the nature, and thus are the sources of environmental pollution, (Lata et al., 2014). In soil, heavy metals exist in different forms: dissolved ions (e.g., Cu^{+2}, Cd^{+2}, CrO_4^{-2},$cr^20_7^{-2}$ and MO_4^{-2}) and organic complexes (e.g., Cu^{+2}, Pb^{+2}, and Hg^{+2} binding to dissolved organic matter) in soil solution, exchangeable ions (e.g. Cu^{+2}, Zn^{+2}, Cd^{+2}, Ni^{+2} and Pb^{+2}) adsorbed on soil solid particles, and (co) precipitates as part of soil solids (e.g., $Cd_3(PO_4)_2$, ZnS, $PbCO_3$, and $HgSO_4$).The categories of heavy metals remain in thermodynamic equilibrium with each other, and with insoluble substances like the principal groups. The presence of poisoning metals in the soil can

prevent the biodegradation of organic pollutants. This is attributed to the possible chemical alteration and the associated bioavailability. The contamination of soil by heavy metals negatively influence ecosystem and humanity when consuming or contacting the polluted soil directly, consuming polluted groundwater, food degradation via phytotoxicity, food chain of soil, plants, animals and human, minimizing land utilization for producing agriculture resulting in food insecurity. The presence of heavy metals in plant excessively can prevent its productivity and growth or even its death (Hananingtyas et al., 2022)

1.2 Technologies used to remediate contaminated soil

There are two methods for treating polluted soil, which are the in-situ technique, and ex-situ method. In the first method, the treatment of the soil of contaminants occurs in the same place. This method is adopted to discard pollutants from soils with no transportation of the soil. On the other hand, the ex-situ method involves excavating the soil, which need remediation, and moves it outside the polluted location. Recently, many in-situ and ex-situ methods have been utilized to clean soils from pollutants or minimize the negative influences of the polluted soils. These methods can be categorized into five groups based in the treatment processes, which is utilized which is physical, thermal, biological, chemical and combined. Add to that they can be classified in accordance with action of the technology, which are transport, containment and transformation see Figure (1.1) (Thomé et al., 2018).

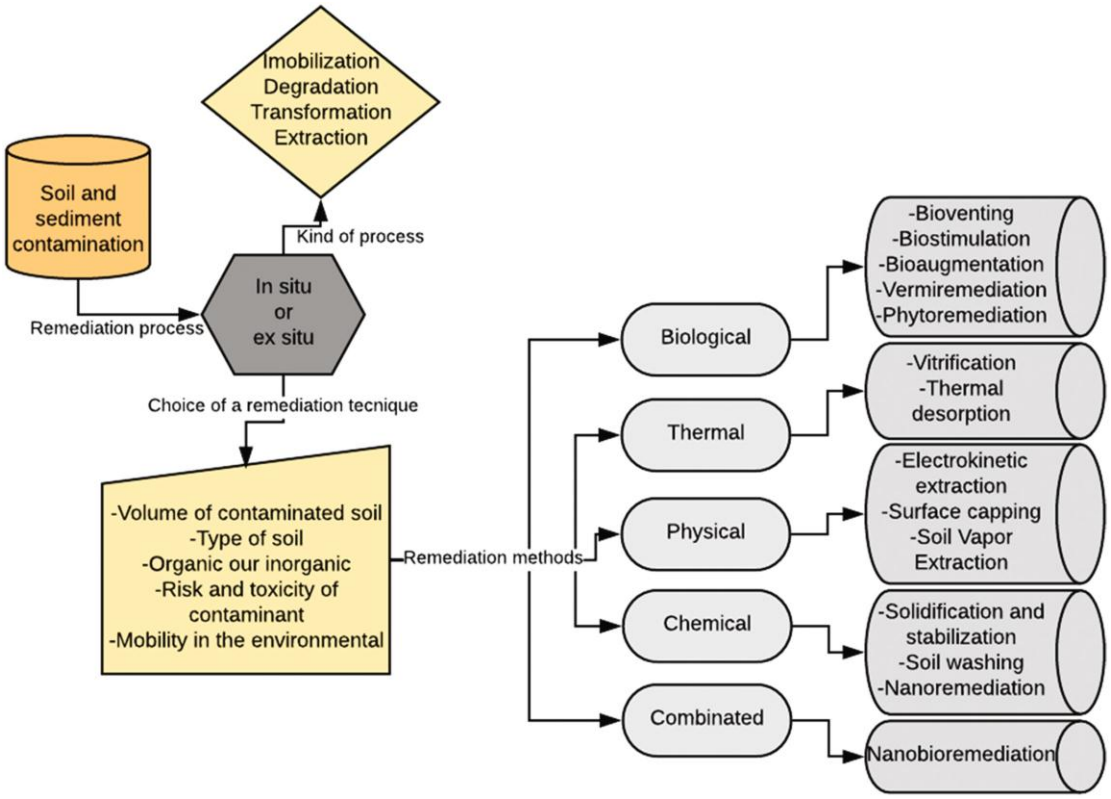


Figure 1.1: Methods commonly utilized for treating polluted soils and sediments (Thomé et al., 2018).

In this concern, experts and industry administrators have been interest by some methods that described below, as cited by (Rashid, 2015).

- **Thermal desorption;** it can be used for remediating the soils, which are contaminated by organic pollutants like pesticides, fuel hydrocarbons, volatile compounds …etc. The experimental works proved that this method could not be used effectively for treating soil polluted with metals.
- **Bioremediation;** it can be used for remediating the soils contaminated with organic pollutants such as pesticides, volatile compounds …etc. However, it is not showed good results in the removal of HMs from polluted soils.

- **Soil vapor extraction;** experimental results proved that this technology causes a significant reduction in the HMs of treated soils. However, it cannot reduce their toxicity.
- **Washing of Soil,** It is the technique, which has confirmed probable role in the removal of HMs from contaminated soil.
- **Flushing of Soil;** In accordance with the experiments of lab scale, this method is effective in remediating the soils contaminated with HMs, but it cannot reduce their concentration toxicity.
- **Electro kinetic;** (EK) treatment can be utilized for discarding organic and inorganic pollutants from soils via electronic adsorption. The application of electrical current with low intensity in soils via electrodes leads to the migration of anions from soil to the anode and cations to the cathode via the produced electrical field. This method is very effective for partially or fully saturated soils having low electrical conductivity (Thomé et al., 2018). In spite of the significant outcomes, this method is associated with some negative aspects. Firstly, the high reliance of the electro kinetic treatment on acidic environment when being applied which is preferable for releasing the heavy metals pollutants into the solution phase. Nevertheless, there is difficulty in producing the acidic environment while the buffering capacity of the soil is elevated. Add to that, there is environmental restrictions on acidification of soils. Moreover, the treatment technique consumes lots of time ranging from couples of days to years (Virkutyte et al., 2002).

In the multi-anode technology, there is a principle point, which is the electrodes arrangement in soil, which assist in surrounding the

contamination or move it to the gathering points. Hence, the configuration of electrodes in the remediation process is the principal operational factor since it influence the amount and direction of the electro-kinetic methods and in consequence the efficiency of transportation of contaminants. Recently, this subject has been gaining favor with lots of researches concentrating on assisting the electrode configuration (Risco et al., 2016).

In the EK treatment, to enhance the effiency of removing contaminants and minimize the required time and the consumption of energy, researchers have investigated the technology of approaching anode. In this method, sequential approaching anode placed near the fixed cathode following the beginning EK remediation (Li et al., 2012). The pH close to the cathode lowered consistently during approaching anode treatment with compression to the area where heavy metals precipitate. In compared with the fixed anode technique, the approaching anode method is more efficient and less time-consuming (Zhang et al., 2014).

1.3 Problem Statement

In several Iraqi governorates, a number of studies were completed to assess the soil pollution caused by heavy metals. (Al-Rifaie et al., 2021) were selected three sites; in site 1, 2 and 3, it is situated at distance of 10 m, 20 m and 30 m respectively from the landfill edge, its location is in the north of city of Hillah/ Babylon Province, close to the borders between city of Babil and Qadhaa-Al-Mahaweel district. This landfill gathered different types of municipal solid waste (MSW) from household waste to the building waste. Table (1.1) gives the content of Chromium metal in the collected soil samples from the three sites (I_1, I_2 and I_3). It is clear that

the concentrations exceeded the maximum permissible limits for heavy metals in soil by United Kingdom (UK)(6.4 mg/kg) and World Health Organization (WHO)(0.002- 0.2 mg/kg), as cited by (Ediene and Umoetok, 2017)

Another study was achieved by (Alrubaiee and Al-Owadi, 2022) determined the concentration of heavy metals (Mn, Ni, Cr, Cu, Zn, As, Zr and Pb) at residential and industrial area. Ten samples from industrial and fourteen samples from residential were collected from Hilla city. Figure (1.2) shows the enrichment factor and pollution categories to the industrial and residential area for heavy metals (As, Cr, Ni, Cu, Zn, Zr Mn, and Pb). It is clear that the enrichment factor values for the trace elements such as Lead, Nickel and Zinc were significant enrichment, and this reflects the high pollution. In contrast, the elements like Manganese, Zinc ion were deficiency to minimal enrichment, which indicates low pollution, but the other metals such as Copper, Chromium, and Arsenic are moderate pollution, in the industrial area of the study area. Whereas the heavy elements in the residential area such as Nickel and Arsenic were highly polluted, while the moderate pollution is Lead, Chromium and Zinc.

Table 1.1: The content of the chromium metal in the gathered soil specimen (Al-Rifaie et al., 2021)

metal	Site	Content
Cr	I_1	22.9 mg/kg
	I_2	19.3 mg/kg
	I_3	15.5 mg/kg
Average		19.2

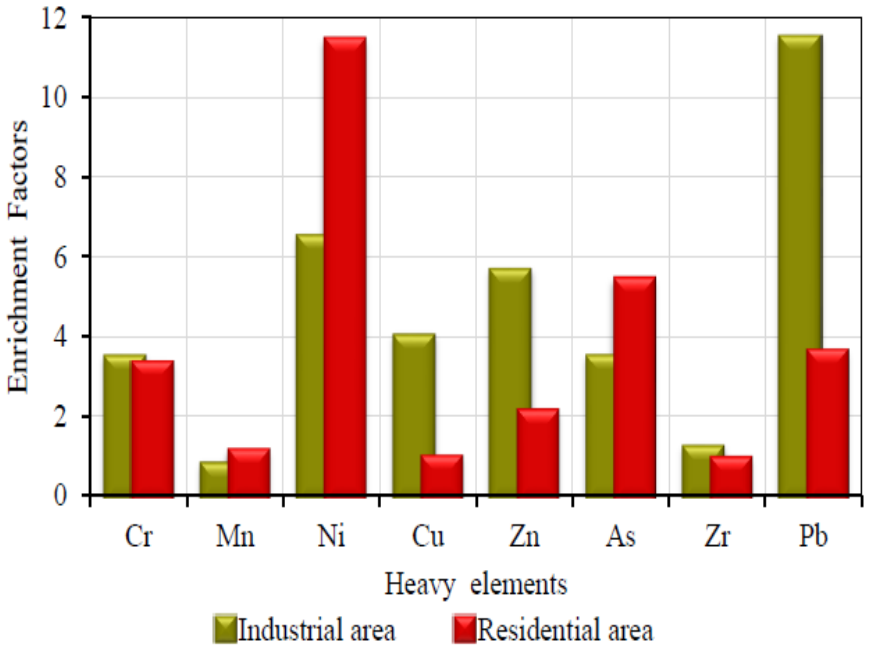


Figure 1.2: Enrichment factors mean values in the industrial area and the residential area (Alrubaiee and Al-Owadi, 2022).

1.4 Objectives of the present study

1- Evaluate using double anode electrodes through electro-kinetic remediation on removal efficiencies of the Chromium and Zinc from the contaminated sandy loam soil.

2- Evaluation of the use of acetic acid (AA) and Ammonium citrate (AC) as chelating agent on the removal of Chromium and Zinc from contaminated soil through electro-kinetic remediation.

3- Effect of approaching anodes electrode on the efficiency removal of Chromium and Zinc through electro kinetic remediation.

4- Effect of approaching cathode electrode on the efficiency removal of Chromium and Zinc through electro-kinetic remediation.

1.5 Methodology

In the research, the electro-kinetic experiments allowed to investigate the effect of influent purging solution (acetic acid (AA) and Ammonium citrate (AC)) in combination with the fixed anode (FA) and approaching electrode (anode (AAs) or cathode (ACs)) technique, on the removal efficiency of zinc (Zn^{+2}) and total chromium Cr(III) from contaminated soil under non-uniform electric field.

Measured parameters are grouped into two categories: parameters complied during the experiments such as (pH and current) and parameters obtained across the length of the soil samples from S1 to S4 after the end of the experiments such as (Zn (II) or Cr (III) concentrations and pH). All final reports for concentrations of Cr (III) or Zn (II) carried out in Ibn Al-betar Research center/ Ministry of industry and Minerals Corporation for Research and Industrial Development was showed in Appendix (A).

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

This chapter gives and discusses the basic concepts and definitions of electro-kinetic process. This includes the understanding of the electro-kinetic phenomena, which comprise adsorption, desorption, precipitation and migration of contaminant when an electric field presented. In addition, the source, toxicity, and mobility of heavy metals like Zinc and Chromium were discussed. In addition, a brief discussion about electro-migration, electrophoresis, and electro osmotic are introduced.

2.2 Soil contaminants

Soil contamination is a serious issue which may comes from various sources like heavy metals and metalloids accumulation via emission from industries which are expanded massively, discard high metal wastes, mine tailings, gasoline which contained lead and paints, animal sources, the treatment of soil with pesticides, sludge of sewage, depending on waste water in irrigation, spilling of petrochemical materials, residues of coal combustion as well as atmospheric accumulation. Heavy metals consists of inorganic chemicals with potential to causes serious illness. Heavy metals that are commonly presented in polluted locations are Chromium (Cr), Arsenic (As),Zinc (Zn), Cadmium (Cd), Lead (Pb), Mercury (Hg), and Copper (Cu). Heavy metals are mainly found in soils and released to the atmosphere by the aforementioned sources. These metals do not undergo chemical or microbial degradation that occurs in the organic pollutants,

which oxidize forming carbon oxide. In addition, the amount of heavy metals in soil remain constant for long period (Wuana and Okiemen, 2011).

There are major causes by which heavy metals can incorporate into soils: natural activities and anthropogenic processes. As showed in Table (2.1) the sources of heavy metal in the environment. Many studies have been carried out proving that natural resources of heavy metals cause only slight contamination to the environment in compared with anthropogenic sources (Dixit et al., 2015). Many soils gained the metals from their parent substances containing background of heavy metals that formed naturally that adversely influence organism and plants since the parent substances normally incorporated high amount of the metals. The parent material is the major source of heavy metals in soils. Generally, ingenious rocks contains heavy metals in significant amount most commonly Cu, Ni, Cd and Co whereas the other metals (Pb, Zn, Mn, Cd) present in shale's. Through natural processes like biogenic, terrestrial and volcanic activities, leaching, meteoric, heavy metals of rocks incorporate into soils (Muradoglu et al., 2015).

Table 2.1: Origins of different heavy metal pollution presented in the environment (Lone et al., 2008)

Heavy metals	Sources
Cd	Metal smelting and refining, combustion of fossil fuel, use of fertilizer, wastewater sludge and anthropogenic processes.
As	Preservation of wood, plants using coal, volcanoes, animal feeding, semiconductor and mining and smelting processes.
Cr	Wastewater sludge, solid waste, electroplating manufacture.
Hg	Emission from caustic soda manufacture, volcano detonation, combustion of wood and peat
Cu	Electroplating manufacture, smelting and refining processes, volcanic detonation, and weathering of soils, industrial sludge, and manufacture of steel alloy, batteries, and surgical instruments.
Ni	Landfill, weathering of soils, volcanic detonation, manufacture of batteries, surgical instruments and steel alloy and gas exchange in batteries.
Zn	Electroplating manufacture, mining, refining and smelting processes

2.3 Background information of metals

2.3.1 Chromium (Cr)

Chromium is a first-row d-block transition metal of group VIB in the periodic table with the following properties: atomic number 24, atomic mass 52, density 7.19 g cm^{-3}, melting point 1875◦C, and boiling point 2665◦C. It

is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary product in the form of the mineral chromite, $FeCr^2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr containing wastes. Chromium (VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the III oxidation state, depending on pH and redox conditions. Chromium (VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. Chromium (VI) can be reduced to Cr (III) by soil organic matter, S^{-2} and Fe^{+2} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr (VI) species include chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$) which precipitate readily in the presence of metal cations (especially Ba^{+2}, Pb^{+2}, and Ag^{+}). Chromate and dichromate also adsorb on soil surfaces, especially Iron and Aluminum oxides. Chromium (III) is the dominant form of Cr at low pH (<4). Cr^{+3} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{-2}, and soluble organic ligands. Chromium (VI) is the more toxic form of Chromium and is also more mobile. Chromium(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3$ (s). Chromium mobility depends on sorption characteristics of the soil, including clay content, Iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed Chromium complexes can leach from soil into groundwater. The leach ability of Cr (VI) increases as soil pH increases. Most of Cr released into natural waters is particle associated, however, and is ultimately

deposited into the sediment .Chromium is associated with allergic dermatitis in humans. (Wuana and Okieimen, 2011)

2.3.2 Zinc (Zn^{+2})

Zinc can be considered as transition metal having 4 periods, IIB group, 30 atomic number, with 65.4 atomic mass, density of 7.14 g cm^{-3}, and 419.5 °C melting point while the boiling point is 906. Zinc forms in soil in natural manner (in crustal rocks, there is 70 $mgkg^{-1}$ approximately) nevertheless the amount of Zn increase in unnatural way due to anthropogenic activities. Significant amount of Zn in soils come from industries such as combustion of coal and waste, mining and steel manufacturing. Many foodstuffs incorporate specific amount of Zn. In addition, drinking water has Zn in certain percentage, which could be increase when storing in metal tanks. Toxic waste location or industries result in increase in the Zn amount in drinking water reaching unacceptable level, which can causes health issues. Zinc is a trace substance being crucial for human health. The lack of Zinc results in birth defects. The production of Zn increase continuously throughout the world. This means that more and more Zn would be released to the environment. Zinc is found in of industries in high concentration, hence high Zn sludge will be produced which released to water causing increase in the pollution of water by Zn. Acidity of water can be increased by Zn^{+2}. Zinc can be accumulated in the fish bodies when living in Zn polluted environment. The intrusion of zinc to fish bodies causes bio magnify the food chain. Groundwater can also be polluted by water-soluble Zinc of soil. Attributing to zinc accumulation in soil, plants can usually have Zinc uptake, which cannot be treated in their

system. Zinc can interrupt the activities in soils since it adversely affects the earthworm and microorganisms activities hence minimizing the breakdown of organic substances (Wuana and Okieimen, 2011)

2.4 Harmful effects of heavy metals

Heavy metal contamination causes health risks if its concentration exceeds permissible limits. Even when the concentration of these minerals does not exceed the permissible limits, the risk of these pollutants remains large in the long term because they are accumulated within the biotic systems (Hussein, 2019). Where the toxicity of heavy metals can be arranged in the order of decrease toxicity as Co< Al< Cr< Pb< Ni< Zn< Cu< Cd< Hg (Hussein, 2018). Nevertheless, the influences of pollutants affect by factors like the chemical and mobility activities in soils in particular when contamination percentage is higher than specific levels (Karkush and Ali, 2019). Heavy metals differ from organic pollutants, as they do not degrade over time into non-harmful products of the biological system (Hussein, 2019). Shear strength parameters of soil decrease when it is contaminated with HMs. Add to that, soil contaminated with HMs has higher degree of compressibility and raise in the maximum dry density (MDD) but the optimum moisture content (OMC) and permeability minimized (Karkush and Ali, 2019).

2.5 Geochemical reactions in soil

Metals in soil solution can be either free (un complexes) such as Cd^{+2}, Zn^{+2} and Cr^{+3} in different soluble complexes with organic or inorganic ligands like $CdSO_4$, $CdCl^{-3}$, and $ZnCl^{+}$, or combined with organic and inorganic mobile colloidal substance. The complex is indicated as a unit

consists of central part surrounded by number of associated molecules or atoms in a specific geometric form such as $CdHCO^{+3,}$ $ZnSO_4$ and $Cr(OH)^4$. Ligands are the term given to the associated molecules or atoms. In the aforementioned examples, the ligands are $SO4^{-2}$, OH^- and HCO^{-3}. In soil solution, the total amount of a metal equal to the sum of soluble organic, free ion percentage (Mez^+), and the percentage of metals associated with mobile organic and inorganic collides. Metals combine with organic and inorganic ligands forming soluble complexes. Influenced by metal speciation, metal bioavailability is affected by a number of environmental factors (Figure (2.1)), including soil cation exchange capacity, pH, and redox potential (Hussein, 2012).

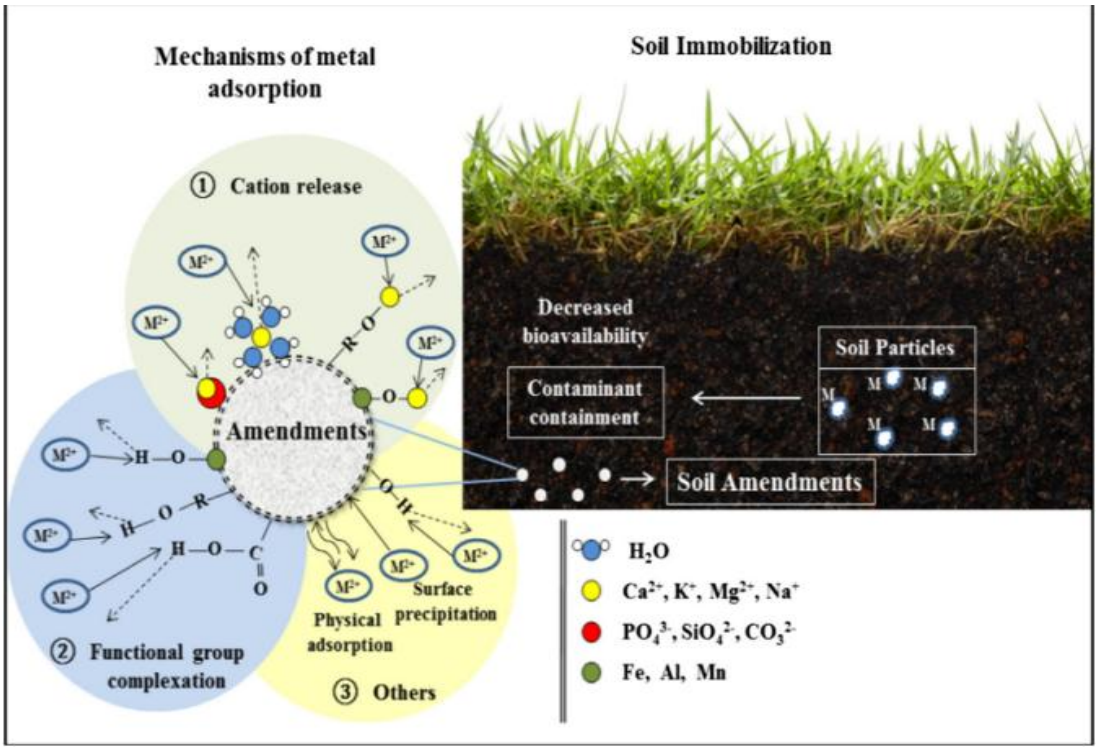


Figure 2.1: Methods of remediating soil contaminated with heavy metals. (Yvonne et al., 2022)

2.5.1 Sorption and desorption

Sorption is the process by which chemical species partitioning from solution to soil surface or solid phase. Sorption mechanism is ion exchange or complexation. There is high attraction between positively charged heavy metals and the negatively charged clay particles presented in the surface. The sorption properties and mechanisms of heavy metals vary widely. Sorption is a function of clay minerals, valence and size. Reverse to sorption is desorption which causes ion release from soil surface. pH variation affects both sorption and desorption processes. pH of soil alters due to the migration of OH^- and H^+ ions from electrolysis process. The increase in H^+ level causes desorb of cations from the clay surface controlling by soil type. These mechanisms also influence by clay minerals properties, most importantly surface charge density, amount and percentage of cationic species and the presence of organic substances and soil carbonation (Acar & Alshawabkeh, 1993).

2.5.2 Precipitation and dissolution

Precipitation is the process of separating a substance from a solution as a solid and dissolution refers to the process by which a solute forms a solution in a solvent. Precipitation and dissolution reactions, which are influenced by pH of soil and pore fluid and species concentration, have significant effect on the transportation of fluid and solute via porous media. In high pH (alkaline environment), there will be accumulation, precipitation, soil pores clogging and hinder of EK process of heavy metals. While, in low pH (acidic environment), the majority of precipitates undergoes dissolution

and formation of new precipitate in some cases (Acar & Alshawabkeh, 1993).

2.5.3 Oxidation and reduction

Significant alterations in soil electrochemistry throughout EK treatment cause various chemical reactions like oxidizing and reducing of chemical species. In oxidation -reduction reaction, electrons would be exchange between two reactants. Oxidation occurs to the species that loss electron while reduction takes place for the species that gain electron. These reactions are highly influenced by pH of soil. Thus, the adjustment of soil pH is important to decrease the detrimental influences on infrastructure in highly acidic and alkaline environment and to preserve plant growth (Jayasekera, 2008).

2.5.4 Cation exchange capacity (CEC)

The determination of cation exchange capacity (CEC) is an important tool in studies of erosion, retention of pollutants and waste, and has wide applicability in soil mechanics. Studies on agricultural productivity, includes determining the degree of fertilizer and soil adjustment practices necessary before a crop. The CEC is now widely used in the characterization and study of soil fertility. By analyzing the CEC of a soil, the cost of application of nutrients (NPK) and calcareous can be significantly reduced. The CEC is defined as the ability of a particle to change positive bases with the environment in which the particle interacts. Cations have the ability to be exchanged for another positively charged ion from the surfaces of clay minerals and organic matter. The most important exchangeable cations in the soil are Calcium (Ca^{+2}), Magnesium (Mg^{+2}), Sodium (Na^{+}), Potassium (K^{+}),

Hydrogen (H^+), Aluminum (Al^{+3}) and Ammonium (NH_4^{+2}). The CEC can directly influence the changes in soil pH, because every time the clay particles capture cations release H^+ and Al^{+3} ions, which in high concentrations acidifies soil. Generally, tropical soils have low CEC, especially for high sandy and low pH soils. Minerals as oxides of Aluminum, Iron and Manganese that are very abundant in tropical soils also contribute to the low CEC. In these cases a greater investment in fertilization, especially with humic compounds becomes necessary. (Aprile and Lorandi 2012)

2.6 Electro kinetic (EK) remediation

Is a group of treatment methods using the processes of transportation gained from the application of an electronic DC field to soil. The significant of EK is the ability to apply for fine-grained soils while the other treatment methods fail in that. In EK method, ions can transport by electro migration (EM), while water by electro osmosis (EO) and charged molecules by electrophoresis (EP) as show in Table 2.3. Recently, to overcome the deficiencies of already practiced treatment in fine grained soil research, development and implementation within EK have been carried out which involve combing these two methods (Lima et al., 2017).

2.6.1 Electrochemical transport processes

There are four principle mechanisms of contaminant transport under an applied electrical field (Merkx, 2011): (1) Electro-migration, i.e. the movement of an ion in solution due to the electrical current; (2) Electro-osmosis, i.e. the transportation of water with respect to the solid particles and matrix of the soil; (3) Electrophoresis, i.e. the transportation of charged

solid particles relative to the solution; and (4) Molecular diffusion of constituents in solution. Figure (2.2) shows the electro-kinetic process in soil treatment. The transport processes can be briefly described in Table (2.3).

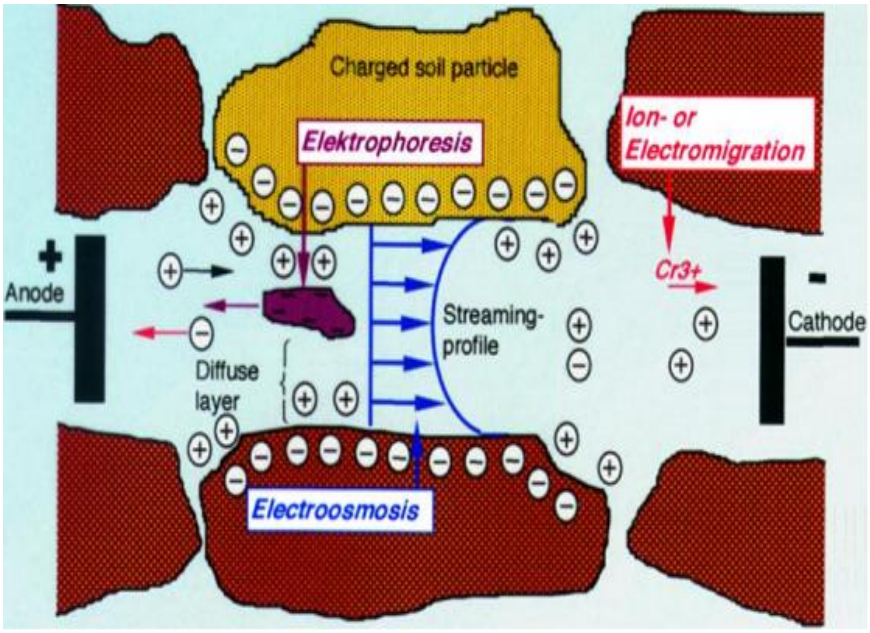


Figure 2.2: Schematic diagram of the electro kinetic treatment technique (Iyer, 2001).

Table 2.2 : Soil properties and reactions in soil affecting electro migration, electrophoresis and electro osmosis in the electric field. (Ottosen et al., 2019)

Transport technique	**Transportation of:**	**transportation velocity relies on**
electro migration (EM)	Ions	mobility of ions precipitation and dissolution, desorption, and adsorption water content, geometry and pore volume
Electro osmosis (EO)	Water	Potential of soil zeta, chemistry of pore water and conductivity
Electrophoresis (EP)	Colloids, Particles, bacteria	Potential of soil zeta, chemistry of pore water, pore sizes, and moisture content

Electro migration EM is due to electric current while EO and EP are electro kinetic transport processes. The ions in soil solution have current. Cations migrate to the cathode while anions move to the anode. In systems with no flowing and dispersion tensor in flowing systems, the ionic mobility of an ion has a close relation with the aqueous diffusion coefficient. Nevertheless, in soil, the velocity is very low because ions are unable to transport to the electrodes via EM by the shortest path. The direct path is blocked by soil and air voids. In a particular ion, the efficient ionic mobility is a function of tortuosity factor, molecular diffusion coefficient, porosity, and charge (Reddy and Cameselle, 2009). In addition, desorption and adsorption and dissolution and precipitation affect the type and the ions concentration in solution subjecting to various circumstances, and hence EM of the particular ions.

Electro osmosis EO according to (Heister et al., 2005) is a coupled flow. The application of electric field to soil causes movement to ions in the diffuse layer. In general, cations are the main elements in the soils. They transport towards the cathode pushing and drugging water particles to cathode as shown in Figure (2.3).

Electrophoresis the transportation of charged molecules is done by EP. The electric field setting ions in the multiple layer on the molecule itself in association with an electrostatic force because of the surface charge. The direction of EP is the same as that of cathode in case of the positive charge of the particles moving to the negatively charged anode. The boundary retarding influence calculated as decrease in EP mobility become more profound when the particle is closer to a solid surface (Tsai et al., 2011). It

is noticed that the thickness of the multiple layer around the particle would be reduced in up to 90% mobility, and this reduction is comparable to the radius of the particle in case the particle is closer to the solid plane. This retarding influence is more profound when the permeability of the medium is lower (Tsai et al., 2011).

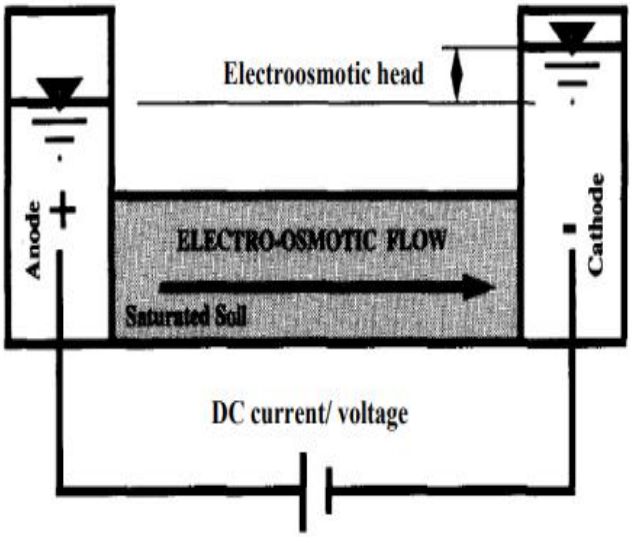


Figure 2.3: A diagram schematically showing electro-osmotic movement of fluid via a soil sample (Acar et al., 1995).

Charged particles will move by electrophoresis. Ions is set in double layer by the electric field. Because of the surface charge, the electric field works with the electrostatic force on the Particles. Cathode would attract the electrophoresis in case the molecule contains a net positive charge on the surface, nevertheless it moves to the anode in case of the negative surface charge. Decreased rates of movement of electrophoresis of bacteria in clay and silt comparing with sand give indications of the importance of pore size on the mobility of Electrophoresis. The boundary influence is more profound when the particle is close to a solid surface. It is noticed that the thickness

of the multiple layer around the particle would be reduced in up to 90% mobility, and this reduction is comparable to the radius of the particle in case the particle is closer to the solid plane. This retarding influence is more profound when the permeability of the medium is lower (Ottosen et al., 2019).

Usually, in environmental requests, electrophoresis is fewer important than electro-osmosis and electro-migration in case of mass flux; but, in specific conditions, electrophoresis contributes in decontamination, e.g. if the travelling colloids have the chemicals adsorbed on them (Mosavat, 2014).

Diffusion is a solutes flow governed by gradient of concentration. Electrophoresis and electromigration are unlike electroosmosis, chemical diffusion has a tendency to refabricate a homogeneous distribution of the solute in the pore water. When electrochemical is applied in soil remediation, it is possible to neglect the role of chemical diffusion (Ferrarese, 2008).

2.6.2 Electrokinetic reactions

At the electrodes, electrolysis reactions take place during the electro-treatment processes. The reactions given in Eqs.2.1 and 2.2) are the dominant chemistry at the boundaries and in the electro-treatment in the soil. If there is no control on the chemistry of the boundaries, hydroxide ions would be formed at the cathode and hydrogen at the anode due to the electrolysis reactions. Through the electro-migration, the ions move to soils resulting in alteration the soil chemistry. The greater ionic mobility of hydrogen ions and the electro-osmosis flow causes them to move towards cathode at the completion of the Electro-kinetic treatment methods, nearly

all soil is subjected to acid environment while small parts of soils masses close to the cathode stay in alkaline environment (Asavadorndeja and glawe, 2005).

At the anode: $2H_2O - 4e^- \rightarrow O^2(g) + 4H^+$ (2.1)

At the cathode: $4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^-$ (2.2)

The consequence of this condition is very important that could influence the Electro-kinetic treatment process. The increase in pH of the soil close to cathode could result in adverse complexation of metal ions within the pH jump zone in which they could precipitate as insoluble substances in case of unimproved electro-kinetic treatment. It is possible to avoid the creation of low conductive area that lead to metal precipitation by utilizing various acidic purging solution in order to make cathode depolarization. The process is indicated as improved electro-kinetic treatment (Ferrarese, 2008).

2.7 Survey of previous studies

Kim et al. (2001) examined a new electro-kinetic method to purge heavy metals from soil. The results showed there are many factors affecting the removal efficiency of Pb (II) and Cd (II) including the kind of purging solutions, zeta potential of soil, soil pH, voltage and current and permeability. In kaolinite clay, the removal efficiency of Cd (II) and Pb (II) was 75-85%, while I am the tailing soil was 50-70% over the 4 days.

Lee et al. (2003) investigated the properties of metal removal experimentally, set the pH profile of the soil and the citric acid role as an electrolyte solution and tendency of electro-osmosis. In the study, the mine

tailing soils are used collected from two abandoned mines. The main pollutants in the soils were Zn (II), Pb (II), Cu (II), and As (II). The results indicated by applying 0.25 mA/cm^2 of current density utilizing 2.5 mS/ conductivity of electrolysis for 2 weeks, 37 to 41% of metals were removed.

Turer and Genc (2005) utilized electro process to treat soils artificially contaminated by a single metallic pollutants (Cu, Pb, and Zn) and multiple metallic pollutants (Zn^{+} Pb). The sequential extraction outcomes indicated that these metals have removal efficiency, which is highly influenced by contamination types. The removal efficiency of soil polluted by lead only was 48%. Nevertheless, the removal efficiency of Lead in the soil contaminated by all the other contaminants was 32%. Similar results were shown for copper and zinc. The removal efficiency was 34%, 31%, 92%, 37% for copper and zinc respectively.

Shen et al. (2007) showed the improved EK in remediating soil. During cation exchange membrane (CEM), the H^+ concentration and the redox potentials are very high near the anode. Speeding up Cd electro-migration is made when pH is low and redox potential is high. Usually, EK process can work with one fixed anode (FA). A novel CEM improved EK technique with approaching anodes (AAs) is incorporated to speed up electro-migration influence. In turn, they were moved from the anode to cathode. Hence, migration of high redox potentials and high H^+ concentration to the cathode become quickly. In consequence, remediating of soil can be done very quickly and approximately 44% of the energy and 40% of time can be saved.

Buchireddy et al. (2009) examined the discard of copper, arsine and chromium from the polluted soil by using electro-kinetic method. The

removal efficiencies were 77%, 72%, and 65% for Arsine, Chromium and Copper respectively. These results showed the advancement of removing metal from soil via using acid front favored desorption in which metals can be transported as metal complexes or free cations.

Shen et al. (2009) showed that Wanshan Mercury mine is the largest cinnabar deposit in Guizhou, China. Few effective methods had been achieved to remedy Hg heavily contaminated field soils. In this paper, a modified EK method with approaching cathodes (AC-EK) and an I-/I2 lixiviant was described to remedy mercury-contaminated field soils near Wanshan mercury mine. Paddy Soil I and Paddy Soil II were sampled and contained 576.73 ± 45.50 and 491.35 ± 4.73 mg/kg Hg, respectively. Although they contained 6.9 and 9.4% organic matter respectively, more than 92 and 89% Hg were removed by AC-EK within 5 days. Removal ratio increased by 0.21 and 0.68 times using EK process with ACs over that with one single cathode (SC-EK). AC-EK method saved nearly 26.4–28.1% electric power as compared to SC-EK method. As an I-/I2 lixiviant solution was used to solubilize HgS (HgO) during EK process, the bonding of Hg to organic functional S groups should be less important than the binding to inner sites of organic matter in soil. The relationship between EK remediation effect and soil organic matter content was fitted to a linear model. It turned out that when soil OM increased by 1.0%, EK removal ratio (%) of Hg would decrease by 2.63%.

Hosseini et al. (2011) investigated the discard of Lead and Zinc from both natural and alkaline polluted soil by using enhanced solution like EDTA and Ammonium Citrate. The results showed that EDTA is sufficient

for treating soil lead polluted soil and the removal of zinc by utilizing citrate is very efficient.

Lee et al. (2012) remediate shooting-range location by utilizing hexagonal arrangement in electro-kinetic method. Firstly, the soil was sieved in dry way to separate pb^{+2}. This is followed by preparing two cells in a hexagonal arrangement involving two cathods in the middle and ten anodes outside the cell. The target contaminants were Pb (II) and Cu (II) to depth of soil of about 0.5 m. using concentrated HNO_3, the pH of each electrolyte was adjusted causing acid-enhanced electro-kinetics. The monitoring results also showed the achievement of the removal of heavy metal (Pb and Cu) outside the cell. The removal efficiency of Pb (II) was 39.5± 35% and that of Cu (II) was 63.8 ± 12%.

Khalil, (2013) showed that evaluated the feasibility of using an upward electro-kinetic soil remediation (UESR) process with aid a novel acidic injection well technique to enhance the mobility of cadmium and/or phenol in saturated soil subjecting to the influence of uniform electric field. Various tests were carried out on silty loam soil spiked with Cd^{+2} and/or Phenol in concentrations of 500 and/or 250 mg/kg, respectively under voltage gradient of 1.5 V/cm and processing time of 4 days. The experimental results showed that the introducing injection well technique was significantly increased the removal efficiency of contaminants.

Hassan et al. (2015) investigated a novel method of two anodes technique (TAT) and compared with traditional anode-cathode (CAC). TAT proved retarding the advancement of the base front, thus lowering the precipitation of copper during electro-kinetics to improve the discard of copper from the

polluted soil. Solar cell panels were utilized in the electro-kinetic treatment. The results showed that the use of solar cells could provide electric field highly enough to remediate soil contaminated with Cu. In addition, it was indicated that the location of the secondary anode affected the results of TAT test. Locating the secondary anode at 15 mm from the cathode resulted in the highest copper removal, which was 92%.

Rashid, (2015) found that using various purging solutions and configurations of the incorporation, i.e. injection wells, were examined in experimental methods to improve the discard of lead and/or chromium from soil of Iraq through the EK process. These removal efficiencies were increased to 37 and 21.5 % respectively with using of acetic acid. Ethylene diamine tetra acetic acid (EDTA) was also used as the purging solution in the cathode compartment and the removal of lead and chromium into the anode compartment was increased to become 42 and 34 % respectively. In addition, the residual concentrations of Pb^{+2} and Cr^{+3} were less than their initial values in all sections of the treated soil and the achieved removal efficiencies of lead and chromium were 29 and 21% respectively when ammonium citrate used as catholic purging solution.

Ng et al. (2016) explained that the study evaluated the feasibility of electrokinetic process in concentrating Lead (Pb) and Chromium (Cr) in a co-contaminated soil using different types of wetting agents, namely 0.01M $NaNO_3$, 0.1M citric acid, and 0.1M 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%.

Risco et al. (2016) examined the removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D) from spiked soil utilizing an electrode configuration in electro-kinetic soil flushing (EKSF) technologies. It consists of one cathode surrounding by six anodes and one anode surrounding by 6 cathodes .The water volume obtained from 1a6c cathodes was seven times higher than that gained from the 1c6a cathodes. Through electro migration, herbicide was moved to the anode wells and by electro-osmosis fluxes, they dragged toward cathode wells. The first process is the most important one. The most effective configuration was 1c6a giving a removal efficiency equal to 70% in 35 days. The other configuration which is 1 a6c gave herbicide removal of about 8% in 58 days.

Wei et al. (2016) utilized chelating agents as electrolyte solution to increase the mobility of metal. This research examined the mobility of different heavy metals such as (As, Cd, Cr, Cu, Ni, Pb and Zn) with the use of various chelating agents like ethylene diamine di succinic acid (EDDS), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) or citric

acid (CA) in modifying EK remediation efficiency. The results proved that EDTA is more efficient in removing Ni (52.8%), Pb (60.1%), and Zn (34.9%) when used in the same concentration (0.1 mol L^{-1}). EDDS increases the efficiency of the removal of Cu to 52%. Meanwhile, the removal improvement of EDTA and EDDS is similar to that of EK remediation (30.5∼31.3 percentage).

Song et al. (2019) carried out experiment to test the influence of the complexation and migration of metal-ethylene diamine tetra acetic acid (EDTA) complexes during EK treatment and the metal accumulation process gained. The red soil contaminated by Pb-EDTA and Cd-EDTA was remediated using six tests with the electrolyte pH and utilizing membrane. The results showed the due to the low pH and electrochemical degradation at the anode, part of free metal cations could be de complexed from the metal-EDTA complexes. Through the electro-migration, these cations can return into the soil and accumulate in separate area in accordance to the hydrolysis ability and the distribution of pH of the soil in various sections. In 7 days, the Cd^{+2} and pb^{+2} were removed from the soil in 61% and 83% respectively.

Wan et al. (2019) investigated the influence of moving polygonal electrodes in remediating cadmium-polluted soil, which was prepared in the laboratory. For the purpose of the research, a regular hexagon electrode electric restoration experimental instrument was fabricated. A comparison and analysis of the influence of approaching anode technique and fixed anode technique were made under constantly shortening distance between anode and cathode. The results showed similarity in the current variation trend between the fixed anode method and the approaching anode method.

There is also similarity in the pH variation for both methods. In the approaching method, there is significant decrease in the pH value at the later stage of restoration. At type A2 sampling points, the removal rate of Cd (II) by fixed anode method was 69% and by the approaching anode, method was 95%. In compared with the fixed anode method, the energy consumption of the approaching anode method was minimized by 65%. All these proved that the approaching method is more efficient and effective.

Xu et al. (2022) remediated as Cr/Co polluted soil using the permeable reactive barrier (PRB) assisted electro kinetic (EK) in order to examine the best treatment situations and the migration of as/Cr. The influence of PRB active particle, voltage gradient and running time, and PRB position on the transportation and as/Cr polluted kaolin clay were examined. The significant parameters were PRB location, as locating PRB close to the anode (PRB A, the media of PRB was hydrocalumite with one V/cm initial voltage gradient and running time of 96 hours. Subjecting to the optimal situation, the efficiency of the removal was 40.1% for total arsine (TAs) and 81.0% for total chromium (TCr)

Wang and Hou (2022) investigated the discard of Cd, Cu and Ni from the polluted soil using Electro-kinetic remediation via utilizing acetic acid, oxalic acid and citric acid as catholytes. Four tests were conducted to indicate the influences of the acids on pH and total dissolved solids (TDS), content, distribution, removal performance and alteration in speciation of heavy metals (reducible, exchangeable, residual and oxidizing fragments). The utilization of these acids as catholyte in association with EKR increased pH significantly and enhanced the removal efficiency of the heavy metals.

The remediation of soil contaminated with Cu, Cd and Ni remarkably improved when applying these acids and CK, and the most efficient acid was citric acid then acetic acid, oxalic acid and finally CK. With the use pf citric acid, the removal efficiency of Cd, Cu and Ni was 61±1.6%, 41±0.5% and 52±1.3% respectively. According to the heavy metal speciation analysis, the reducing and exchangeable fragments minimized close to the cathode for all the acids treatment in compared with CK remediation.

CHAPTER THREE
EXPERIMENTAL WORK

3.1 Introduction

The experiment studied the effect of arranged two anode electrodes and one cathode electrode on movement of contaminants (Chromium and Zinc) through technique of the fixed and approaching anode and approaching cathode electrode, mainly by the electro-osmotic and electro-migration. The developed experiments were adopted to determine an optimal purging solution to remove contaminants in horizontal reactor set-up.

3.2 Materials

3.2.1 Contaminants

The simulation of the Zinc and Chromium contamination in the soil, Zn $(NO_3)_2$ and Cr $(NO_3)_2$ solution was utilized which produced by BHD limited people England. The prepared solution was incorporated with the sample to gain a representative concentration. The molecular weight and the atomic weight of Zn $(NO_3)_2$ is 189.38 gram/mole and 65.38 gram/mole respectively. For instance, to prepare soil specimen containing Zinc with 850 mg/kg concentration and 40% initial water content by weight of 1.8 gram of $Zn(NO_3)_2$ dissolves in distilled water about 400 ml and the solution is incorporated with 1 kg of dry soil. Atomic weights of Cr $(NO_3)_2$ is equal to 51.9961 g/mole. The weight is necessary to determine the mass of the compound needed to fabricate the artificially polluted soil samples. The contaminated soil was left for 72 hr. before it was packed into the reactor cell to attain equilibrium, this is accordance to the same procedure adopted by (Faisal and Rashid, 2015).

3.2.2 Soil

In the experiment carried out in this research, naturally Iraqi soil was utilized as a porous medium. The soil was taken from a depth of (40 - 50) cm from agricultural land and subjected to cleaning, drying and storing with further sieving to gain the optimal uniformity. Table (3.1) showed the physiochemical characteristics of the utilized soil. It is essential to prepare and characterize the soil properly to achieve the highest accuracy in these experiments.

Table 3.1: Constituents and characteristics of the soil.

Property	Value
Particle size distribution	
Silt (%)	36.4
Sand (%)	39.9
Clay (%)	16.2
Atterberg limits	
Liquid limit (%)	30.5
Plastic limit (%)	21
Plasticity index (%)	9.5
$CaCO_3$ (%)	11.432
pH	8.5
Chloride ions, Cl^{-1} (mg/l)	1.859
Organic content (%)	3.8
EC (ms/cm)	2.2
Soil classification	Sandy loam

3.2.3 Purging Solutions

Chemical leaching is washing the polluted soil utilize reagents, fresh water, and others liquids or gas that can leach the contaminant from the soil. Heavy metal was moved from soil to liquid level through the chelation, adsorption, precipitation and ions exchange, and then recovered from the leachate. The leachate using essentially consist of surfactant, inorganic eluent, and chelation agents, etc (Yao et al., 2012). The purging solutions utilized in this study are Acetic acid and ammonium citrate as illustrated below:

- **Acetic acid (AA):** it was utilized as purging solution in the cathode compartment. Acetic acid is monoprotic acid having CH_3COOH chemical formula. This acid partially dissociate into the hydrogen ions in the aqueous solution as well as the CH_3COO^- which is the acetate ions. The pH of the solution and dissolve metal can be lowered by the fabricated hydrogen ions (H^+). Nevertheless, the acetate ions could be connected with various metal ions found in the solution (Rashid, 2015).

In the cathode chamber of the electro-kinetic cell, acetic acid was added so that the hydroxyl ions produced by different cathode electrolytic reduction treatments can be depolarized. The selection of acetic acid principally affected by the following reasons: 1) the high solubility of most metal acetates, 2) the fabrication of other insoluble salt in cathode can be eliminated by acetate ions, 3) it is biodegradable thus it is environmental, hence eliminate the formation of a low electrical conductivity (EC) area and in consequence dissipating the excessive power in the soils close to the cathode (Hahladakis et al., 2016).

●**Ammonium citrate (AC):** Ammonium citrate with the chemical formula, $C_6H_8O_7 – 2NH_3$, is a salt where two H^+ ions in the carboxyl groups of the citric acid are replaced by ammonium. It is dissolved in water, forming citrate and ammonium ions. Ammonium citrate can be used as alkaline reagent for forming both anionic and cationic complexes.

3.3 Equipment& Reagents

A- Equipment

1. Atomic Absorption spectrophotometer (AAS) (GBC 933 plus (Australia)): utilized to calculate soluble Zinc and Chromium concentration.
2. pH meter (pH 315i (Romania)): used to calculate the soil pH obtained from the electro-kinetic experiment.
3. Sensitive balance (AZ214, Germany): used for material weight.
4. Oven (A00711, Italic): used for sample drying.
5. Conductivity meter (WTW Cond 720 (Germany)): used to calculate soil electrical conductivity.
6. Electro-kinetic cells and their apparatuses.
7. DC power supply (LODESTAR-LP3005D) used for the application of constant voltage by electrodes.

B- Reagents

All chemical reagents used in this study were of analytical grade as given in Table (3.2).

Table 3.2: Chemical Reagents Data.

Chemical Reagent	Chemical Formula	Purity %	Provided by
Ammonium citrate (AC)	$C_6H_8O_7.2NH_3$	99	Piedel-dehaen, Germany
Acetic acid	CH_3COOH	99	Piedel-dehaen, Germany
Hydrogen chloride	HCL	99.9	Houston, Texas
Nitric Acid	HNO_3	99.9	Houston, Texas
Zinc nitrate	$Zn(NO_3)_2$	99	BHD limited Poole England
Chromium nitrate	$Cr(NO_3)_2$	99	BHD limited Poole England

3.4 Electro-kinetic Experiments

3.4.1 Reactor setup

Figure (3.1) (a and b) illustrates schematically the electro-kinetic diagram and the experimental setup as present in the research by using fixed anode technique (FAs). The setup experiment (Figure (3.1)) consist of rectangular cell (14 cm D*10 cm W* 26 cm L), three electrode compartments and an energy supply. In the edge of the cell is cathode chamber's was placed, which was dimension as 7 cm L, 10 cm W and 14 cm D. The valve was mounted at end of the cathode chamber (to control flowing of purging solution to the cell). Whereas, in other side two anode chambers (which is cylindrical tube made of plexiglass with 3.5 cm diameter and 12.5 cm height**).** According to the cited by Peng et al. (2013) the adopting the different electrodes arrangements in the electro-kinetic technique enable the

expansion of the base zone and decrease the area of the base, increase the removal of the heavy metals and the efficiency of the remediation. To improve the acid front propagation (i.e. at the , H^+ ions produced) toward the cathode chamber, two perforated plexiglass cylinder for anode chamber (D 3.5 cm; 0.3 cm holes No.8) was implanted in the soil specimen to the bottom vertically in the other side for the rectangular cell. The cylindrical graphite electrodes which were three having no chemical reaction utilized two electrodes at the anode (the electrodes have diamante of 2.5 cm and length of 12.5 cm). In the cathode, there is only one cathode with diameter and length of 3.5 cm and 12.5 cm respectively. The introduction of additional chemical species can be eliminated by utilizing inert electrodes, which can make the electrochemistry more complex during processing. At the anode, their utilizations are particularly essential because of the high corrosive influence of the oxidation process on the electrode (Acar and Alshawabkeh, 1996). In this cell, the length of the soil sample is 13 cm. The cathode chambers have a perforated surface to eliminate electro-osmosis flow of water caused by applying electric field. In addition to covering the chambers surfaces with filter paper so that no soil pass into the electrode cell as described by (Turer and Genc, 2005). The top of the cell is opened to the air to permit the discard of gases formed during the electrolysis reaction. Each electrode is linked to the DC power supply (application of a persistent voltage) by power cable linked to the electrodes at the top with the use of multi meter to supervise the voltage and determine the flow of the current via the soil specimen during the treatment.

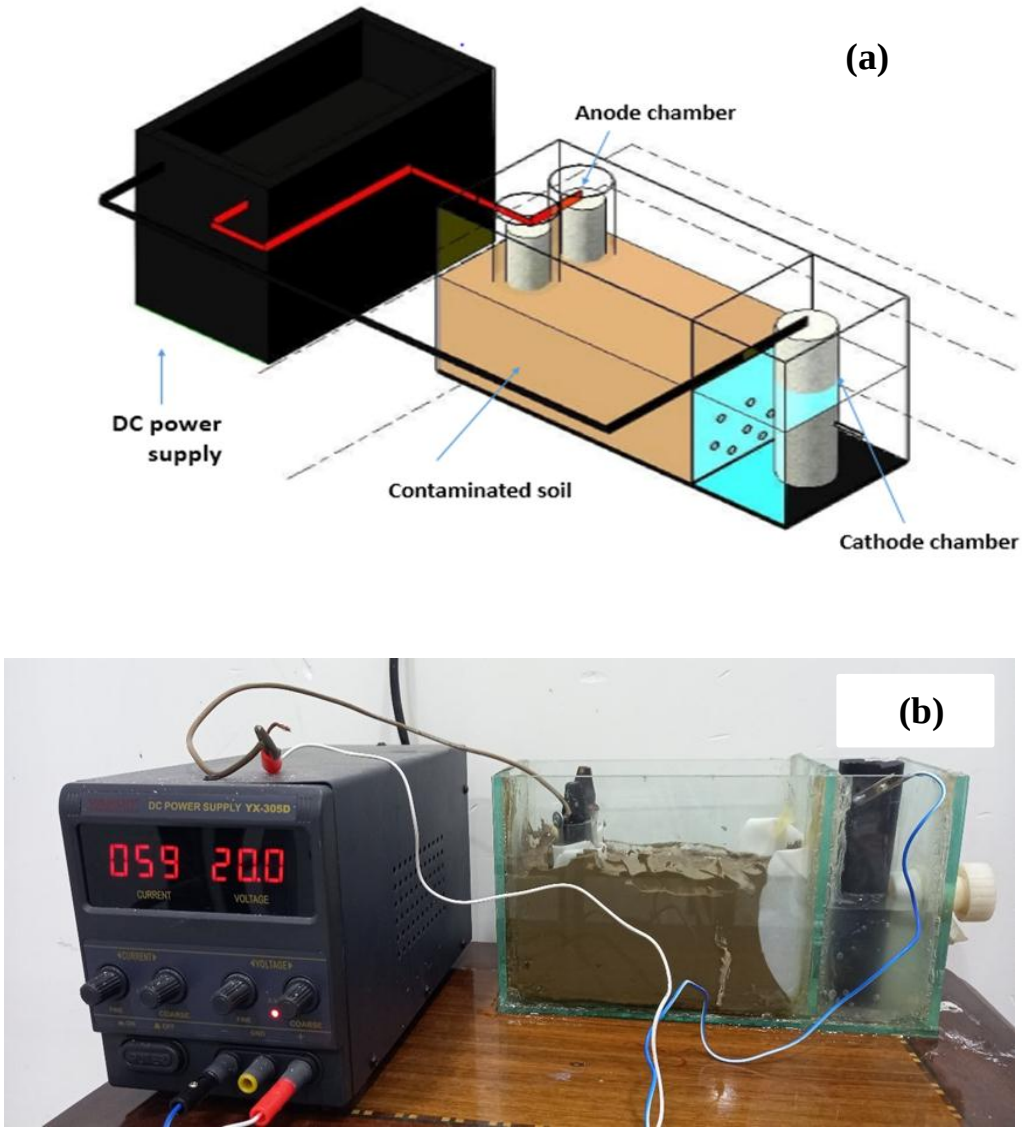


Figure (3.1): The experimental electro-kinetic cell (a) Schematic diagram of electro-kinetic experiments setup and (b) the experimental setup of electro-kinetic cell in the fixed anodes technique (FAs).

Figure (3.2) (a & b) presents schematically the set-up of electro-kinetic processes and the experimental setup by utilizing approaching anodes technique.

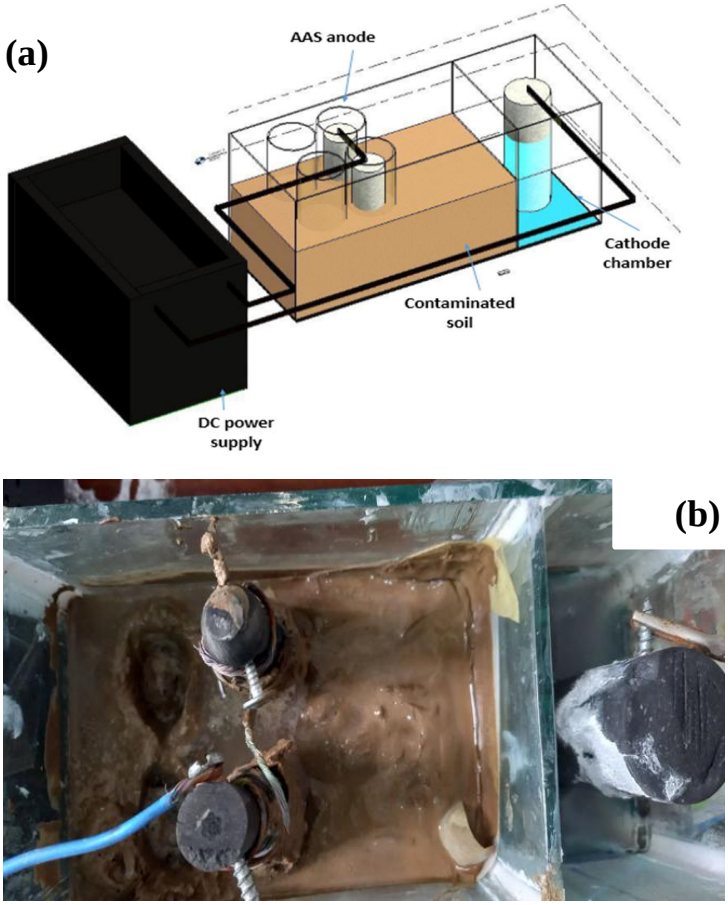


Figure (3.2): The experimental electro-kinetic cell (a) Schematic diagram of electro-kinetic experiments setup and (b) the experimental setup of electro-kinetic cell in the approached anodes technique (AAs).

Figure (3.3) (a & b) presents schematically the set-up of electro-kinetic processes and the experimental setup by utilizing approaching cathode technique.

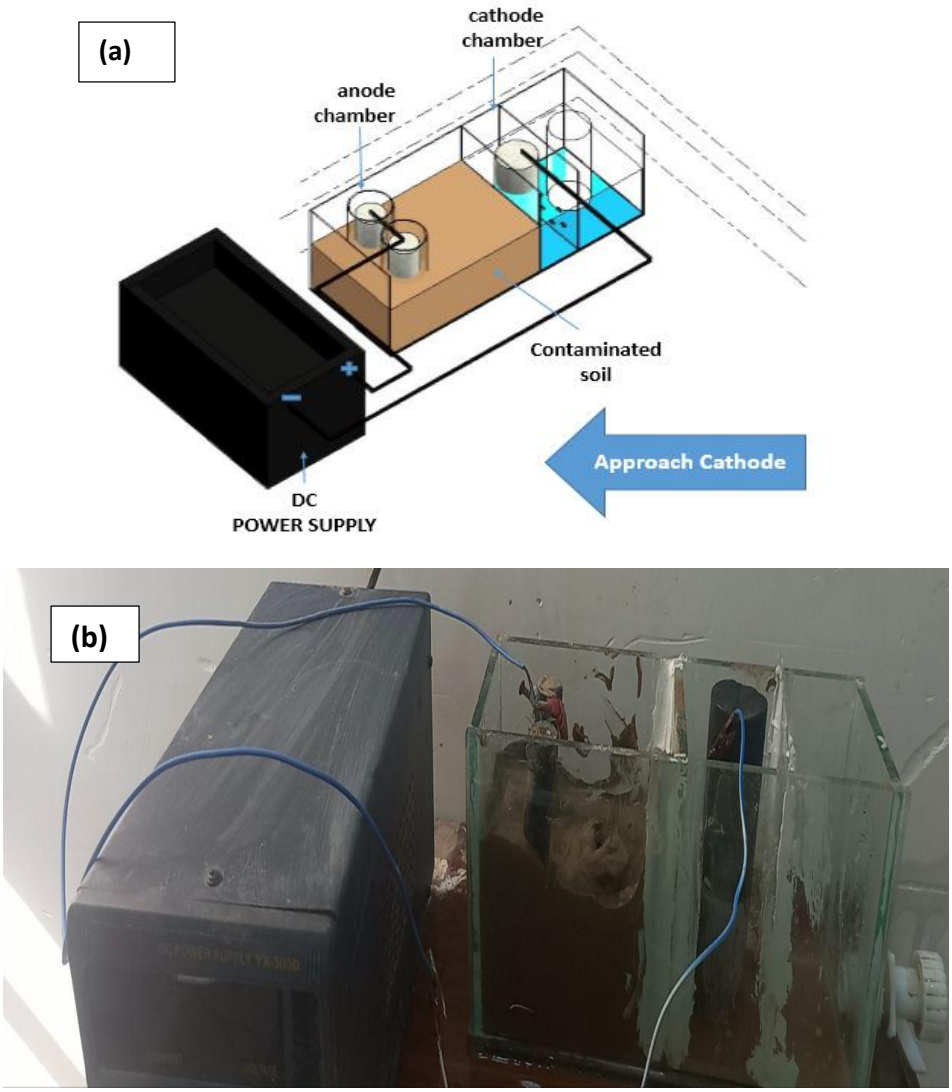


Figure (3.3): The experimental electro-kinetic cell (a) Schematic diagram of electro-kinetic experiments setup and (b) the experimental setup of electro-kinetic cell in the approached cathode technique (ACs).

3.4.2 Testing Procedure

A determined mass of artificially contaminated soil specimen with Zinc or Chromium was prepared as described in 3.2.1 and then, introduced into the EK cell in uniformly compacted layers using a wooden rod to minimize the void ratio. In the chamber anode influent and cathode chamber

effluent, purging solution was utilized to fill them to the same level and maintaining so that no hydraulic gradient produce in the sample. Then, the EC cell was linked with the energy supplier with the application of constant DC voltage gradient to the soil sample. In the cell, the weight of the soil utilized was measured then it left for equilibrium for 24 hours, which is needed to obtain uniform redistribution of pollutants (Faisal and Hussein, 2015). Throughout the experiments, the electric current passed in the specimen followed by calculating the pH of the cathode chamber effluent at various periods. The tests continued till the current reduced significantly and the effluent volume decreased remarkably (Reddy et al., 2003).

Finally, soil samples were discarded from the cell based on the sampling point's layouts, as given by (Zhang et al.,2014), and sliced into four sections (S1– S4), each of which was 3.25 cm long, as shown in Figure (3.4). From each soil sampling points, 3g following drying, was mixed with 30 ml distilled water. Then, shaking the mix in thorough way by hand couples of minutes. After that, the particles were to settle for 1 hrs. pH of the supernatant was then measured representing the soil's pH (Faisal and Hussein, 2015). Additionally, the overall treatment efficacies were calculated as follows (Zhang et al., 2014):

$$w = \frac{C_o - C_1}{C_o} \qquad \ldots\ldots\ldots\ldots 3.1$$

Where:

C_0 is the initial ratio of metals (Zn (II) or Cr (III)) in the soils (mg/kg) and C_1 is ratio of metals (Zn(II) or Cr(III) that remains in the soils after treatment (mg/kg).

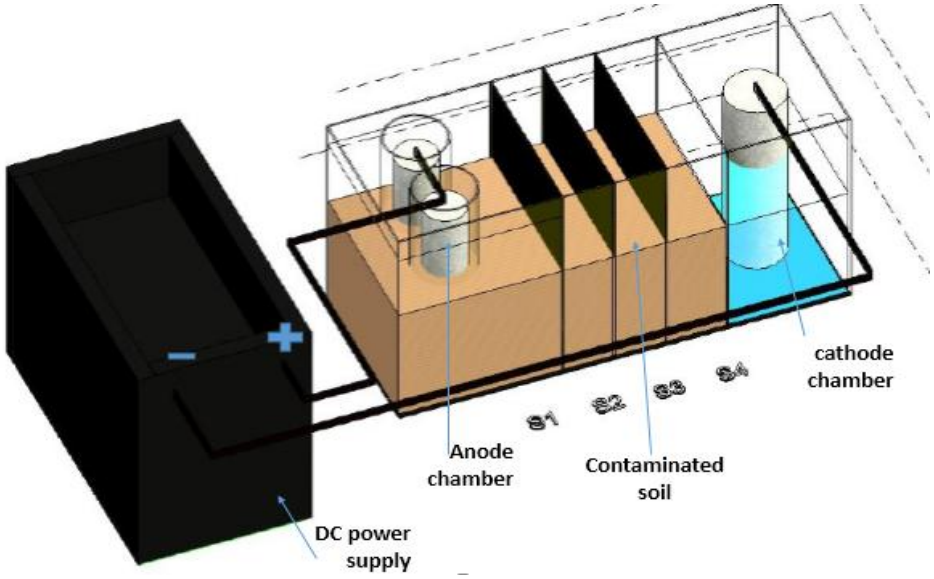


Figure (3.4): The layout of the sampling points.

3.4.3 Experimental design

To achieve the objectives of the current research, five experimental series were established which are (1, 2, 3, 4 & 5) (see Table 3.3) showes these series being carried out utilizing a strict methodology. Series-1 was represented as Fixed Anode (FAs), that EK process is operated with fixed anode (i.e., electric field with 1.5 V/cm potential gradient), which was included the processes from EK-1 to EK-3 for study the removal of Zinc ion from contaminated soil. Then, the processes from EK-4 to EK-6 were implemented in the Series-2 for clean up the soil contaminated with total chromium Cr (III) or Cr (total). While the experiments from EK-7 to EK-12 were implemented in the Series-3 & series 4 for clean-up the soil contaminated with zinc or chromium by approaching anodes (AAs). At last series 5, which include EK-13 and EK-14. For the experiments for approaching cathode electrode, the cathode were located at distance equal to 3.25 cm from S4 (i.e., the cathode were switched from S4 to the S3 electrode

after 50 hour operation and the voltage (14.625 V) used was adjusted accordingly to maintain 1.5 V/cm). This procedure was similar to that adopted by (Shen et al., 2007; Zhang et al., 2014; Ng et al., 2016 and Wan et al., 2019).

For experiments [EK-1/Series-1, EK-4/ Series-2 and EK-7 &EK-10/series-3&4], distilled water [EC=22 µS/cm, pH=7.8] was utilized in each cathode and anode parts. Each experiment served as a baseline experiment for its series. The significant fault of the traditional EK is hydroxides precipitation in the soil near the cathode, resulting in a decrease of remedial efficiency. This is because water electrolysis leads to the formation of hydroxide ions in the cathode compartment. In order to prevent this precipitation, has been used the double anodes method with the help of Chelating agents. The experiments [EK-2 and EK-5] were conducted using 1M acetic acid as catholyte to make buffering the hydroxide ions and pH remained low [~3]. The metals solubility can be improved by incorporating reagents which produce metal complexes like chelates. Chelating agents have ligands which are either two or more bonding with the metal for formation of stable compounds named chelates. The chelate can be extracted with no need to low pH, so the experiments [EK-3 & EK-6] and [EK-9, EK-12, EK-13 and EK-14] were conducted using the 1 M Ammonium citrate (AC).

Table 3.3: Summary of electro-kinetic treatment tests.

Series-	Name Of Experiment	Initial Conc. (mg/kg)	Time (hours)	PS (pH)	
				Anodes	Cathodes
1-(FAs)/(Zn)	EK-1	850	100	DW	DW
	EK-2	850	100	DW	1 M AA (~3)
	EK-3	850	100	DW	1M AC (~9)
2-(FAs)/(Cr)	EK-4	220	100	DW	DW
	EK-5	220	100	DW	1 M AA (~3)
	EK-6	220	100	DW	1M AC (~9)
3-(AAs)/(Zn)	EK-7	850	100	DW	DW
	EK-8	850	100	DW	1M AA (~3)
	EK-9	850	100	DW	1M AC (~9)
4-(AAs)/(Cr)	EK-10	220	100	DW	DW
	EK-11	220	100	DW	1 M AA (~3)
	Ek-12	220	100	DW	1M AC (~9)
5-(ACs)/(Zn)	EK-13	850	100	DW	1M AC (~9)
(ACs)/(Cr)	EK-14	220	100	DW	1M AC (~9)

DW: Distilled water, AA: acetic acid , AC: ammonium citrate, AAs: approach anode technique, ACs: approach cathode technique, FAs: fixed anode technique, Ps: purging solution.

3.4.4 Chemical analysis

All final reports for concentrations of Cr (III) or Zn (II) carried out in Ibn Al-betar Research center/ Ministry of industry and Minerals Corporation for Research and Industrial Development. In addition, some of the soil analyses were conducted at the environmental Engineering Department / University of Babylon. The results of SEM and EDS it was examined at Al-Nahrain University, Faculty of Science. Pollutants in various soils were collected by conducting acid digestion following a procedure similar to that of (Haswell, 1991). Total concentrations of zinc and chromium were determined by acid digestion procedure, as cited by (Ng et al., 2016). By

following the procedure, the soil specimens were subjected to crushing then about 1 gram of representative specimen was measured precisely in a breaker with capacity of 250 ml. This is followed by mixing with 4 ml of hydrochloric acid and nitric acid by 1 ml then leaving for two hours. On paper No.42, the specimen was filtered and placed in volumetric flask having 100 ml capacity. After that, utilize distilled water to wash the precipitation, incorporate this washed water to filtration and add more water till having a size of 100 ml. At the end, determine the metal concentration by atomic Absorption spectrophotometer (AAS).

The results of the experiment should be as precise as possible, thus the work should be carried out carefully and with precautions. The precaution steps involved the following: 1) for each test, utilize a new filter paper and electrodes, 2) soaking the compartment and the electro-kinetic cell in dilute acid solution for 24 hours rinsing with water and distilled water to present the passage of pollutants during the tests.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results of native soil analyses

The original soil has a pH equal to 8.5 and the amount of chloride ions and calcium carbonate equal to 1.859 mg/l and 11.432% respectively. The soil is classified as sandy loam soil in accordance with particle-size distributional analyses. As explained in Table (3.1) in section 3.2.2, the liquid limit is 30.5% and plastic limit was 21%. The EDS (Energy Dispersive X-Ray Spectroscopy) curve of the original soil is as given in Figure 4.1. This technique gives an overall mapping of the sample by analyzing near-surface elements and estimates the elemental proportion at different positions.The Figure elucidates that that relatively high concentrations are as follows: Si, Al, Au, Mg, Ca, Na and K.

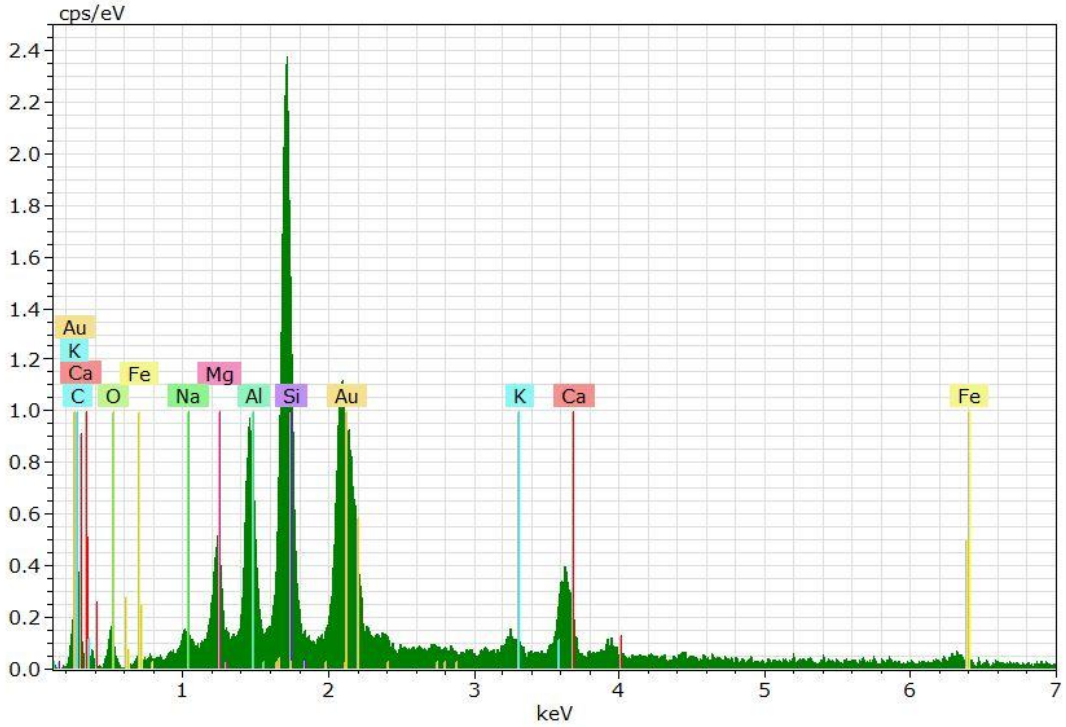


Figure 4.1: EDS for the composition of the native soil sample.

4.2 Effect of different types of the leaching solutions on the migration of metals through fixed anode electrode technique

A) Series -1 (Zinc ions)

The experiments that used of the electro-kinetic fixed anode technique to remove zinc from sandy loam soil are conducted using distilled water (DW), 1 M acetic acid (AA) and 1 M ammonium citrate (AC) as the purging solution (leaching solution). In these experiments, clean soil was spiked with 850 mg/kg zinc and a voltage gradient of 1.5 V/cm was applied. According to Table (3.3) in section 3.4.3, the experimental plan for series-1 included three electro-kinetic remediation tests (EK-1 to EK-3).

Figure (4.2) shows the profile of electric current during electro-kinetic process with fixed anode technique (FAs) for experiments in series-1 (EK-1 to EK-3). For EK-1, the electric current in the process varied from 29 to 429 mA within ranged between 1 to 46 hr. At 46 hr., electrical current was at its highest, then decreasing gradually, and finally stabilizing to 95-71 mA. It is seen during the test (EK-2), the initial value of the current increased from 26 mA to peak value of 492 mA in about 40 hr. Then, it minimized to value of 92 mA in 100 hr. While for EK-3 (when utilizing 1 M AC as catholyte solution), the initial value of the current clearly increased from 37 mA to a peak value of 440 mA in about 46 hr. After that, the current lowered to a low value and fixed at about 252 mA. Saeedi and Moradi (2013) indicated that the decrease in the current in the first hours of the experiment (first 30 hours) is higher than that occurred at the late hours of the experiment. As time pass, the electrical currents reaches more stable levels. During the tests, the decrease in electrical current through soil is attributed to the increase in soil matrix electrical resistance because of ions precipitation as insoluble

products, especially next to electrodes. The electrical current presented in the soil shows high affinity of ions to migrate toward the other electrodes, which created during the tests because the precipitation of reaction products increase the sensitivity of the soil.

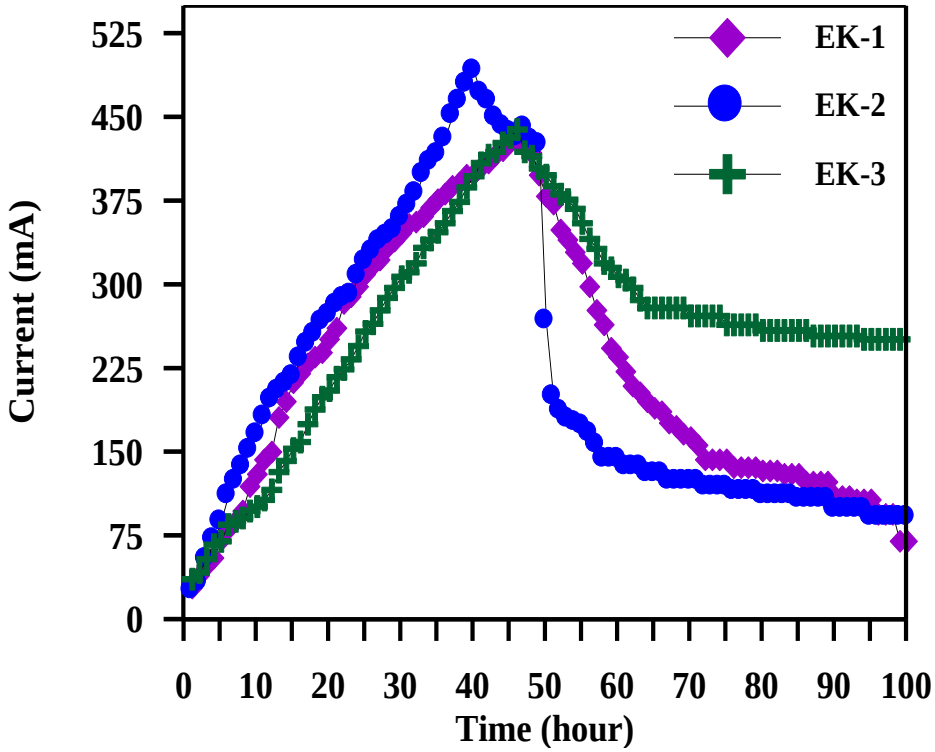


Figure 4.2: Effect of types of the leaching solutions on variation of current of electro-kinetic with time for experiments in series-1 (EK-1 – EK-3).

Figure 4.3 (a, b and c) together with Table (4.1) illustrates zinc residual concentration profile and pH of the soil as a distance function from the anode compartment of the treated soil for experiments EK-1, EK-2 and EK-3 after the completion of the electro-kinetic treatment time, which was 100 hr. As given in Figure 4.3 (a, b and c) in which the electrolyte for the anode and cathode chamber was the distilled water, there is no pH control imposed. Therefore, the pH distribution in the EK-1 as follows:

1- It was noticed that the soil at S1 (close to the anode) for the EK-1 has a pH equal to (8.6) low than at S1 for the EK-2 and EK-3 (7.6 and 8.9, respectively).

2- It was determined that the pH in the section S2, S3 and S4 of the treated soil for test EK-1 equal to 9.6, 10.1 and 11.6, respectively, was higher than the same section points for the tests EK-2 and EK-3 .

In each section of the treated soil (S1-S4) for tests (EK-1 – EK-3), (The residual concentration of Zn^{+2} in the each section of the treated soil were calculated and plotted in 4.3 (a, b and c). The residual amount of Zn^{+2} in the S1 (close the anode) was 580 mg/kg and S4 (close the cathode) for the treated soil for EK-1 was 722.5 mg/kg, which were higher than in EK-2 (403.46 & 514.44 mg/kg, respectively), and in EK-3 (637.5, 629, 620.5 and 618 mg/kg, respectively). Clearly, the amount of Zn^{+2} started accumulating from S2 toward S4 for EK-1. This is related directly to soil pH, in the EK-1 test was used DW as an electrolyte for the anode and cathode chamber, and in the cathode and anode compartments, there is no pH control imposed. Hence, there was relative increase in the amount of carbonate and calcite in the soil sample in each section of the treated soil (S1-S2) which was the reason behind this buffering capacity of the soil as compared with the initial amount of calcium carbonate for native soil, as shown in Figure (4.4). Thus, the achieved removal of zinc was low in compared with EK-2 and EK-3, as explained in Table (4.1). It is clear from the same figure that the final concentration of Zn^{+2}, which is related directly to soil pH, was decreased in the sections of pH ~7.3 close to the anode electrode and raised in the sections of pH $\geq$ 8.33 close to the cathode electrode for tests EK-2 (Figure 4.2 b). Some of the zinc species in the sections of pH ~ 7.3 was probably

soluble and can present in Zn^{+2} cationic forms. These ions could migrate by electro-migration, and possibly by electro-osmosis to some extent towards the cathode. However, the accumulation of zinc in the sections close to the cathode was due to the high pH conditions which result in precipitation Zn^{+2} as Zn $(OH)_2$ Because of reduction soil pH in the each section of the treated soil, which was lower than initial soil pH (8.5), which was leading to decreases the amount of calcite and carbonate in the soil specimen. Therefore, the buffering capacity for the soil was decreased. This will be the basis for formation and development of acid front phenomena. Therefore, a relatively high removal of zinc can be achieved. Maria et al. (2014) studied the effectiveness of addition of an acid (strong and weak acids) to the cathode chamber to enhance the EK remediation by neutralization of the alkaline front generated at the cathode. Also, reported the chemical equilibria, considering no gaseous phase, when used 1 M acetic acid (weak acid) as catholyte solution to control catholyte pH in the cathode chamber are the following:

$$HA_C \leftrightarrows H^+ + A_C \quad \text{..... (4.1)}$$
$$A_C + M^{+2} \rightleftarrows MA_C{}^+ \quad \text{..... (4.2)}$$
$$2A_C^- + M^{+2} \leftrightarrows MA_C \quad \text{..... (4.3)}$$

Where $MA_C{}^+$ represented formation of complex species with any metallic ion (M) is more favorable for acetic acid. Based on the above chemical equilibria may be expected that the complex specie as $ZnA_C{}^+$formed therefore the trend of distribution of measured contaminant toward the cathode as cleared in Figure 4.3 (b). The obtained results agreed with previous study. Rashid, (2015) showed that the using acetic acid in the cathode was beneficial and the introduction of acetic acid allowed

significantly higher removal and migration of lead toward the cathode in comparison with unenhanced condition when distilled water was the purging solution.

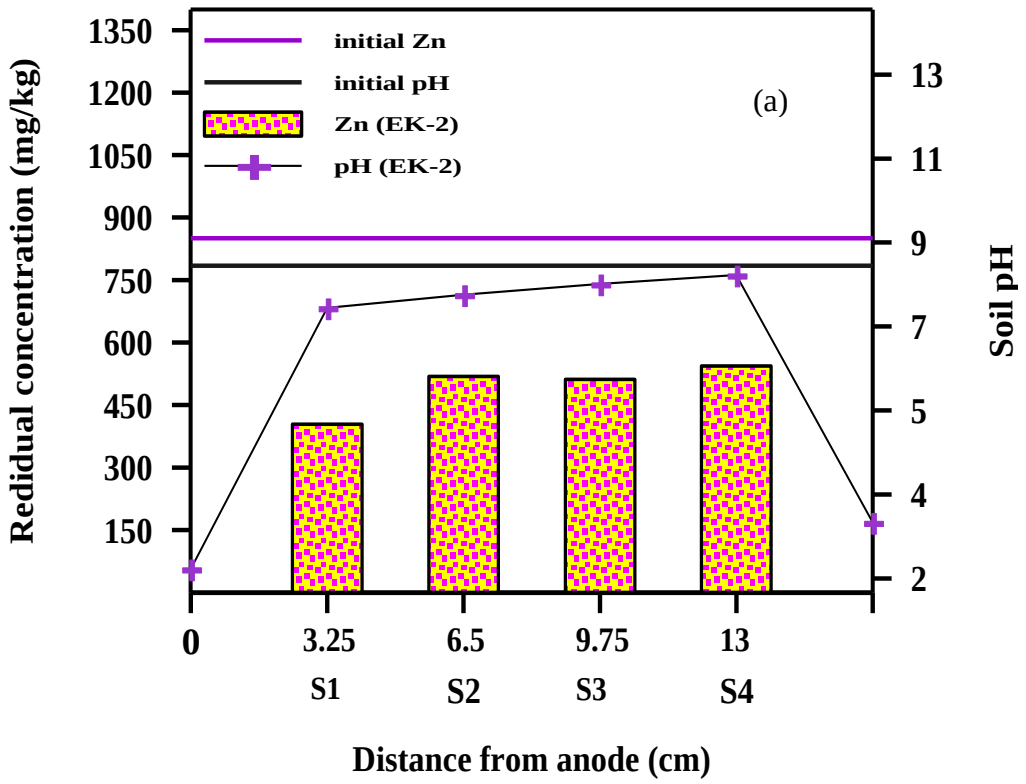
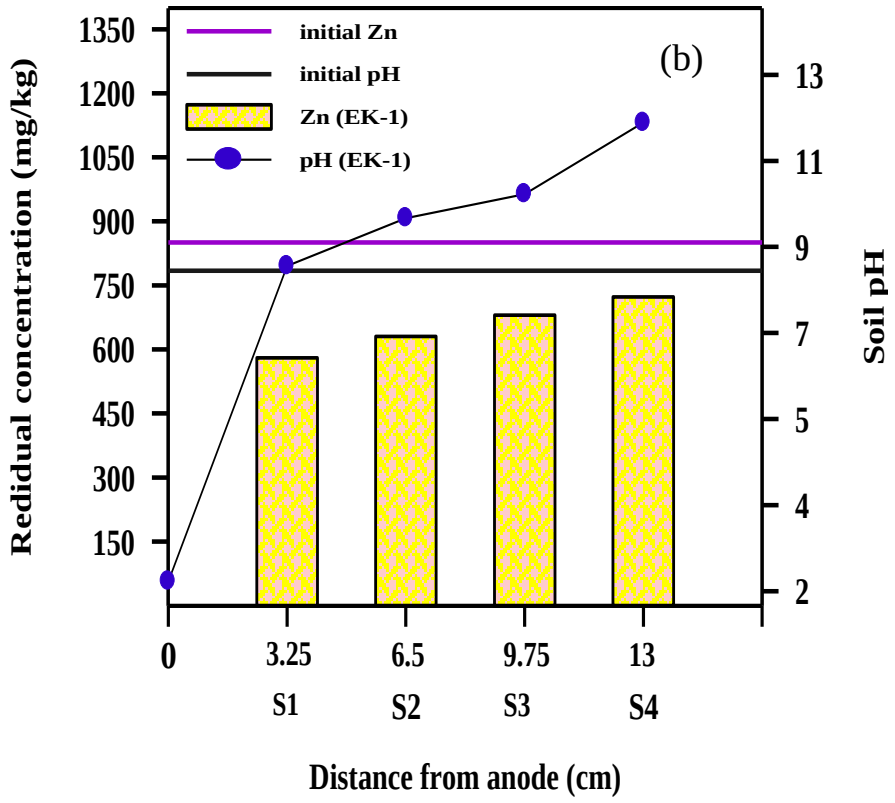


Figure 4.3: Zinc and pH profiles in the treated soil by fixed anode -electro kinetic technique (FAs-EK) for Ek-1 - EK-3.


(b)
initial Zn
initial pH
Zn (EK-1)
pH (EK-1)
Redidual concentration (mg/kg)
Soil pH
1350
1200
1050
900
750
600
450
300
150
13
11
9
7
5
4
2
0
3.25
6.5
9.75
13
S1
S2
S3
S4
Distance from anode (cm)

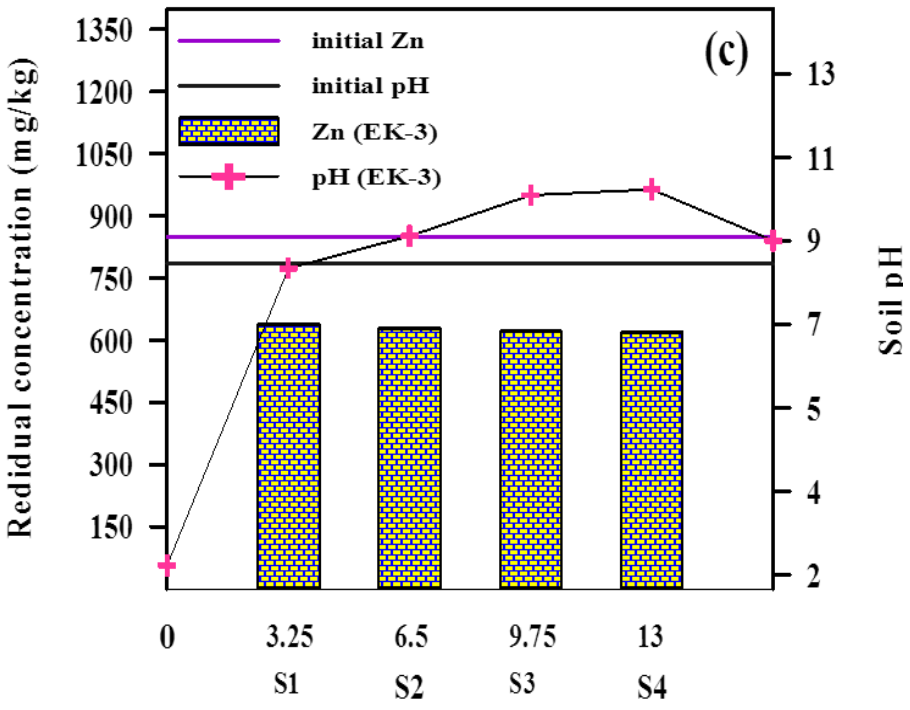

(c)
initial Zn
initial pH
Zn (EK-3)
pH (EK-3)
Redidual concentration (mg/kg)
Soil pH
1350
1200
1050
900
750
600
450
300
150
13
11
9
7
5
4
2
0
3.25
6.5
9.75
13
S1
S2
S3
S4

Table 4.1: Residual zinc (II) concentrations and percentage of calcium carbonate for every part of the treated soil for (EK-1-EK-3) tests (series1).

Experiments	Parameters	points of samples			
		S1	S2	S3	S4
EK-1	Initial concentration of Zn (II) (mg/kg)	850			
	Zn (II) residual concentration (mg/kg)	580	630	680	722.5
	Reduction (%)	31.7	25.8	20	15
	Average reduction (%)	23.125			
	Initial CaCO3 (%)	11.432			
	Residual $CaCO_3$ (%)	11.8	12.768	13.149	13.89
EK-2	Zn (II) residual concentration (mg/kg)	403.46	518.56	511.15	543.2
	Reduction (%)	52.5	39	39.8	36.1
	Average reduction (%)	42			
	Residual $CaCO_3$ (%)	9.98	10.432	10.6	11.03
EK-3	Zn (II) residual concentration (mg/kg)	637.5	629	620.5	618
	Reduction (%)	25	26	27	27.3
	Average reduction (%)	26.325			
	Residual $CaCO_3$ (%)	13.6	13.4	13.7	13.9

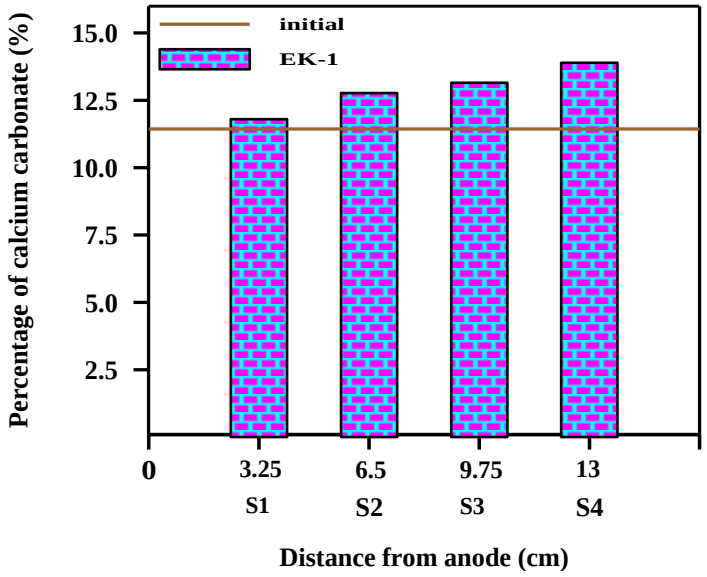


Figure 4.4: Variation of residual carbonate along the specimen of the treated soil.

The scanning electron microscope (SEM) was given in Figure (4.5) together with EDS Spectra. For 20-μm magnification scale, SEM images, presented in Figure 4.5 (a), are important for identification of the morphological properties for adopted the soil amended with zinc ions before electro-kinetic remediation. It can be seen that the shape of the initial soil amended with zinc ions is separated aggregates with large pore spacing (Khodary et al., 2021). Figure 4.5 (b) elucidates that Silicon (Si), Antimony (Au), Aluminum (Al) and Calcium (Ca) forms the predominant element in the composition of the initial soil amended with zinc ions. Figure 4.5 (c) shows EDS mapping for Si and Zn. It was noticed that the Si heavily distributed, while Zn was randomly distributed. (Wang et al., 2017) showed heterogeneous distribution to the S, Fe and P in the SEM-EDS mapping, while homogeneous distribution occurred in Cu and Zn and there is no association between Cu and Zn in the sediment and the components incorporating P and S.

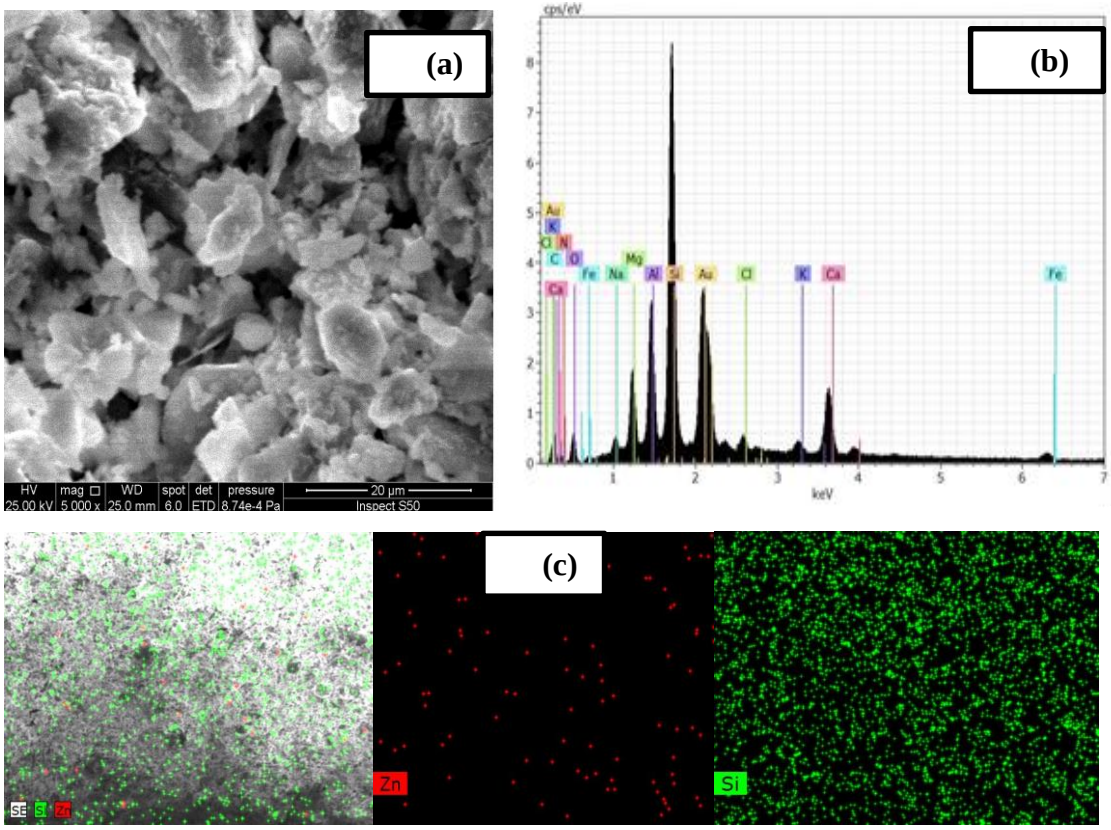


Figure 4.5: Mapping spectra, EDS and SEM of the soil amended with zinc ions before electro-kinetic remediation: (a) SEM. (b) EDS spectra; and (c) mapping spectra of element.

Figure 4.6 (a) and (b) gives the scanning electron microscope (SEM) of sample points S1 (near the anode) and S4 (near the cathode) for EK-2 (when used 1 M AA as catholyte solution), had magnification to a 20 µm scale. Figure 4.6 (a) indicates that the surface shape of soil in S1, whereas the void between soil particles for the region near the anode was larger as compared with it's in the region near the cathode (sample point S4). This indicated that stacking of large platy shape soil particles with large pores after being blended utilizing distilled water as leaching solution in the anode and 1 M AA as leaching solution in the cathode chamber. It is thought that the acidic environment or other chemical reactions occurred close to the anode led to the dissolution of coating substances. While on the background

closed to the randomly arranged small modules, the large inter-connected soil particles present (Ahmad et al., 2006).

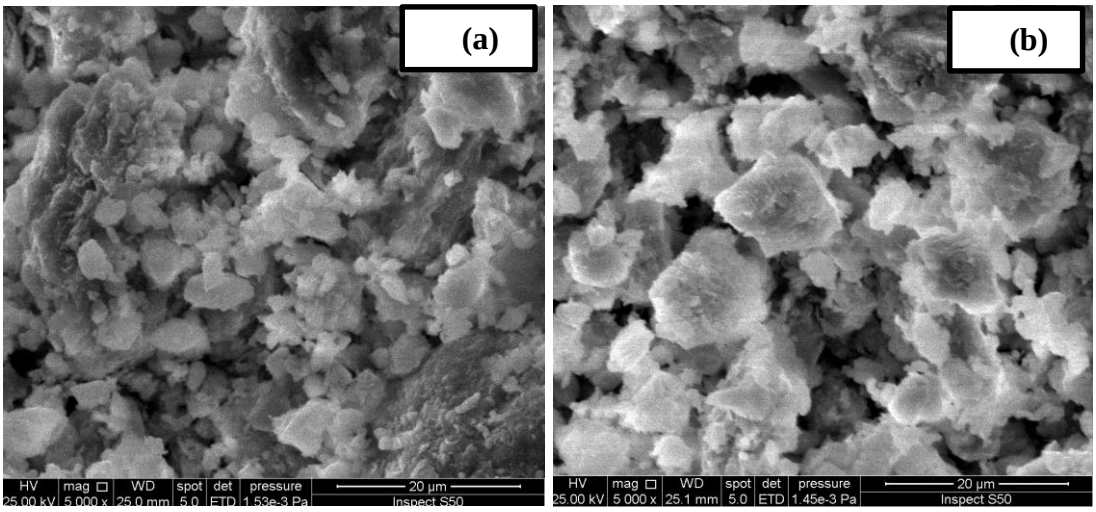


Figure 4.6: SEM images for the (a) S1 (close to the anode) and S4 (close to the cathode) samples soil for EK-2 test.

Figure 4.7 (a, b and c) shows the effect different types of the leaching solutions (when DW, 1 M AA and 1 M AC were used as catholyte solution in the EK-1, EK-2 and EK-3 tests, respectively), on the decreasing of residual carbonate across the length of the soil specimen. Consequently, the removal of the salts from the sample which increased by utilizing 1 M AA of leaching solution in cathode chamber can be distinguished by acceptable contents from the salts that gathered on the cathode electrode surface. It is noticed from Figure 4.7 (c), the quantity of salts that accumulated on the cathode electrode of the surface in EK-3 test was lower than these in the EK-2 and EK-1 tests.

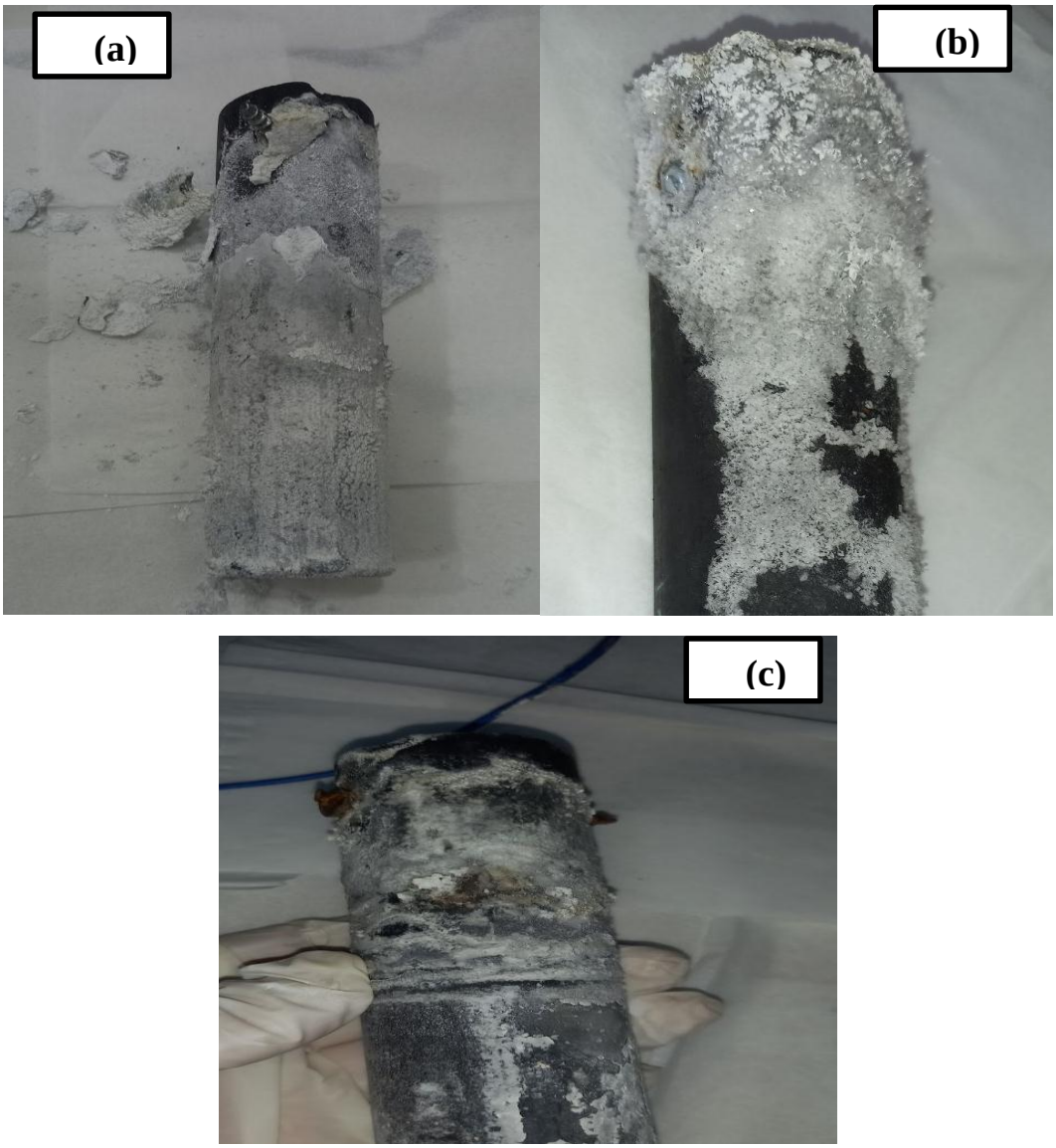


Figure 4.7: gathering of salts on the cathode electrode surface after the completion of electro-kinetic process: (a) in EK-1 test, (b) in EK-2 test and (c) in EK-3 test.

B) Series -2 (Chromium ions)

The removal of Chromium and Lead is remarkably influenced by the precipitation of the metals in the soil close to the cathode when the purging solution is the distilled water. The precipitation is caused by the high pH environment, which is developed from the water electrolysis at the cathode (Rashid, 2015). In order to obtain high discard of heavy metals from the

polluted soil during the EK remediation process is used chelating agents so that the pH of the soil remain fixed and the heavy metals are mobilized. Since the chelating agent is capable of converting heavy metals in the soil into soluble metal (Paramkusam et al., 2011). In this series-2, EK-4, EK-5 and EK-6 tests (when sandy loam soil was spiked with 220 mg/kg chromium (Cr(III)) was conducted with the same experimental conditions for EK-1, EK-2 and EK-3 tests in the series-1, where the sandy loam soil spiked with 850 mg/kg zinc.

Figure (4.8) shows the variations of the current for three tests (EK-4 to EK-6) as a function with time. The trend of the current variations for EK-4 and EK-5 is the same: the current initially increased to high value of 340 mA for EK-4 test and 514 mA for EK-5 test in the first hours of the experiments (first 35 and 30 hours), is higher than later during the experiments. As time passed, the electrical current tends to become highly stable (140 mA for EK-4 and 170 mA for EK-5 test). Whereas, the current in EK-6 increased with time up to 57 hr to reach higher value equal to 642 mA, and then reduced to about 163 mA when the test is completed (100 hr.). Also, it noticed from the same figure that the current for EK-4 test (with the utilization of distilled water as leaching solution in the anode and cathode chamber) was lower than its for EK-5 test (when used 1 M AA as catholyte solution) and EK-6 test (when 1 AC was used as catholyte solution)**.** These changes in the current can be attributed to the following: (i) the high initial current which is caused by the incorporation of an electrolytic solution in cathode and anode areas. As time goes on, the contents of free ions in the electrolytic solution reduces because of participating or migrating toward the specimen region resulting in current reduction; (ii) the migration of H+ ions is very fast which

produces an acid condition and results in high releasing of metal ions, at the end, this increase the current because of the existence of a free ions in high amount; and (iii) the reduction of current is gradual which caused by precipitation which minimizes the free ions content and increase the resistance (Xue et al., 2017).

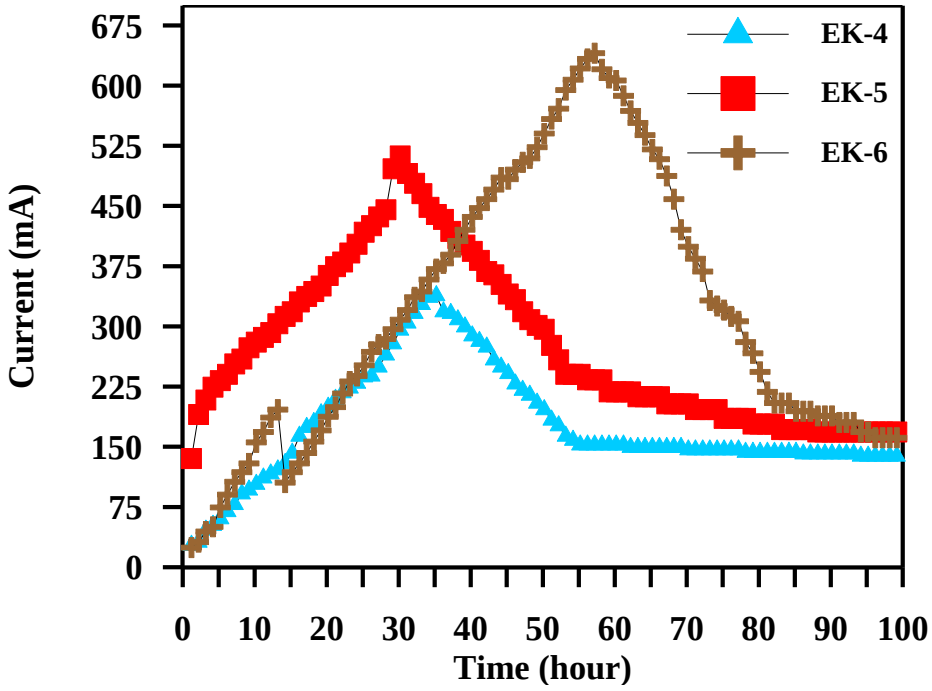


Figure 4.8: Effect of types of the leaching solutions on variation of current of electro-kinetic with time for experiments in series-2 (EK-4 – EK-6).

The distribution of Cr (III) concentration and pH is given in Figure 4.9 (a, b and c). The figure shows their detection after the completion of the EK treatment period for EK-4, EK-5 and EK-6 tests which took 100 hr., for four samples points Located at a distance from anode (S1 to S4): 3.25, 6. 5, 9.75 and 13 cm. As explained in Table (3.3) in section 3.4.3, in EK-4 test was used DW as anolyte and catholyte solutions, the initial value of the pH of anolyte in EK-4 reduced from 6.8 (pH of distilled water) and fixed at nearly 2 as shown in Figure (4.9) where the line started from part zero in Figure

(4.9) (which represented the position of the anode chamber) due to production of H^+ ions. While, there is no pH control imposed in the cathode chamber and expected to increase from 6.8 and stabilized at approximately 12.5 because of the production of OH^- ions (Rashid, 2015). The generated H^+ ions at the anode compartment have lowered the pH in the anode zone. In contrast. The OH^- ions formed in the cathode compartment has increased the pH in the cathode zone. The hydrogen and hydroxyl ion are migrated during the soil to cathode and anode electrode under an electrical field, producing an acidic and basic front. When the acid and base fronts meet, the soil inside the cell was classified into the acidic and basic zone with a sharp pH peak in between (Zhang et al., 2014). The acid region advanced faster than the base one since the electro-osmotic flow is counteracted in addition to the ionic mobility of H^+ which higher than that of OH^- by about 1.76 (Saeedi et al., 2009). As displayed in the same Figure in the EK-4, the pH of the soil profiles increased above the native soil pH value 8.7, where started from the second section (S2) beginning at the anode to the last section vicinity of the cathode (S4) to become equal to 10.89. It was noticed there was no change in the soil pH between anode region and cathode region for EK-4 test (when was used DW as catholyte solution). Based on the previous study (Fansheng et al., 2018) showed that in the EK treatment, there is no acidic region migration phenomena. This can be attributed to consumption of H+ formed in the anode in the interaction with the buffer substances when they migrate to the cathode.

The initial concentration of Cr (III) throughout the soil, which is plotted in each Figure as horizontal line was 220 mg/kg. The removal efficiency of Cr^{+3} in EK-4 experiment (when used distilled water as anolyte and catholyte

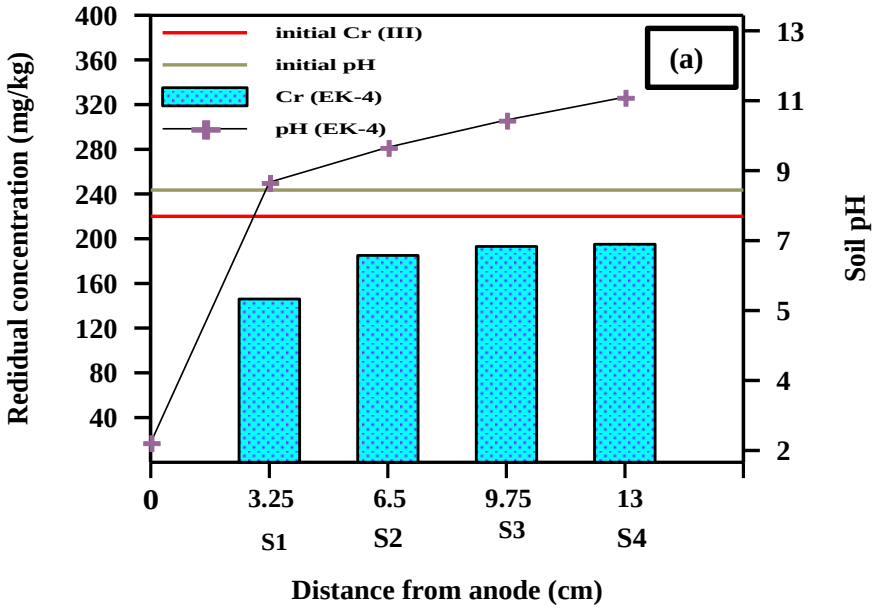
solutions) decrease towards the cathode as 33.6%, 15.9% and 12.3 %and 11.36 for S1, S2, S3 and S4 sampling points, respectively (the residual concentration of chromium as 145.9, 185, 193 and 195 mg/kg for S1, S2, S3 and S4 sampling points, respectively), as given in Figure 4.9 (a). Finally, the trend of migration of Cr (III) throughout soil towards the cathode region. Saeedi et al. (2013) illustrates that chromium is present as: most commonly, hexavalent chromium is found in hydro chromate anions like as $HCrO_4^{-2}$, $Cr_2O_7^{-2}$ and CrO_4^{-2}, while Cr (III) can be presented in the form of cationic, anionic and molecular like Cr $(OH)^{+2}$, $Cr(OH)^{-4}$, Cr $(OH)_2^{+1}$, and $Cr(OH)_5^{-2}$. The observed migration of Cr was consistent with the changes in the soil pH (Rashid, 2015). In EK technique, the ions of Cr (III) mainly transport to the cathode region while Cr (VI) moves to the anode area. In the soil matrix, the Cr ion species act differently because of their geotechnical variations; whears Cr (III) can be adsorbed or precipitated into high pH soil particles, the adsorption of Cr (VI) onto these particles is very low (Saeedi et al., 2013).

The residual concentration of Cr^{+3} and pH in the every part of the treated soil (S1-S4) for tests (EK-5 and EK-6) were determined and plotted in Figure 4.9 (b and c) together with Table (4.2). As displayed in Figure 4.9 (a), the profiles of the soil pH in the EK-5 test for each section samples soil below background value 8.5. The soil pH at S1, S2, S3 and S4 that are located at a distance 3.25, 6.5, 9.75 and 13 cm from the anode, were 8.2, 8.25, 8.31 and 8.45, respectively. The residual amount of Cr^{+3} in the S1, S2, S3 and S4 for the treated soil for EK-5 test (when used 1 M AA as catholyte solution so that the pH at the cathode region remains low (about 3) approximately 125.7, 129, 138.9 and 143 mg/kg, respectively, respectively,

corresponding to the achieved of removal efficiency were equal to 42.8%, 41.4%, 36.8% and 35%, respectively (Table 4.2), were lower than in EK-6 test (165, 158.4, 154 and 147.7 mg/kg, respectively), and in EK-4 test (145.9, 185, 193 and 195 mg/kg, respectively. It was clear from the figure 4.9 (a) that the trend of migration Cr^{+3} in the test of EK-5 through soil sections after the completion of the electro-kinetic treatment time toward the cathode region. These results are agreed with the previous research. (Meng Fansheng et al., 2018) showed that close to the cathode region, the highest C/C0 value of Cr (T) could be gained, which is opposite to the minimizing trend of Cr (T) from anode to cathode in the EK treatment test. This can be attributed to the citric acid, which is a weak acid works as complex agent. This acid can react with Cr (III) initiating complexation reaction in order to enhance the discard of Cr (III). On the other hand, in the electric removal treatment, there is migration to the Cr (III) to the cathode region resulting in high amount of Cr (T) gathered close to the cathode. Based on the profile of the pH at each sections for the treated soil for EK-5 test were below the initial soil pH (8.5). This is lead to lower the buffering capacity and, as a result reducing the concentration of carbonate and calcite in the soil sample. Table (4.2) shows the residual carbonate of the soil was decreased during two-thirds of the soil being at the anode region.

In Ek-6 test, when used 1 M AC as catholyte solution with pH adjusted to (~9, according to procedure adopted by Rashid, 2015) in the cathode chamber. As displayed in Figure 4.9 (c), the concentration of Cr^{+3} residual for treated soil in S1 (close to the anode) for EK-6, equivalent to 165 mg/kg, were higher than in S4 (147.4 mg/kg)(near the cathode). It was clear that the concentration of chromium removed from the region close to the cathode

and the anode. However, the amount of contaminant accumulated in the section near the anode is relatively more than in the section close to the cathode. Therefore, Figure 4.10 (a, b and c) show the accumulation of salts on the cathode surface when using distilled water, 1 M AA and 1 M AC as purging solution, from Figure 4.10 (c) could be distinguished by low quantities of these salts on the surface of cathode electrode. Finally, it is evident from Table (4.2) the average decrease for chromium (III) that indicated for the EK-5 being approximately 39%, higher than those for the EK-4 and EK-6 (18.29 and 29%, respectively). The reason for this, the profile of the pH at each sections for the treated soil for EK-5 test were below the initial soil pH (8.5) was unlike for EK-6 (i.e., the profile of the pH at each sections for the treated soil for EK-6 test were higher the initial soil pH (8.5)), therefore the concentration of and calcite in the soil sample for EK-6 was increased above its initial value (11.342%).



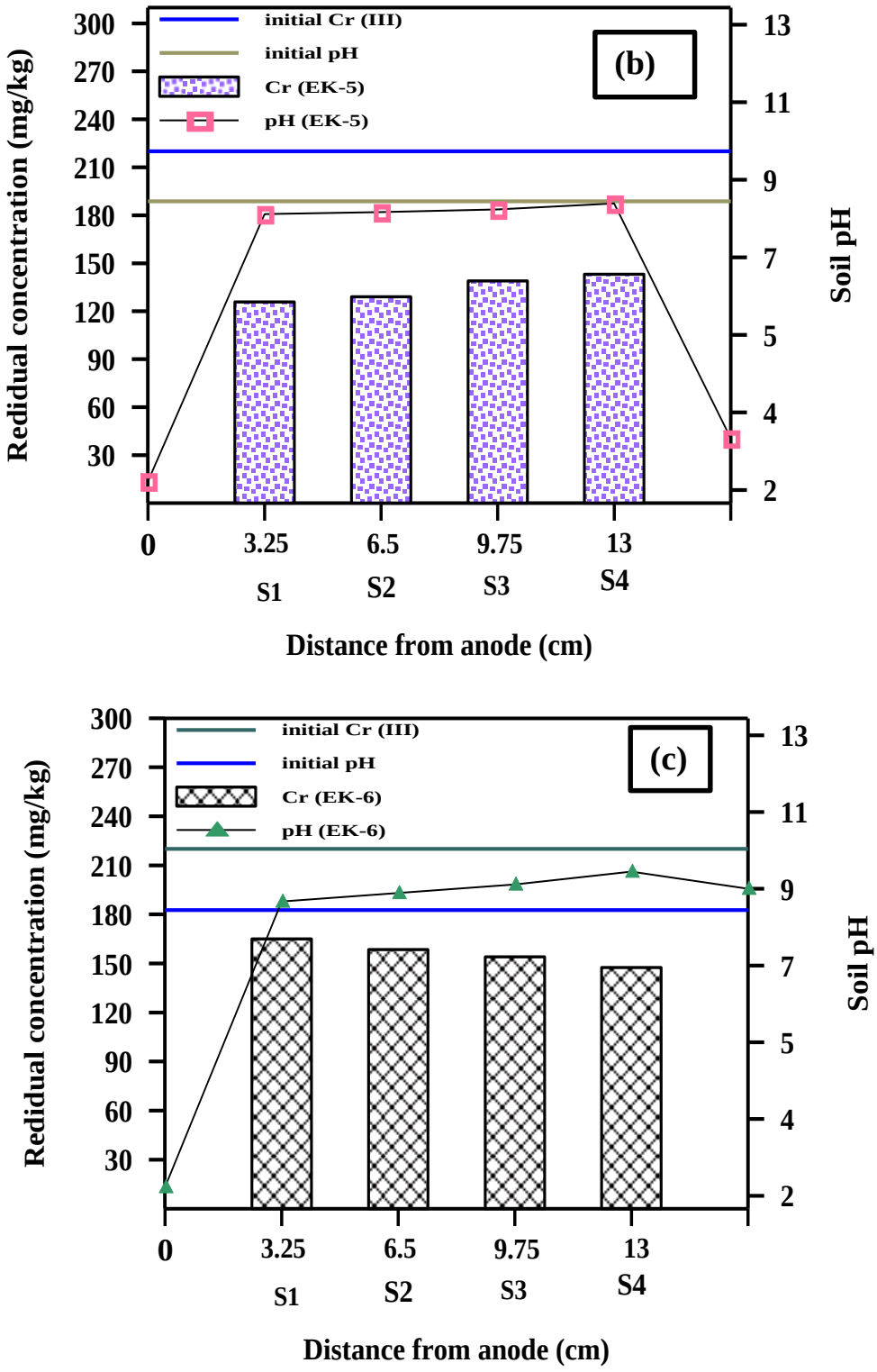


Figure 4.9: Chromium and pH profiles in the treated soil by fixed anode electro kinetic technique (FAs) (a) EK-4 test; (b) EK-5 test and (c) EK-6 test.

Table 4.2: Residual chromium (III) concentrations and percentage of calcium carbonate for each part of the contaminated soil for EK-4 - EK-6 tests (series-2).

Experiments	Parameters	points of samples			
		S1	**S2**	**S3**	**S4**
EK-4	Initial concentration of Cr (III) (mg/kg)	220			
	Cr (III) residual concentration (mg/kg)	145.9	185	193	195
	Reduction (%)	33.6	15.9	12.3	11.36
	Average reduction (%)	18.29			
	Initial CaCO3 (%)	11.432			
	Residual $CaCO_3$ (%)	11.87	12.56	13.85	14.11
EK-5	Cr (III) residual concentration (mg/kg)	125.7	129	138.9	143
	Reduction (%)	42.8	41.4	36.8	35
	Average reduction (%)	39			
	Residual $CaCO_3$ (%)	10.418	10.616	11.54	11.57
EK-6	Cr (III) residual concentration (mg/kg)	165	158.4	154	147.4
	Reduction (%)	25	28	30	33
	Average reduction (%)	29			
	Residual $CaCO_3$ (%)	13.32	13.66	13.87	13.98

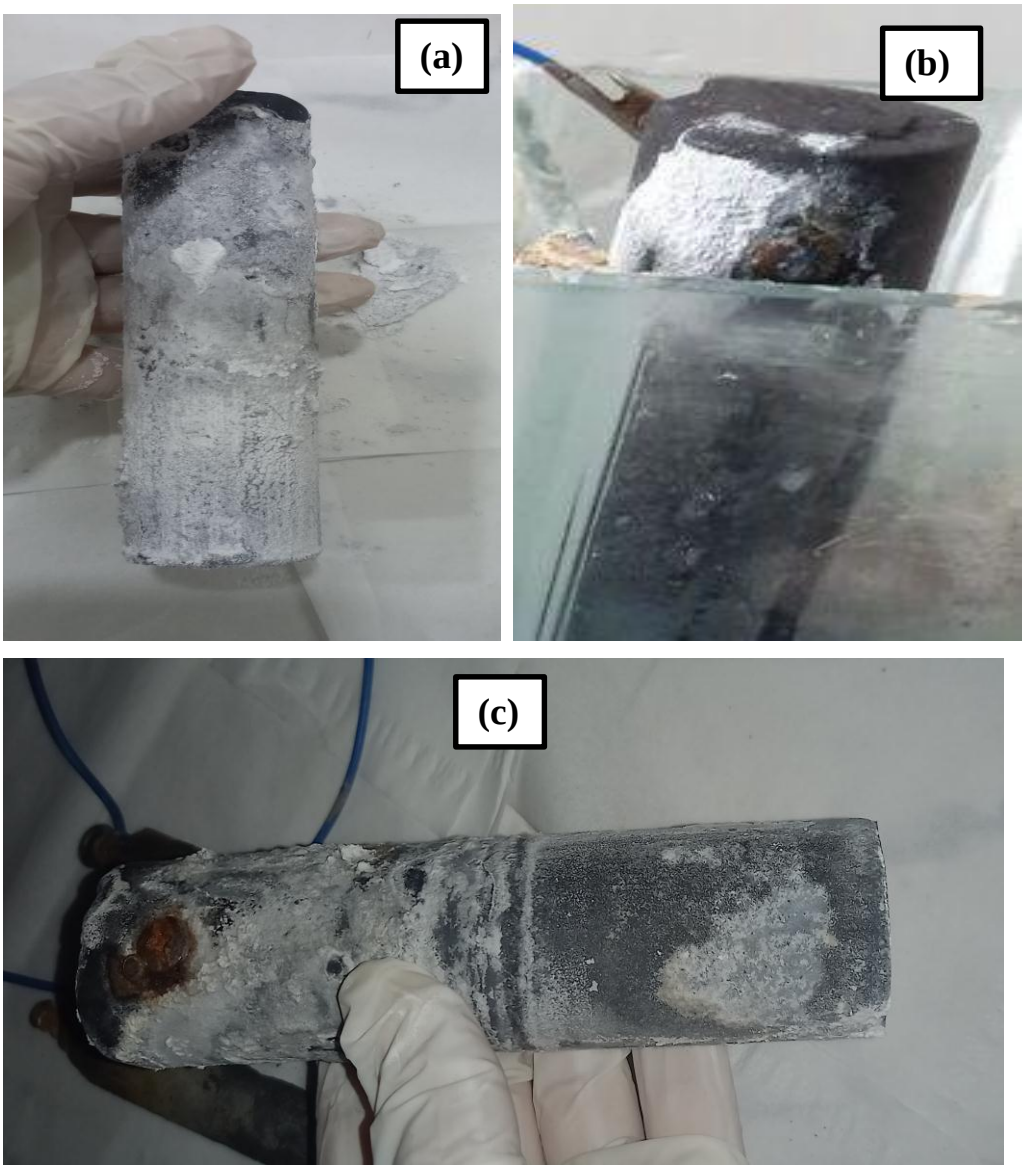


Figure 4.10: Salts accumulated on the cathode surface after the completion of electro-kinetic process: (a) in EK-4 test, (b) in EK-5 test and (c) in EK-6 test.

Figure 4.11 (a1) elucidates that silicon (Si), antimony (Au), chloride (Cl), aluminum (Al), Magnesium (Mg), and calcium (Ca) forms the predominant element in the composition of the treated soil in the section S1 for EK-5 (when used 1 M AA as catholyte solution). In addition, other elements, specifically Cr, Na, K, C, and Fe with certain percentages, can be

observed in the S1 composition of the soil spiked with chromium. While it was clear from Figure 4.11 (a2) that Si, Au, Al, Mg, Cl and Ca are a major element in the composition of the treated soil in the section S4 for EK-5 with other element such as Cr, K, Na, O and C represented minor elements. Figure 4.11 (b1 and b2) shows EDS mapping for Si and Cr in the section S1 (close to the anode) and in the section S4 (close to the cathode). It was noticed in both Figures that the Si heavily distributed, while density of the distributed of the Cr in the S1 section was low as compared in section S4 (Figure 4.11 (b2)) where density of the distribution of the Cr higher. This is attributed to the concentration of the Cr (III) observed in S4 (close to the cathode) was higher than it is in S1 (near the anode), as explained in Table (4.2).

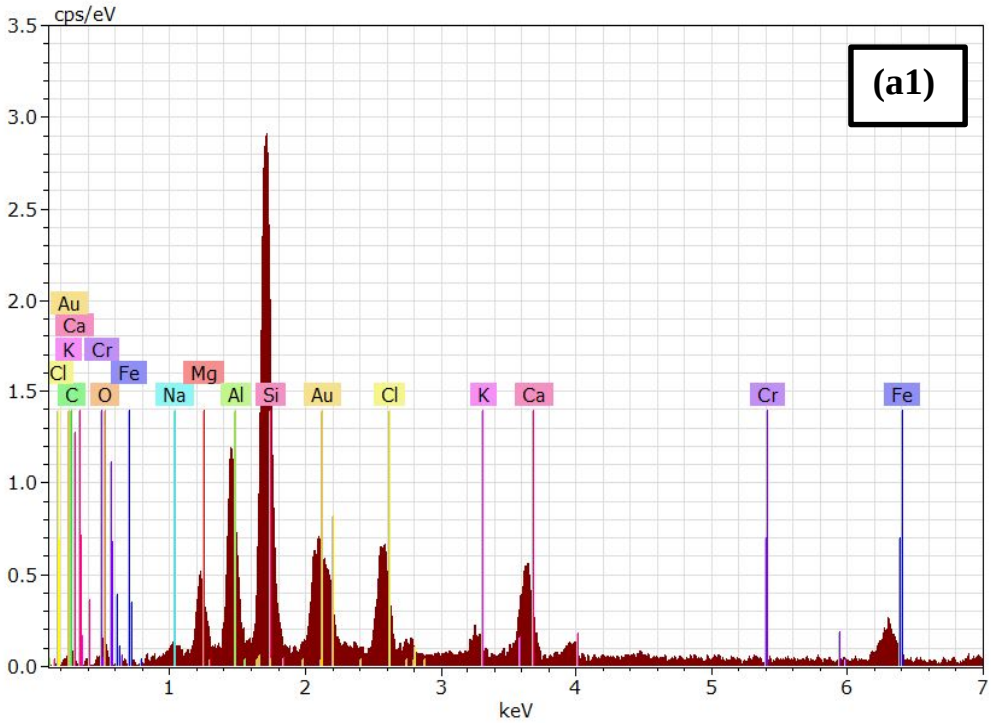
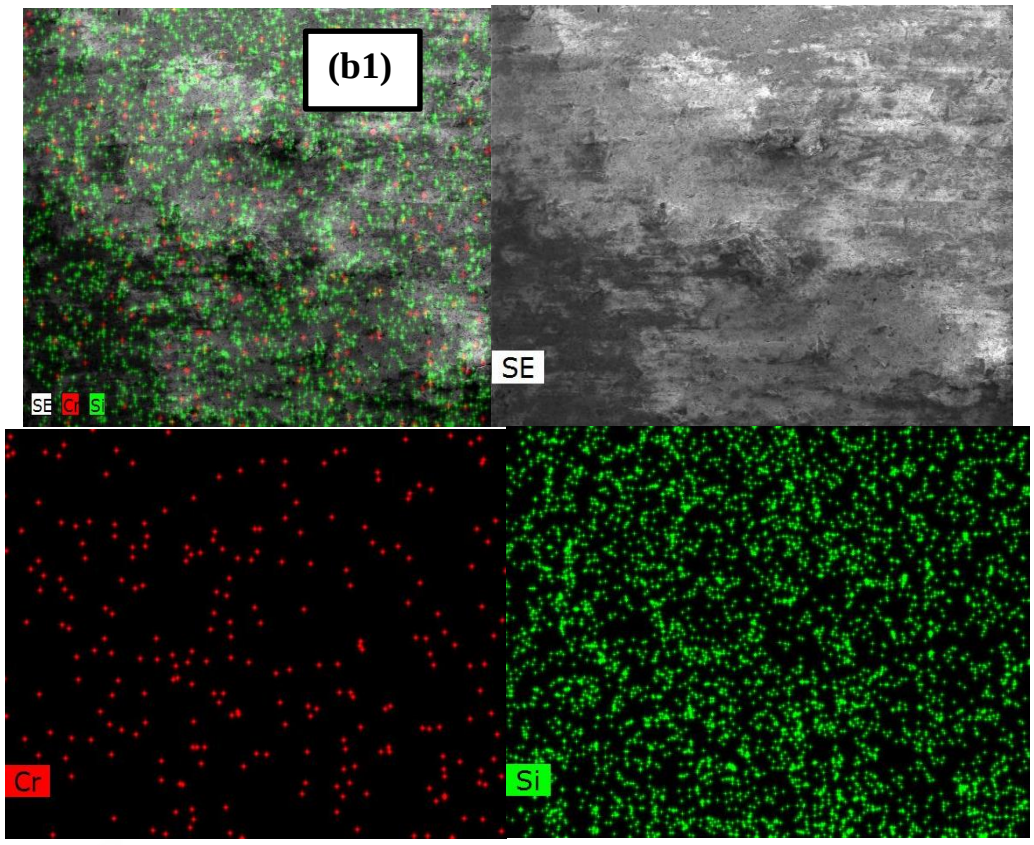
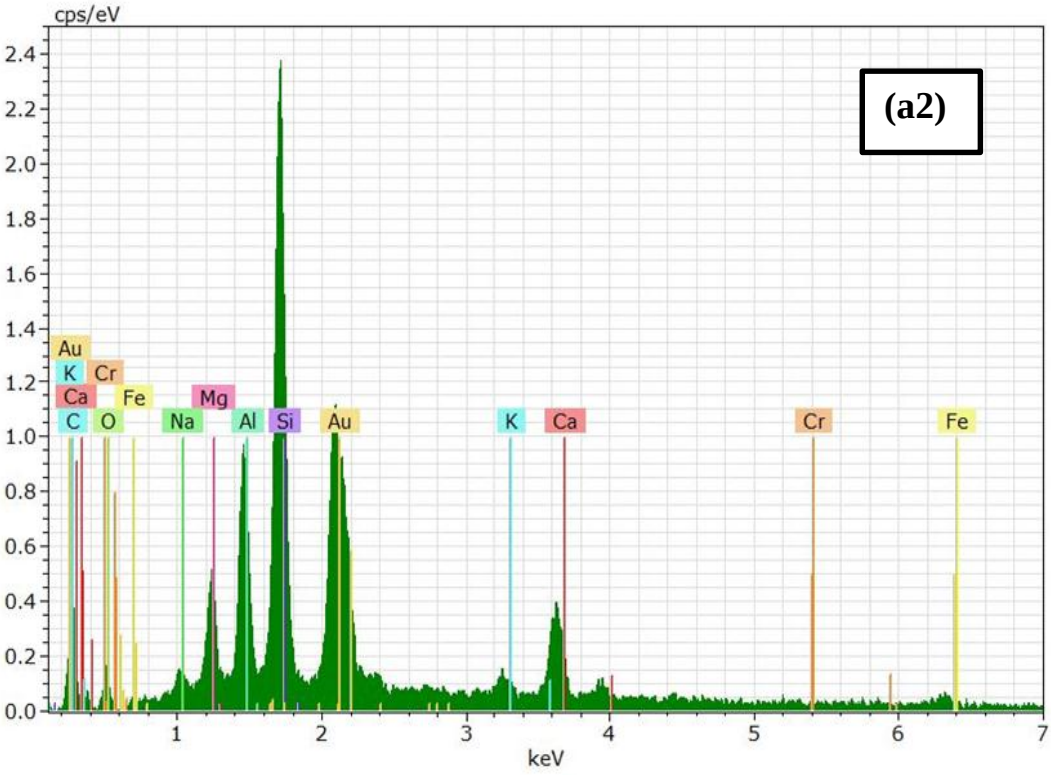
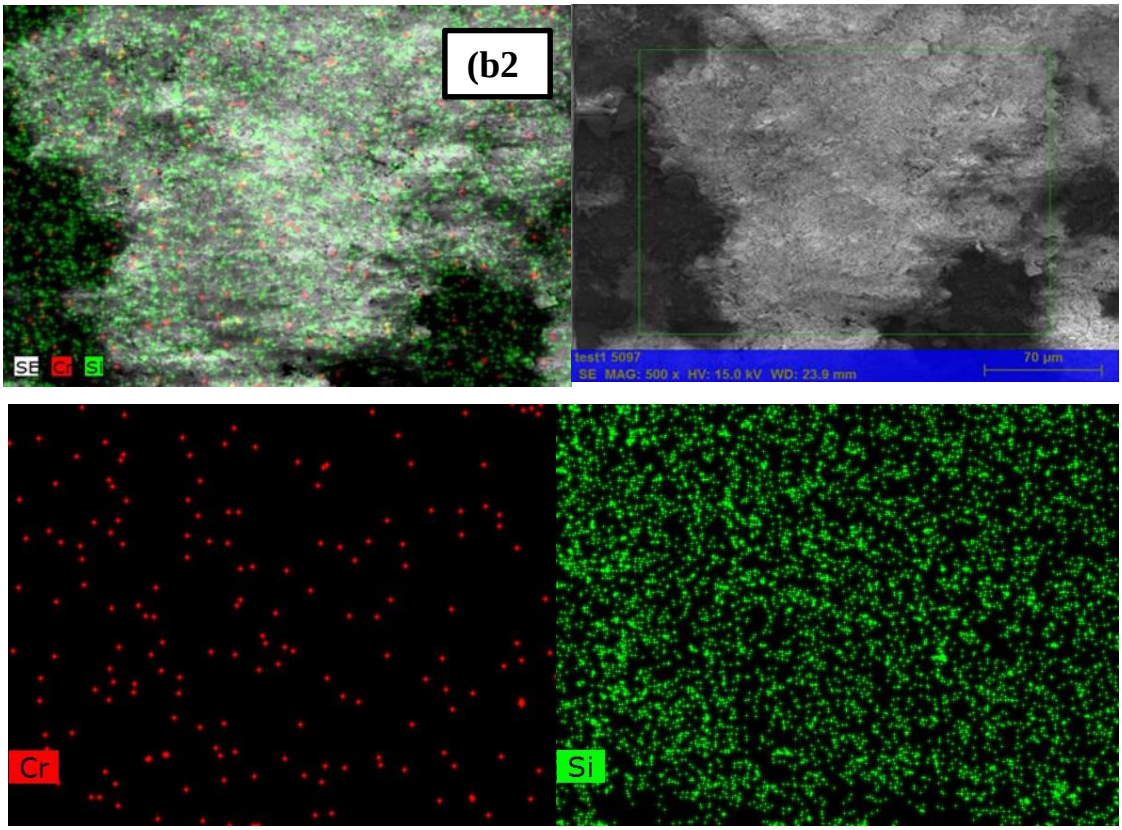


Figure 4.11: EDS and Mapping spectra of the treated soil at S1 and S4 section for EK-5: (a1) EDS spectra and (b1) mapping spectra of element at S1 section; (a2) EDS spectra and (b2) mapping spectra of element at S4 section.


(b1)
SE
SE Cr Si
Cr
Si


(a2)
cps/eV
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Au
K
Cr
Ca
Fe
Mg
C
O
Na
Al
Si
Au
K
Ca
Cr
Fe
1
2
3
4
5
6
7
keV



4.3 Behavior of the metals migration under approached anode electrode technique and approached cathode electrode technique

4.3.1 Series -3 (Zinc ions)

A) Electric current

In all experiments, sandy loam soil was artificially contaminated with 850 mg/kg of zinc ions. The potential gradient of 1.5 V/cm was chosen in this study, according to **(**Zhang et al., 2021) stated that the current of the soil would be great if the voltage is higher. The migration rate of contamination enhance with the high voltage, nevertheless the consumption of the power would be elevated. Thus, finding appropriate voltage gradient is essential.

To examine the influence of FAs and AAs on the electric current change upon time, the laboratory results of EK-7 are compared with that of EK-1 (Figure 4.12, a). These experiments were carried out at the same operating parameters (i.e. distilled water is utilized in the anode and cathode regions). These experiments were carried out at the same operating parameters (i.e., used distilled water in both the anode and cathode chambers). For EK-1, the electric current in the process varied from 29 to 429 mA within ranged between 1 to 46 hr. At 46 hr., electrical current was at its highest, then decreasing gradually, and finally stabilizing to 95-71 mA. While, For EK-7, the initial value of the current raised from 26 mA to a highest value of 441 mA in about 47 hr. then it lowered to value 426 mA in 49 hr. After 50 hr, it decreased from 268 mA to a low value and remained constant at about 92 mA.

Acetic acid (AA) is biodegradable, and it was used in the concentration of 1 M (pH~3) as the catholyte in EK-2 and EK-8 (Rashid, 2015). The reason for using of acetic acid that it is often adequate to reduce soil pH, as well as being weak and not capable of dissociate. Thus, the incorporation of acetic acid in the soil would not increase the electrical conductivity to higher extent (Saeedi et al., 2013). The electric current can be indicated from the amount of ion electro-migration (Shen et al., 2007). The variation in the electric current for EK-2 and EK-8 experiments as a function of the distances from anode for section S1, S2, S3 and S4: 3.25, 6.5 ,9.75 and 13 cm are depicted in figure 4.12 (b). It can be noticed that in the first hours of the experiment (first 26 for EK-2 and 30 hours for EK-8), the current increase is greater than later during the experiments. As time goes on, the electrical current appears to reach more fixed levels (92 mA and 190

mA for EK-2 and EK-8, respectively). In addition, (Saeedi et al., 2013) cited that some materials like acetic acid when dissociated, the electrical conductivity of the soil could be increased throughout the laboratory experiments. Thus, the improved electrical current of the acetic acid in the soil is positive. The experiment of EK-8, where the two anode electrodes inserted in S2, therefore the distance between anode and cathode was short (9.75 cm from cathode) and the voltage between electrodes applied was equal to 14.625 V, was slightly higher than in the EK-2 and decreased again until it attained its steady state. The results of this part had provided significant agreement with the previous study by (Shen et al., 2007) exhibited electrical current in the CEM-EK (cation exchange membrane (CEM) improved electro-kinetic (EK)) with approaching anode electrodes (AAs) was higher than in the fixed anode electrodes (FA) experiments. These data inferred from the experiments referred that electro-kinetic with approaching anodes (AAs) method can sustain highly mobile ions in the soil. The possible mechanism of improved Cd removal in the AAs laboratory experiments can be partially explained by this phenomenon. Also, (Wan et al., 2019) indicated that the current variation in the approaching anode method (The voltage between electrodes was decreased due to the decrease in the distance between cathode and anode), has similarity with the restorating fixed anode, the value of the current is higher than that in the fixed anode technique.

The electric current variations for EK-3 and EK-9 experiments as a function of the time from anode for section S1, S2, S3 and S4: 3.25, 6.5, 9.75 and 13 cm are depicted in Figure 4.12 (c). In first 48, the electric current during the method of approaching anode (EK-9), which increased

from 78 mA to high value 520 mA, was higher than it's of the fixed anode technique (EK-3), in the next time of the process, the current in the AA method nearing more remarkable to the EK-3.

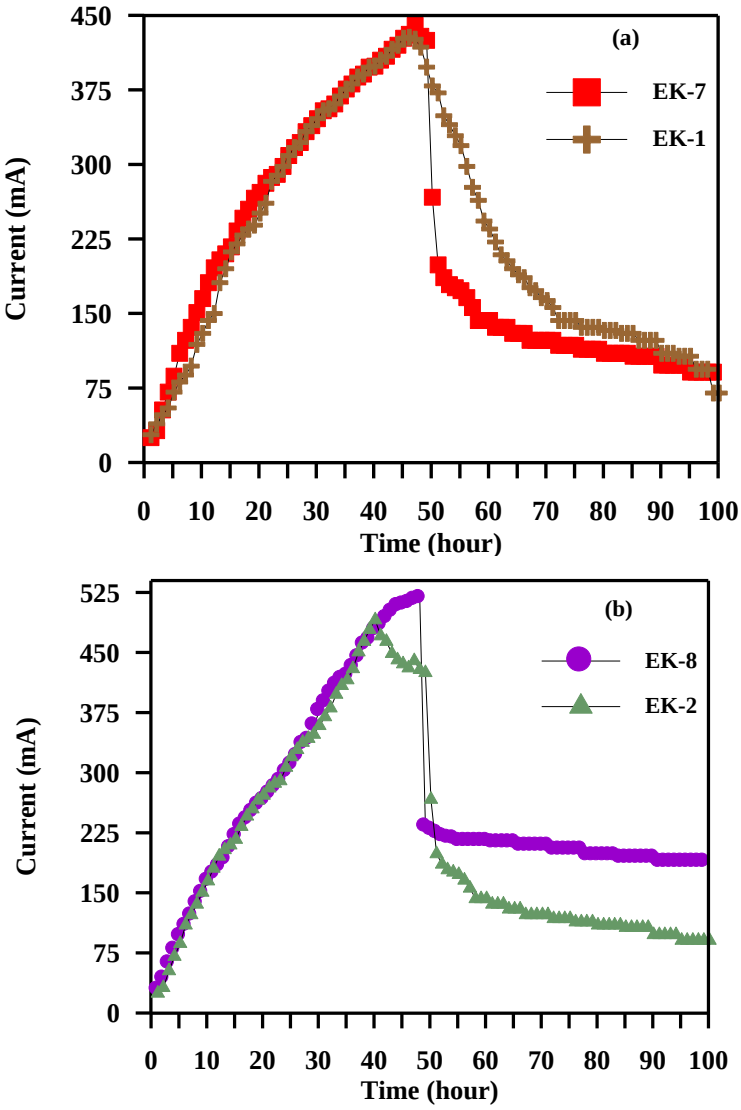
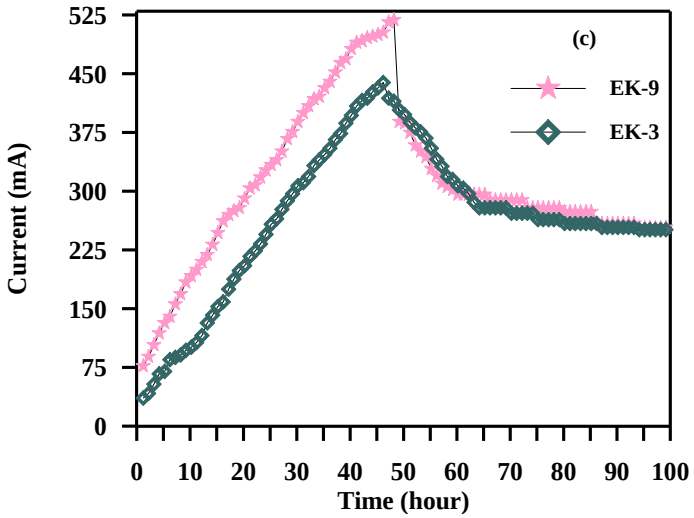


Figure 4.12: Effect of FA and AAs on variation of current of electro-kinetic with time for experiments: (a) EK-1 – EK-7 ;(b) EK-2-EK-8; (c) EK-3 –EK-9.



B) Treated Soil

Figures 4.13 (a, b and c) illustrate the zinc distributions profile and pH of the soil as a function of distance from anode for section S1, S2, S3 and S4: 3.25, 6.5, 9.75 and 13 cm after the electro-kinetic treatment. The acid in the electric field created via water electrolysis in the anode moves to the cathode via electro-osmosis, electro-migration and desorbing pollutants adsorbed on soil. In the soil cell, the desorption and dissolution of species taked place in parallel to the migration of acid front during the remediation process, and the species of the pollutants seemed to be moved slowly to the cathode influencing by the electric field (Rasha, 2013). As shown in Figure 4.12 (a) in which distilled water was utilized as an electrolyte for the anode and cathode chamber, there is no pH control imposed. Therefore, the pH distribution in the EK-1 and EK-7 as follows:

1- It was noticed that the pH for the soil at S1 (close to the anode) for the EK-1 (8.6) was higher than S1 for the EK-7 (8.4).

2- It was calculated that pH of the soil at S4 (close to the cathode) for the EK-1 (11.6) was higher than S4 for the EK-7 (9.33).

The remaining concentration of Zn^{+2} in each sections that were gained for the EK-1 and EK-7 laboratory experiments following treatment is shown in Figures 4.12 (a), in association with Table (4.3). It is clear that the amount of Zn^{+2} remained in the sandy loam soil following the remediation with purging solution being the distilled water as following:

1- The concentration Zn^{+2} remained for treated soil in S4 (close to the cathode) for EK-1, equivalent to 722.5 mg/kg, were more than in EK-7 (629 mg/kg). It was obvious that the initial value of remaining concentrate of Zn^{+2} in S1, S2, S3 and S4 for EK-1 and EK-7 lowered.

2- It can be noticed that the amount of Zinc (II) at sections S1, S2, S3 and S4 for EK-1, as given in Table (4.3), was higher than in that of EK-7. The experiment for EK-7 (i.e., the anode was put in S2; therefore the distance between anode and cathode was short) was obtained more effectively to discard zinc compared to the EK-1, as is a proof from the decrease for zinc (II) that seen for the EK-7 being 30, 28 and 26% for S1, S3 and S4, respectively, higher than those for the EK-1 (31.7, 25.8, 20 and 15 for S1, S2, S3 and S4, respectively). They can be attributed to the short distance between cathode and another which lead to the movement of H+ formed by the anode to the cathode faster. The desorption and dissolution of lead from soil is highly affected by the migration of H+; the faster the migration, the higher the desorption and dissolution and in consequence the discard would be enhanced (Zhang et al., 2021). While the accumulation of zinc (II) occurred close to the cathode. Because of the high pH at the S4, which may be precipitated of the

Zinc (II) by the reaction of hydroxides ions and Zinc (II) close to the cathode. The high buffering capacity (the high-pH environment) of soil is caused due to the presence of carbonate or calcite in the contaminated soil. Therefore, the efficiency of electro kinetic remediation process has decreased due to retain the heavy metal in the precipitated hydroxide/carbonate forms, as cited by (Faisal and Hussein, 2015).

Table 4.3: Reduction of zinc for every part of the treated soil for EK-1 - EK-7 tests.

Section	S1	S2	S3	S4	Average (%)
Reduction for EK-1 (FAs) (%)	31.7	25.8	20	15	23.125
Reduction for EK-7 (AAS) (%)	30	-	28	26	28

Figure 4.13 (b) together with table (4.4) shows the residual concentration of the zinc profiles and profiles of pH at the completion of laboratory experiments of EK-2 (fixed anode, FA) and EK-8 (approaching anode, AAs). When 1 M AA as leaching solution in the cathode chamber with pH adjusted to (~3) was used as modification solution for soil polluted with initial amount of zinc about 850 mg/kg. The removal efficiency of Zn^{+2} in EK-2 experiment decrease towards the cathode as 52.5%, 39%, 39.8 and 36.1 % for S1, S2, S3 and S4, respectively (the residual concentration of zinc as 403.46, 518.56, 511.15 and 543.2 mg/kg for S1, S2, S3 and S4, respectively). Whereas the residual concentration of zinc in section S1, S3 and S4 for EK-8 where the anode inserted in S2, therefore the distance

between anode and cathode was short (9.75 cm from cathode) and the voltage between electrodes applied was equal to 14.625 V; were equal to 250, 330 and 360 mg/kg, respectively. This means that the removal efficiency of Zn^{+2} in EK-8 experiment decrease towards the cathode as 71%, 61.17% and 57.6 % for S1, S3 and S4, respectively. It is obvious that the optimal discard rate of Zn^{+2} appeared at section S1 because in the soil close to the cathode, the pH as given in the same Figure 4.13 (b) was lower which is indicated to be more effective for Zinc ion migration and desorption (Zhang et al., 2021). While the lowest removal rate of Zn^{+2} appeared at S4. This result was the agreement with reported in a previous study (Wan et al., 2019), in which it was proved that the rate of discard of Cd at A1 and B1 type sampling points that are 4 cm away from the anode reached about 65%, while the removal rate of Cd at A3 and B3 type sampling points that are near the cathode was relatively lower. This is due to that H+ was produced in the anode and migrated, and the closer it was to the anode, the lower the soil pH was.

Figure 4.13 (c) shows that the residual concentration of Zn^{+2} in each section S1-S4 with profiles of pH at the completion of electro-kinetic remediation utilizing 1M of Ammonium citrate with pH modified to nearly 9 in the cathode region as purging solution for EK-3 and EK-9. It was notable that the profile pH of the soil for EK-9 (approached anode technique) exhibited the same trend for it is for EK-3 with a slight decrease. For Ek-3, the pH value were 8.4, 9.1, 9.98 and 10.1 for S1, S2, S3 and S4, respectively. While, the pH value for Ek-9 were 8.1, 8.95 and 9.6 for S1, S3 and S4, respectively. The residual concentration of zinc that observed in each section for both EK-3 and EK-9 tests were decreased than an initial

value of zinc 850 mg/kg. Therefore, the removal efficiency that obtained for EK-3 (Fixed anode technique) (26.325%) was relatively low than it is for EK-9 (approached anode technique), as shown in table (4.5). The results of this part had provided significant agreement with the previous study by (Rashid, 2015) showed that Pb^{+2} discard from the soil mainly as anions i.e. both heavy metals (Pb^{+2} and Cr^{+3}) were moved to the two electrodes throughout the experiments due to the complexation with the citric and ammonia part were produced. Also (Ottosen et al., 2005) cited that ammonia citrate can form both anionic and cationic complexes with Cu and Zn, it is seen that both heavy metals were transported towards both electrodes during the experiment. Thus, complexes with ammonia and with the citric part were formed. The highest amount of both heavy metals was removed towards the cathode, i.e., as ammonia complexes $[Zn\ (NH3)_4]^{+2}$. This is due to the constant stability of complex ammonium citrate with zinc (log k=6.1) was higher, as cited by (Mahsa et al., 2011). Therefore, the positive complex ammonium citrate with zinc migrated under electro migrate mechanism toward the cathode region.

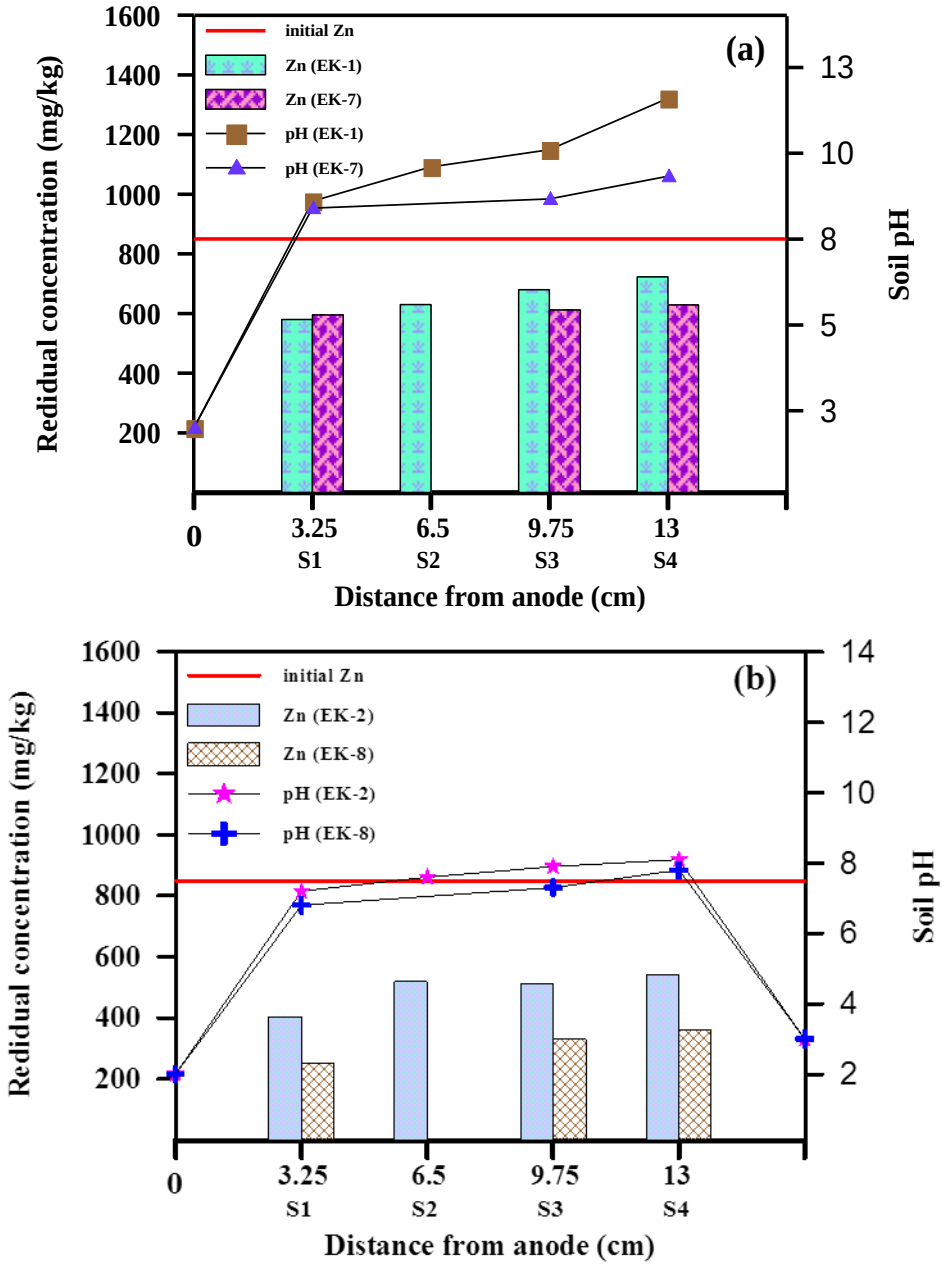


Figure 4.13: Zinc and pH profiles in the treated soil by electro kinetic technique: (a) for Ek-1 and EK-7; (b) for EK-2 and EK-8; and (c) for EK-3 and EK-9.

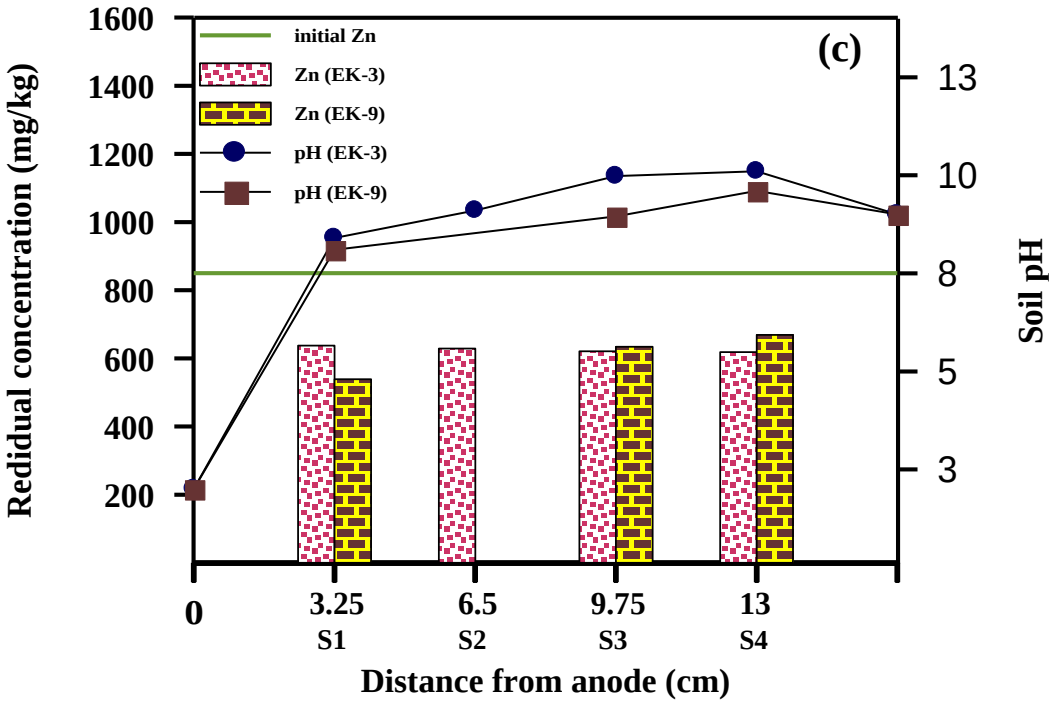


Table 4.4: Removal efficiencies of zinc for every part along soil specimen after electro-kinetic treatment for EK-2 and EK-8.

Section	Removal efficiency (%)	
	EK-2	EK-8
1	52.5	71
2	39	---
3	39.8	61.17
4	36.1	57.6
Average	42	63.3

Table 4.5: Reduction of zinc for every part of the treated soil for EK-3 - EK-9 tests.

Section	S1	S2	S3	S4	Average (%)
Reduction% for EK-3(FAs)	25	26	207	27.3	26.325
Reduction% forEK-9(AAS)	37	-	25.4	21	28

Figures 4.14 (a and b) shows the salts gathered on the cathode surface of the electrode for EK-1 (fixed anode technique) and for EK-7 (approached anode technique). Anyway, the existence of these salts in the soil results in remarkable increase in the buffering capacity. This will be the reason for a delay in the production of acid front phenomena. Thus, a approximately low discard of pollutants can be achieved in this soil (Rasha, 2013).

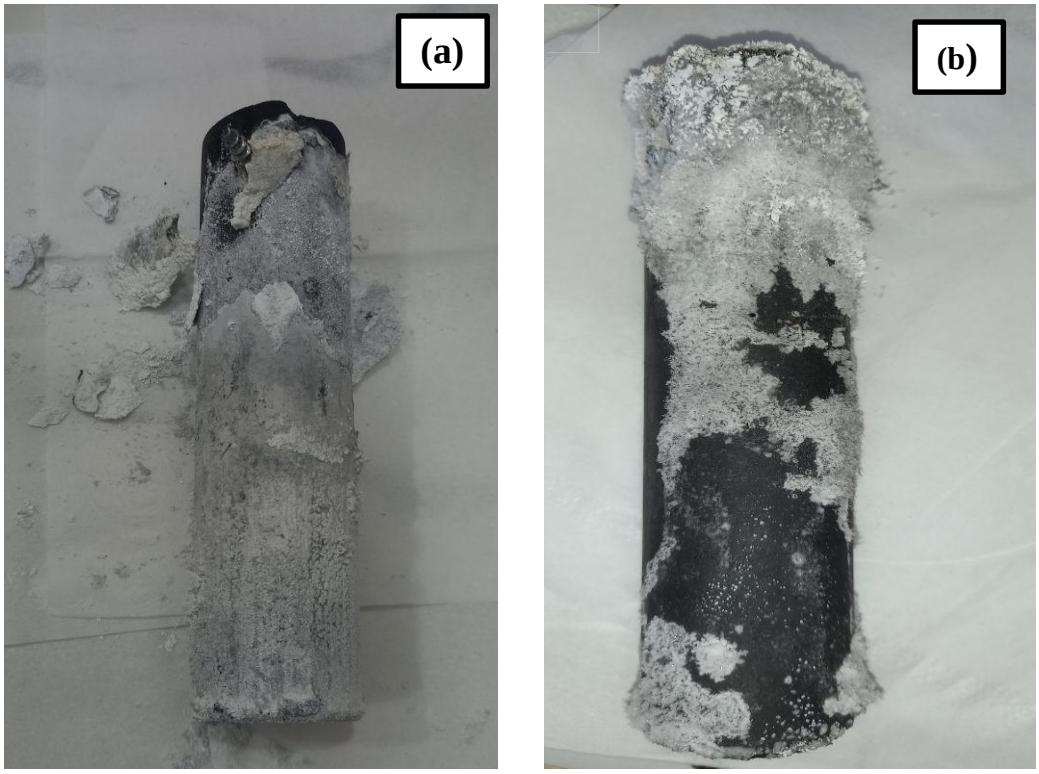
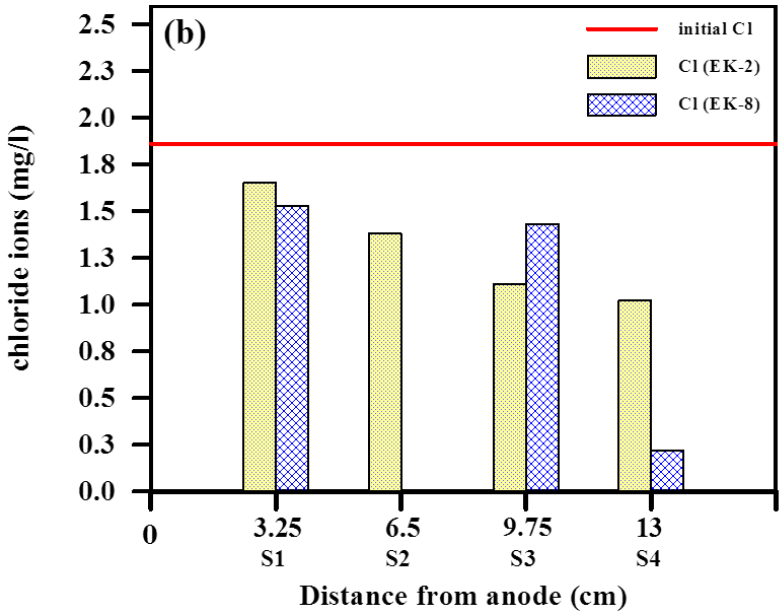
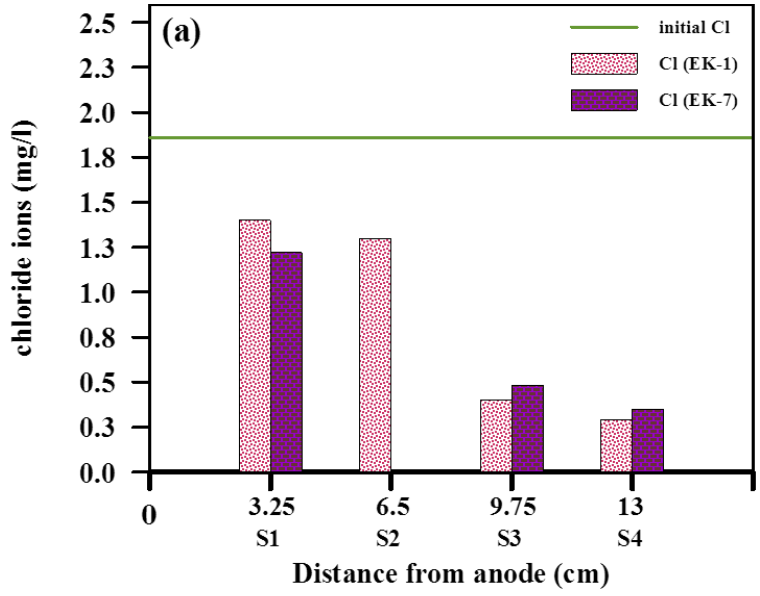


Figure 4.14: Accumulation of salts on the surface of the cathode electrode after the end of electro-kinetic process: (a) in EK-1 test and (b) in EK-7 test.

Species present in the soil pore fluid are transported toward the electrodes in relation to their electric charge. The driving mechanisms for the transport of the species in the soil are the same as those for the acid/base transport. As a result, cations are accumulated at the cathode and anions at the anode (Acar and Alshawabkeh, 1996). This can be observed from Figure 4.15 (a, b and c) show the trend of migrated of chloride ion (Cl^{-1}) (anionic

ion) in each section of the treated soil for EK-1, EK-7, EK-2, EK-8, EK-3 and EK-9 from cathode region toward the anode region. It is noticeable that the concentration of chloride ions in the tests EK-7, EK-8 and EK-9 (experiments with approached anode technique) for section S1 and S4 was lower than it's in the tests EK-1, EK-2 and EK-3 (experiments with fixed anode technique) for the same section.





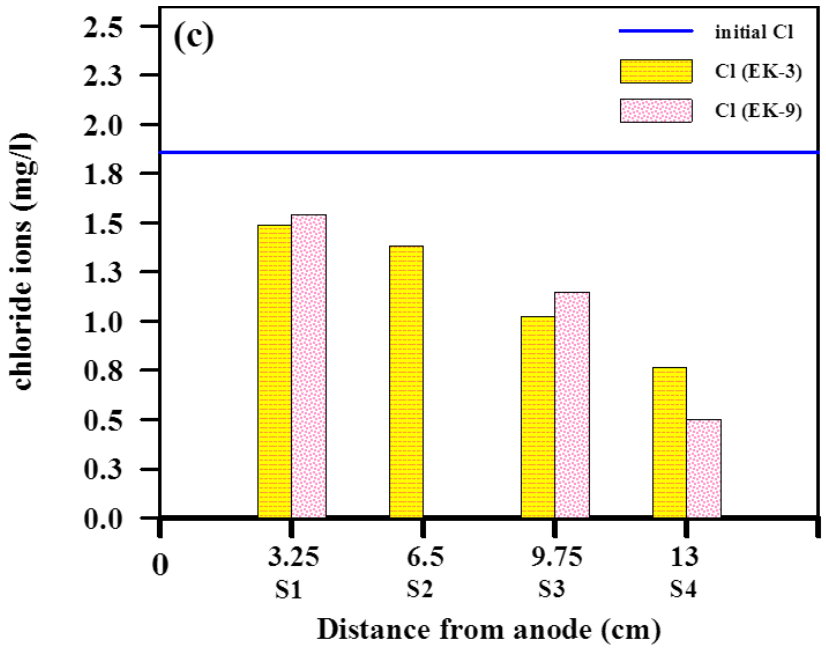


Figure 4.15: Chloride ion profile in the treated soil by electro kinetic technique: (a) for Ek-1 and EK-7, (b) for EK-2 and EK-8, and (c) for EK-3 and EK-9.

4.3.2 Series -4 (Chromium ions)

Approaching anode electro-kinetic treatment (AA-EK) as an improved technique incorporates placing the anode closer to the cathode following the beginning of the EK treatment. The pH close to the anode can be lowered continuously causing compression to the Cr precipitation zone (Li et al., 2012). In series-4, the type of contaminant used for the soil amended was chromium Cr (III) and the initial content of Cr (III) in the polluted soil particles reached to 220 mg/kg. In this series-4, EK-10, EK-11 and EK-12 tests was conducted with the same experimental conditions for EK-7, EK-8 and EK-9 tests, respectively in the series-3, where the two anode electrodes inserted in S2, therefore the distance between anode and cathode was short (9.75 cm from cathode) and the voltage between electrodes applied was equal to 14.625 V. In order to understand the effect of approached anode

technique on migration of chromium in every part of the treated soil (S1, S3 and S4) for EK-10, EK-11 and EK-12 tests and compared with EK-4, EK-5 and EK-6 tests (fixed anode technique),respectively, which corresponds to its operational conditions, as given in Figure 4.16 (a, b and c).

Distilled water was utilized as an electrolyte for the anode and cathode. As given in Figure 4.16 (a), there is no pH control imposed. Therefore, the pH distribution in the EK-4 and EK-10 as follows:

- It was noticed that the pH for the soil at S1 (near the anode) for the EK-4 (8.7) was higher than S1 for the EK-10 (8.3).
- It was determined that the pH for the soil at S4 (near the cathode) for the EK-4 (10.89) was higher than S4 for the EK-10 (9.65).

From the same Figure 4.16 (a) together with Table (4.6), the amount Cr (III) residual for treated soil in S4 (near the cathode) for EK-4, equivalent to 195 mg/kg, were higher than in EK-10 (179 mg/kg), respectively. It was clear that the remaining concentrate of Cr (III) in S1, S2, S3 and S4 for EK-4 and EK-10 decrease from an initial value of 220 mg/kg. It was noticeable that the trend of the migration of chromium toward the cathode region, where the concentration of chromium was decreased in section S1 (145.9 and 153 for EK-4 and EK-10, respectively) and increased in the other sections at the end of the treatment time. Li et al. (2012) indicated that the meeting of acid front with the base front during the EK treatment method resulting in a focusing influence on the heavy metal in the soil. The low pH of the soil (about 4) in part I is preferred to dissociate Cr (III) from the soil. Then, Cr(III) in the soil in part I moves towards part II due to the electric field while the Cr(III) that have been remained in the soil as precipitation

because of the high pH of the soil (approximately 7) in section II for Cr(III) begins in precipitation as $Cr(OH)_3$ at pH more than 5.5.

Throughout the EK treatment, the precipitation of Cr is influenced by soil pH .Figure 4.16 (b) gives the pollutants and the pH profile in the soil sample following electro-kinetic process. In the EK-5 tests (fixed anode technique) and EK-11 (approached anode technique), the pH was about 2 in the anode compartment and ~3 in the cathode compartment, while the pH was below the initial value of 8.5 along each section for soil specimen. It was clear, that the trend of soil pH for EK-5 and EK-11 was similar. (Gang Li et al., 2012) Showed that in the fixed electrodes processes and after 3 days, pH variations in the soil for tests C and D (AA–EK) were the same. Nevertheless, as the electrode was moved toward the cathode, the pH in the region close to the cathode especially in section V raised gradually while in section II, III and IV lowered in evidently. But the soil pH for EK-5 (fixed anode technique**)** in each section for treated soil was higher than its for EK-11 (approached anode technique). The results of this part had provided significant agreement with the previous study by (Cai et al., 2015) indicated that the pH of the soil bed decreased obviously more with AAs rather than FA. This is attributed to the existence of higher H+ ions created from the anode increased the Cr(III) desorption from the soil (Wei et al., 2016) Figure 4.16 (b) shows the residual concentration of the chromium profiles at the completion of experiments EK-5 (fixed anode, FA) and EK-11 (approaching anode, AAs). When 1 M AA as leaching solution in the cathode chamber with pH adjusted to (~3) was utilized as improvement solution for soil polluted with initial chromium amount which is 220 mg/kg. The removal efficiency of Cr (III) in EK-5 experiment decrease towards the cathode as

42.8%, 41.4%, 36.8 and 33 % for S1, S2, S3 and S3, respectively (the residual concentration of chromium as 125.7, 129, 138.9 and 143 mg/kg for S1, S2, S3 and S4, respectively). Whereas the residual concentration of chromium in section S1, S3 and S4 for EK-11 where the anode inserted in S2, therefore the distance between anode and cathode was short (9.75 cm from cathode) and the voltage between electrodes applied was equal to 14.625 V; were equal to 101, 126, and 127.7 mg/kg, respectively. This means that the removal efficiency of Cr (III) in EK-11 experiment decrease towards the cathode as 54.1, 42.7 and 41.9 % for S1, S3 and S4, respectively. This point could explained according to cited by Xue et al. (2017) that the lowering removal rate of total Cr is due to the precipitation of $Cr(OH)_3$ during the migration of Cr(III) towards the cathode. Finally, it was noticed that the trend of chromium migration from anode region toward the cathode region. The results of this part had provided significant agreement with the previous study by (Li et al., 2012) showed the total amount of chromium in the experiment using AAs-EK remarkably reduced, nevertheless was more. The other section, was high concentration of chromium caused by the short treatment time, which is only 3 days. Chromium in particular Cr (III) desorbed from the soil and moved into the cathode under the electric field due to the acidic environment of the soil, which produced close to the approaching anode under throughout the EK treatment. Thus, in section IV, the amount of chromium is highest. In compared with FA EK treatment, the highest of the total chromium in the soil migrated to the cathode as well as lowered remarkably. In consequence, there is improvement in the efficiency of total chromium removal.

Figure 4.16 (c) shows that the remaining content of Cr (III) in each section S1-S4 with pH at the completion of the electro-kinetic remediation with the purging solution used is 1 M of Ammonium citrate with pH modified to (~9) in the cathode region for EK-6 and EK-12. It was notable that the profile pH of the soil for EK-12 (approached anode technique) exhibited the same trend for its for EK-6 with a slight decrease. For Ek-6, the pH value were 8.7, 9.1, 9.54 and 10.3 and 10.6 for S1, S2, S3 and S4, respectively. While, the pH value for Ek-12 were 8.6, 9.4 and 9.65 for S1, S3 and S4, respectively. The residual concentration of chromium that observed in each section for both EK-6 and EK-12 tests were decreased than an initial value of chromium 220 mg/kg. Therefore, the removal efficiency that obtained for EK-6 (Fixed anode technique) (29%) was relatively low than it is for EK-12 (approached anode technique) (44%), as shown in Table (4.7). The results of this part had provided significant agreement with the previous study by (Rashid, 2015) showed that Pb^{+2} discarded from the soil principally as anions i.e. both heavy metals (Pb^{+2} and Cr^{+3}) were moved to electrodes throughout the experiments due to the complexation with ammonia and the citric part were produced. (Wei et al., 2016) cited that there is correlation between the alteration in the remaining total Cr and the distribution of pH in the soil. In area with low pH (less than 4.6), the remaining total Cr is low while it is high in region with high pH. Cr (III) moves to the cathode and gathered near the cathode where the pH is more than 5.5. This takes place since the low pH environment close to the anode raise the Cr(III) solubility hence the migration of Cr to the cathode where the pH is high increases resulting in precipitation of Cr(III) with no further migration.

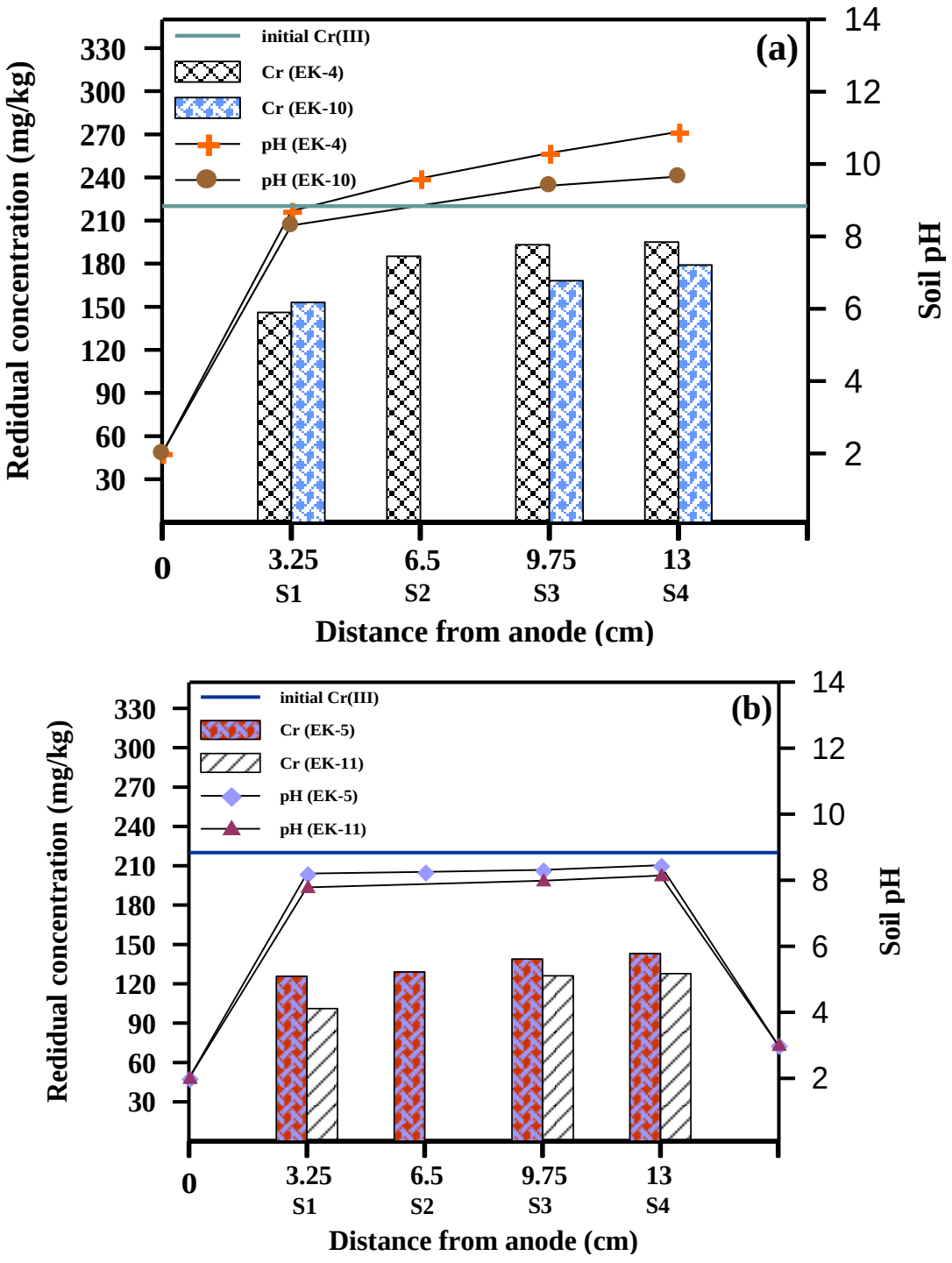


Figure 4.16: Chromium and pH profiles in the treated soil by electro kinetic technique: (a) for Ek-4 and EK-10; (b) for EK-5 and EK-11; and (c) for EK-6 and EK-12.

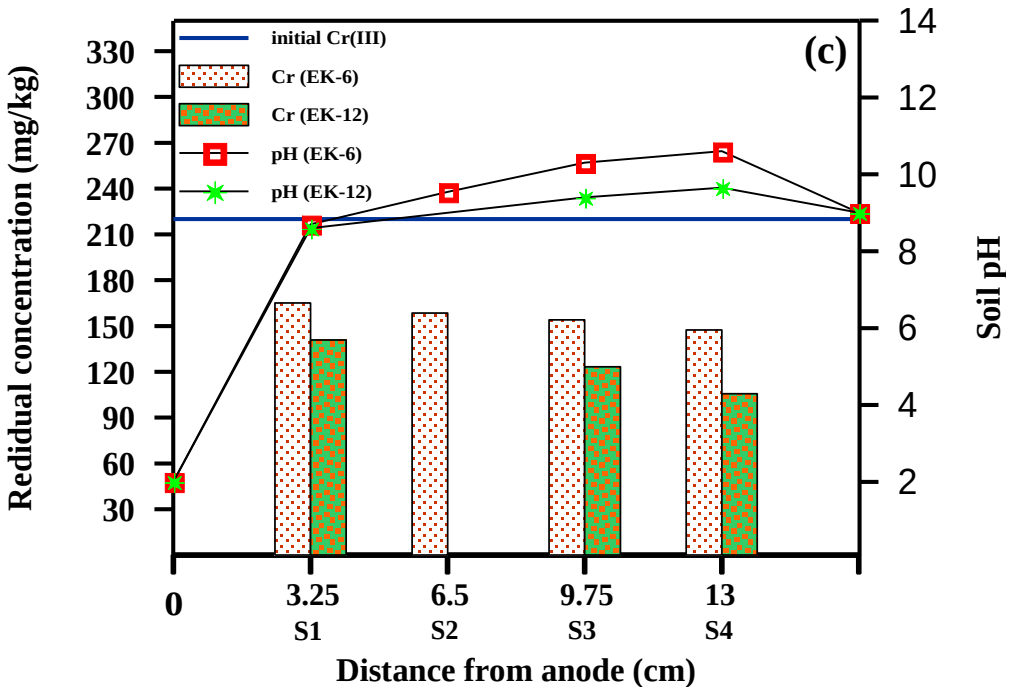


Table 4.6: Reduction of chromium for every part of the treated soil for EK-4 - EK-10 tests.

Section	S1	S2	S3	S4	Average (%)
Reduction for EK-4 (FAs) (%)	33.6	15.9	12.3	11.36	18.29
Reduction for EK-10 (AAS) (%)	30	-	24	19	24.33

Table 4.7: Reduction of chromium for every part of the treated soil for EK-6 – EK-12 tests.

Section	S1	S2	S3	S4	Average (%)
Reduction for EK-6 (FAs) (%)	25	28	30	33	29
Reduction for EK-12 (AAS) (%)	36	-	44	52	44

Figures 4.17 (a, b and c) shows the salts accumulated on the surface of the cathode electrode for EK-10, EK-11 and EK-12.

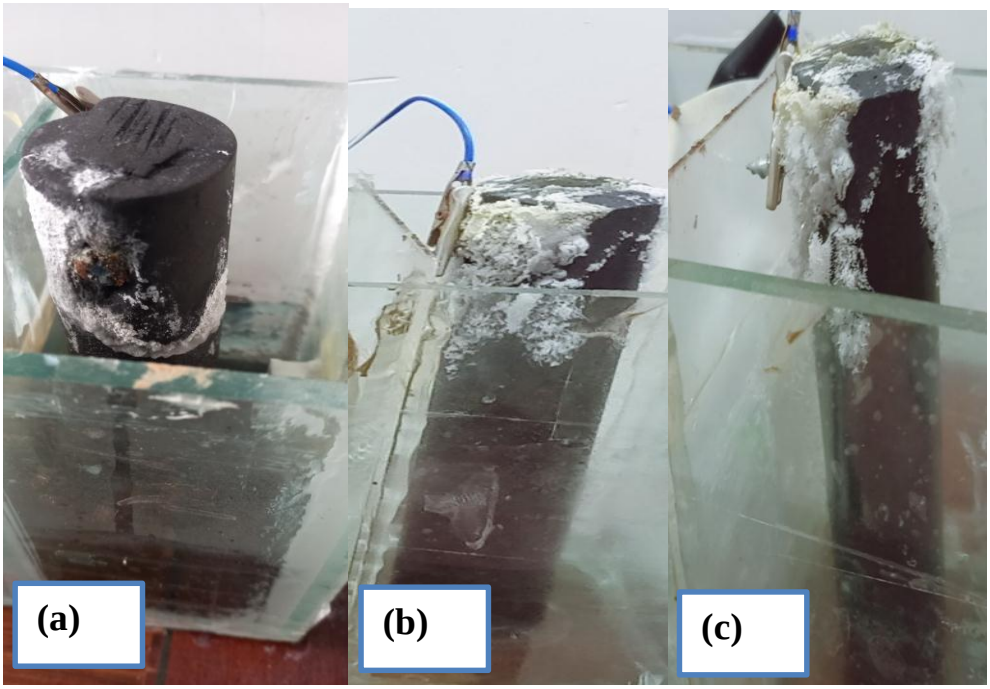


Figure 4.17: Accumulation of salts on the surface of the cathode electrode after the end of electro-kinetic process: (a) in EK-10 test, (b) in EK-11 test and (c) in EK-12 test.

In this study, the major mechanism that responsible for transport of cationic or anionic ions is electro migration. This can be observed from Figure 4.18 (a and b) indicates the migration of chloride ion (Cl^{-1}) (anionic ion) in every part of the treated soil for EK-5, EK-11, EK-6, EK-12 from cathode region toward the anode region.

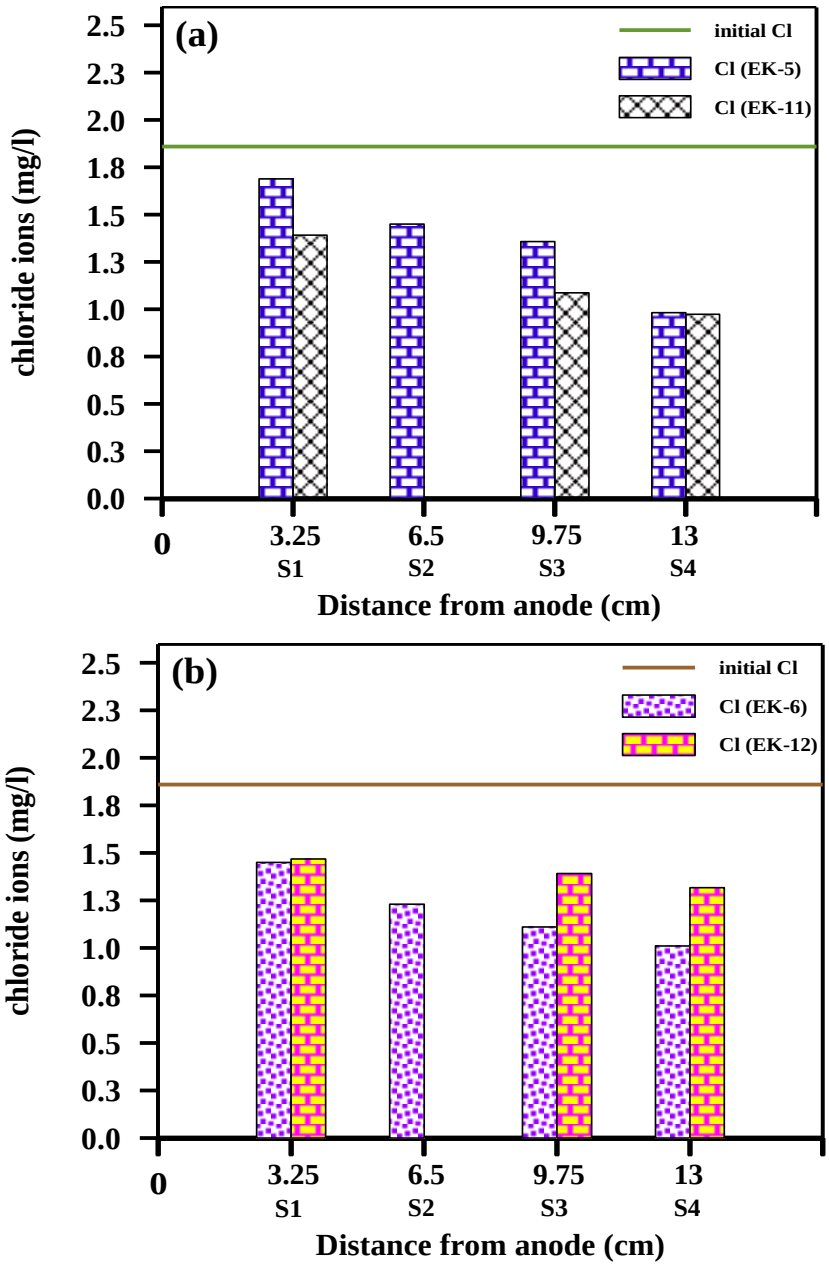


Figure 4.18: Chloride ion profile in the treated soil by electro kinetic technique: (a) for EK-5 and EK-11 and (b) for EK-6 and EK-12.

4.3.3 Series -5 (Zinc and chromium ions)

According to describe by (Ng et al., 2016) the approaching electrode technique involves sequential switching of either anode (approaching anode) or cathode (approaching cathode) close to the other fixed electrode during electrokinetic process. However, it is noted that the investigation of approaching electrode assisted electrokinetic process in treating co-contaminated soil is scarce, especially for the metals that have opposite charge. This is important, as eletromigration would concentrate both metal cations and anions in cathode and anode regions, respectively, which fails the purpose of contaminated soil volume reduction. Thus, an investigation on the feasibility of approaching electrode technique in electrokinetic process in treating co-contaminated soil is necessary. In EK-13 (approached cathode technique, ACs) was carried out to remove zinc ions from the contaminated soil (initial concentration of zinc was equal to 850 mg/kg) by using 1 M AC as catholyte solution with maintain pH (~ 9) at the cathode compartment. In this test the cathode electrode was switched to the S3 section after 50 hr. of start the experiment, therefore the distance between anode and cathode was short (9.75 cm from anode) and the voltage between electrodes applied was equal to 14.625 V.

In order to investigate the effect of FA, AAs and ACs on the electric current variation with time, the experimental results of EK-13 are compared with results of EK-3 and EK-9 (Figure 4.19). These experiments were carried out at the same operating parameters (i.e., used distilled water in the anode and 1 M AC in the cathode chambers). For EK-3, the electric current in the process varied from 37 to 440 mA within ranged between 1 to 46 hr. At 46 hr., electrical current was at its highest, then decreasing gradually, and

finally stabilizing and remaining almost constant at 252 mA. While, For EK-13, the current increased from an initial value of 33 mA to a peak value of 560 mA in approximately 48 hr., then it started decreasing to value 50 mA in 100 hr. It was clear from the same figure the current for EK-13 (ACs) within time ranged from 1 to 48 hr., was higher than it's for EK-3 (FA). (Shen et al., 2009) showed that the electric current in AC-EK is higher than in SC-EK (single cathode). It lied in that ACs (approaching cathodes) method shortened the electrolysis distance, i.e., ion transportation distances. So, more ions that are mobile were maintained in the electric cell. This partly explained the possible mechanism of enhanced Hg removal in the AC-EK tests.

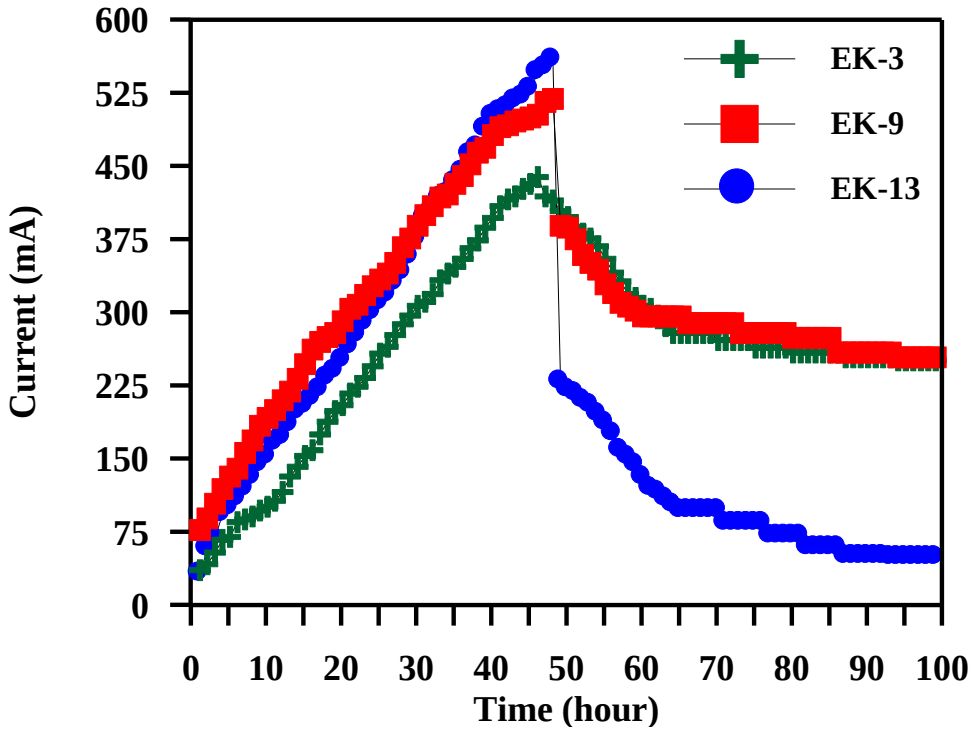


Figure 4.19: Effect of FA, AAs and ACs on variation of current of electro-kinetic with time for experiments (EK-3, EK-9 and EK-13).

Table (4.8) shows the electrical conductivity (EC) for EK-3, EK-9 and EK-13. EC for EK-3 at S1, S2, S3 and S4 was equal to 4.2, 1.44, 0.32 and 5.2 ms/cm, respectively. In this test, the EC at S4 was higher than it is at S1. Jayasekera and Hall (2005) observed that the electrical conductivity of soil is high at the anode and cathode. In general, across the tank, the EC values are gradually reducing from anode towards cathode with cathode end being the lowest electrically conductive zone. The high EC values recorded around the anode and cathode are due to the generation of H^+ ions and OH^- ions in these regions. Accumulation of cations (predominantly Na^+ and Ca^{2+} ions) in the cathode area would also have contributed to higher EC values in this zone. The electromigration of both the hydrogen ions and calcium ions produced at the anode that have reached the middle of the tank are contributing to the high EC valued in the middle of the tank. These ions are also susceptible to migrate from anode towards cathode and interact with clay minerals. Hence, these ions could also contribute to the electrical conductivity of the soil at different regions. While the EC in EK-9 (AAS) and EK-13 (ACs) at S1 (region near the anode) was higher than it's in S4 and S3, which are represented the region near the cathode for EK-9 and EK-13, respectively.(Shen et al., 2009) showed that the electrical conductivity near anode increased gradually and that near cathode decreased simultaneously during the remediation process in both series of tests (AC-EK and SC-EK). It is mainly due to that most anions in soils moved toward the anode and accumulated there.

Table 4.8: The electrical conductivity for each section of the treated soil for EK- 3, EK-9 and EK-13 tests.

Tests	Electrical conductivity (EC), ms/cm			
	S1	S2	S3	S4
EK-3	4.2	6.02	0.32	5.2
EK-9	4.6	-	0.34	0.354
EK-13	3.9	1.44	0.22	-

Figure (4.20) with together Table (4.9) show the residual concentration of Zn (II) after the end time of the treatment process for EK-3, EK-9 and EK-13. The concentration of Zn (II) for EK-13 (ACs) in S1, S2 and S3 was equal to 685.1, 508 and 362.9 mg/kg, respectively, and for EK-3 (FAs) at S1, S2, S3 and S4 was 637.5, 629, 620.5 and 618 mg/kg, respectively. Whereas the residual concentration of Zn (II) for EK-9 (AAs) at S1, S3 and S4 was 538.6, 633.8 and 668.7 mg/kg. It was clear that the trend of migration of Zn (II) (when used 1 M AC as catholyte solution) for EK-3 and EK-13 towards the anode region, but in EK-9 (AAs) it's opposite (i.e., the amount of zinc reduced at anode region and concentrated at the cathode region). It seen from Table (4.9) the average removal efficiency of Zn (II) from the contaminated soil in EK-13 (39%) was higher than it has in EK-3 (26.325%) and EK-9 (28%) when used 1 M AC as catholyte solution. These results were in a good agreement with previously study. Shen et al., (2009) showed that the removal efficiency of Hg from Paddy Soil I and Paddy Soil II after 5 days of SC-EK treatment (EK method with one single cathode), were 82 and 53%, respectively. Simultaneously, after 5 days of AC-EK (EK method with approaching cathodes) treatment, 92 and 89% of Hg were removed. Removal ratio reached 1.21 and 1.68 times, as high as those after SC-EK process. It has been demonstrated that more than half of the removed

Hg was transported to the anode compartment. As for a contaminated field soil, some 50% of the total mercury content had migrated to the anode compartment, and another 25% was recovered from the soil water near the anode. Whereas Ng et al. (2016) showed that 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.

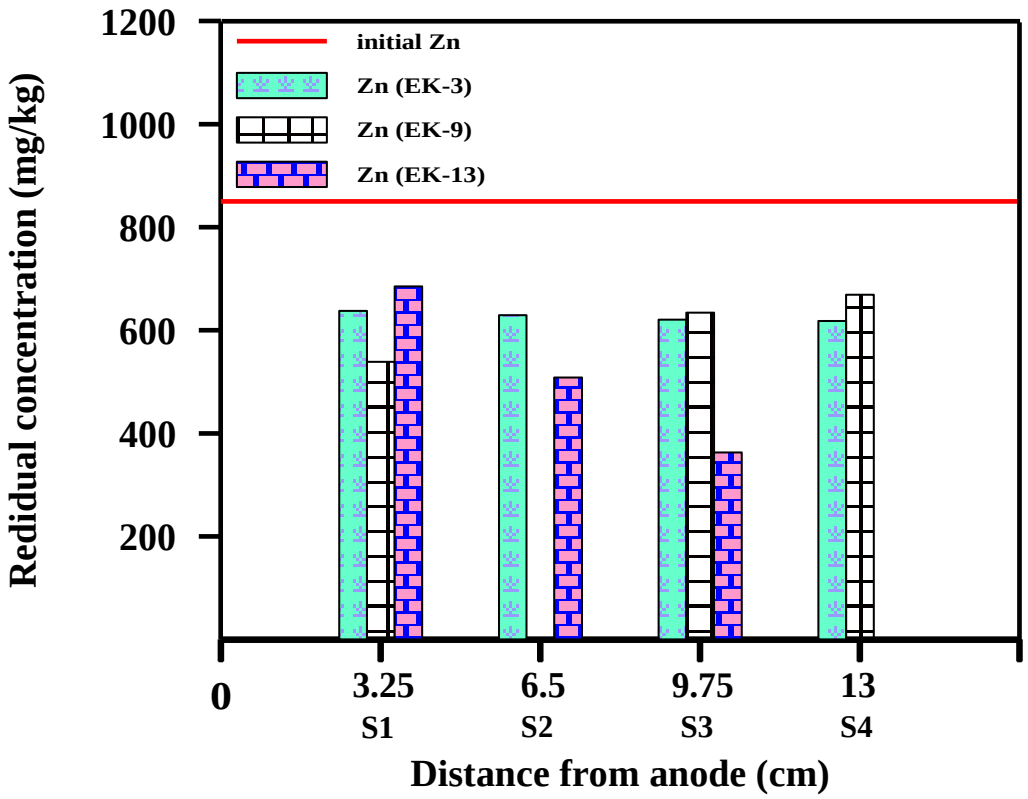


Figure 4.20: Zinc profiles in the treated soil by electro kinetic technique for EK-3, EK-9 and EK-13.

Table 4.9: Reduction of zinc for each section of the treated soil for EK-3, EK-9 and EK-13 tests.

Section	S1	S2	S3	S4	Average (%)
Reduction for EK-3 (FAs) (%)	25	26	27	27.3	26.325
Reduction for EK-9 (AAs) (%)	37	-	25.4	21.3	28
Reduction for EK-13 (ACs) (%)	19.4	40.23	57.31	-	39

In EK-14 (approached cathode technique, ACs) was carried out to remove chromium ions from the contaminated soil (initial concentration of chromium was equal to 220 mg/kg) by using 1 M AC as catholyte solution with maintain pH (~ 9) at the cathode compartment. In this test the cathode electrode was switched to the S3 section after 50 hr. of start the experiment, therefore the distance between anode and cathode was short (9.75 cm from anode) and the voltage between electrodes applied was equal to 14.625 V. Figure (4.21) shows the profile of electric current during the tests (EK-6, EK-12 and EK-14). For EK-6 (FAs), the electric current in the process varied from 26 to 642 mA within ranged between 1 to 57 hr. At 57 hr., electrical current was at its highest, then decreasing gradually, and finally stabilizing and remaining almost constant at 163 mA. While, For EK-12 (AAs), the current increased from an initial value of 78 mA to a peak value of 520 mA in approximately 48 hr., then it started decreasing to value 255 mA in 100 hr. For EK-14 (ACs), the current increased from an initial value of 56 mA to a peak value of 505 mA in approximately 48 hr., and then it started decreasing to value 150 mA in 100 hr.

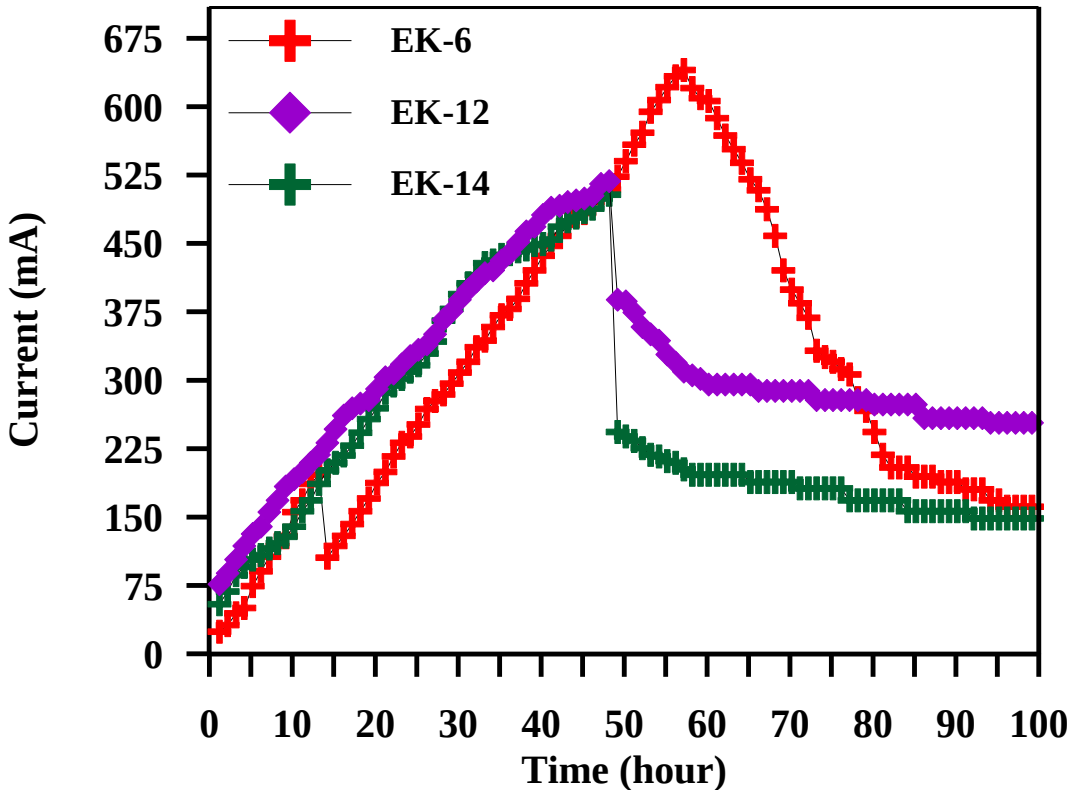


Figure 4.21: Effect of FAs, AAs and ACs on variation of current of electro-kinetic with time for experiments (EK-6, EK-12 and EK-14).

Figure (4.22) with together Table (4.10) show the residual concentration of Cr (III) after the end time of the treatment process for EK-6, EK-12 and EK-14. The concentration of Cr (III) for EK-14 (ACs) in S1, S2 and S3 was equal to 147, 78.6 and 124.5 mg/kg, respectively, and for EK-6 (FAs) at S1, S2, S3 and S4 was 165, 158.4, 154 and 147.4 mg/kg, respectively. Whereas the residual concentration of Cr (III) for EK-12 (AAs) at S1, S3 and S4 was 140.8, 123.2 and 105.6 mg/kg. It was clear that the trend of migration of Cr (III) (when used 1 M AC as catholyte solution) for EK-6 and EK-12 towards the anode region. Whereas in EK-14 test, the amount residual of Cr (III) in S1 (near the anode region) and S3 (near the cathode region) (147 and 124.5 mg/kg, respectively) were higher than it's in the S2 (middle section) (78.6

mg/kg), i.e., the amount of Cr (III) was concentrated in the both anode and cathode regions.

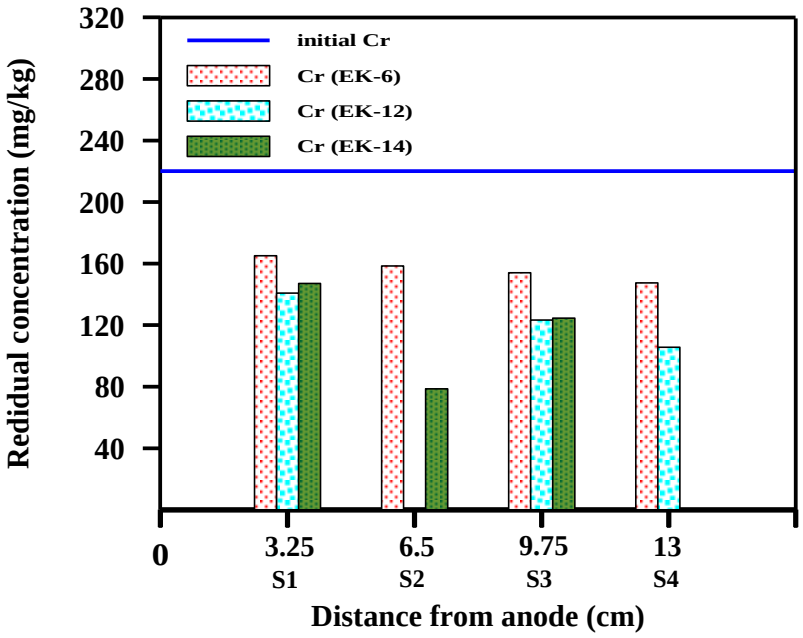


Figure 4.22: Chromium profiles in the treated soil by electro kinetic technique for EK-6, EK-12 and EK-14.

Table 4.10: Reduction of chromium for each section of the treated soil for EK-6, EK-12 and EK-14 tests.

Section	S1	S2	S3	S4	Average (%)
Reduction for EK-6 (FAs) (%)	25	28	30	33	29
Reduction for EK-12 (AAs) (%)	36	-	44	52	44
Reduction for EK-14 (ACs) (%)	33.46	64.3	43.4	-	47

The removal efficiency for each experiment was shown in the Table 4.11

Table 4.11: The removal efficiency for experiments

Series-	Name Of Experiment	Initial Conc. (mg/kg)	**PS (pH)**		**Removal efficiency%**
			Anodes	Cathodes	
1-(FAs)/(Zn)	EK-1	850	DW	DW	23.16
	EK-2	850	DW	1 M AA (~3)	42.71
	EK-3	850	DW	1M AC (~9)	26.3
2-(FAs)/(Cr)	EK-4	220	DW	DW	18.3
	EK-5	220	DW	1 M AA (~3)	39.02
	EK-6	220	DW	1M AC (~9)	29
3-(AAs)/(Zn)	EK-7	850	DW	DW	28
	EK-8	850	DW	1M AA (~3)	63.103
	EK-9	850	DW	1M AC (~9)	27.79
4-(AAs)/(Cr)	EK-10	220	DW	DW	24.23
	EK-11	220	DW	1 M AA (~3)	46.25
	Ek-12	220	DW	1M AC (~9)	44
5-(ACs)/(Zn)	EK-13	850	DW	1M AC (~9)	38.97
(ACs)/(Cr)	EK-14	220	DW	1M AC (~9)	46.95

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- **The primary conclusions are as follows:**

1. In the experiments of EK-1 (Zn+Dw+FAs) and EK-7 (Zn+Dw +AAs) when distilled water was used in the anode and cathode chamber, the average removal efficiency for EK-1was low to about 23.16% while in EK-7 its increased to reach 28%.
2. The average removal efficiency of Zinc in EK-2 (Zn+AA+FAs) was 42%, and in EK-8 (Zn+AA+AAs) was increased to 63.103%, when 1 M acetic acid was used in the cathode chamber and its pH was regulated at approximately three.
3. The average Zinc removal efficiency in EK-3(Zn+AC+FAs) was 26.3% and in EK-9 (Zn+AC+AAs) was rise to 27.79% under using 1M ammonium citrate purging solution in the cathode chamber. In this case, zinc (II) has been removed into the anode chamber direction, which is opposite to the normal direction of metal in unenhanced experiments. While in experiment EK-13(Zn+Ac+ACs) of approaching cathode when used ammonium citrate as purging solution the average removal efficiency was 38.975% and they rang of Pollutants are concentrated at the anode.
4. The chromium was considerably increased in removal from contaminated soil when distilled water was used in the anode and cathode chamber with moving Anode. In this case, removal efficiency in EK-4 (Cr+Dw+FAs) was 18.4%while in EK-10 (Cr+Dw+AAs) it raise to 24.23%.

5. The average removal efficiency of Cr^{+3} according to EK-5 was less than that of EK-11 (Cr+AA+FAs) was 39.02% and 46.25%, respectively, under using 1M acetic acid as purging solution in the cathode chamber.
6. In the experiments of EK-6 (Cr+FAs+AC) and EK-12(CR+AC+AAs) when ammonium citrate was used in the anode and cathode chamber, the average removal efficiency for EK-6 was low to about 29% while in EK-12 was more increase to reach 44%.It noticed the direction of chromium concentration from anode to cathode .While in experiment EK-14 of approaching cathode when used ammonium citrate as purging solution the average removal efficiency was 46.95% and they rang of Pollutants are concentrated at the anode.
7. The approaching anode method had greater Zinc and Chromium removal efficiency than the fixed anode method, which was carried out under identical purging solution circumstances. This might be as a result of the AAs technique keeping more mobile ions in the system. That indicates that the electrokinetic processes will advance as a result of the approach to anode method.
8. The AAs-EK procedures not only increased the removal efficiencies of Cr (III) and Zn^{+2} but also cut down on overall working time, saving energy. A portion of the soil over which the anode moved stopped consuming electricity as the distance between the anode and cathode shrank, resulting in a reduction in voltage between the two. As a result, the approaching anode method's energy usage was decreased during the entire repair procedures.

5.2 Recommendations

1. Future research may be directed towards the treatment of field-contaminated soil.
2. Development of a numerical model for describing the electro-kinetic remediation process as taken into account the effect of enhanced condition.
3. Studying the effect of other factors such as the concentration of purging solutions, soil type, depth variation, temperature, water content, spacing of the electrodes, voltage intensity and many optimizations need to be further investigated.

References

- Acar, Y.B., Alshawabkeh, A.N., (1993). "Principles of electro-kinetic remediation". Environ. Sci. Technol., 27, 2638-2647.
- Acar, Y. B., Gale, R. J., Alshawabkeh, A. N., Marks, R. E., Puppala, S., Bricka, M., & Parker, R. (1995)." Electrokinetic remediation: basics and technology status". Journal of hazardous materials, 40(2), 117-137.
- Acar Y.B. and Alshawabkeh A.N., (1996). "Electro-kinetic remediation I: pilot-scale tests with lead-spiked kaolinite". Journal of Geotechnical Engineering, 122, 173-185.
- Ahmad, K. A. K., Kassim, K. A. K. K. A., & TahaÂ, M. R. T. M. R. (2006)."Electroosmotic flows and electromigrations during electrokinetic processing of tropical residual soil". Malaysian Journal of Civil Engineering, 18(2).
- Al-Rifaie, J. K., Heil, S. M., Khamees, S. K., Alajmi, S., Yeboah, D., Abdellatif, M., & AlKayyat, A. (2021). "Assessment of the effects of municipal landfills on the metal pollution in the surrounding soils: A case study in Iraq". In IOP Conference Series: Materials Science and Engineering (Vol. 1058, No. 1, p. 012008). IOP Publishing.
- Al-Rubaiee, A. K. H., & Al-Owaidi, M. R. (2022). "Assessment of Heavy Metal Contamination in Urban Soils of selected areas in Hilla City, Babylon, Iraq". Iraqi Journal of Science, 1627-1641.
- Aprile, F., & Lorandi, R. (2012). "Evaluation of cation exchange capacity (CEC) in tropical soils using four different analytical methods". Journal of Agricultural Science, 4(6), 278.
- Asavadorndeja, P., & Glawe, U. (2005). "Electrokinetic strengthening of soft clay using the anode depolarization method". Bulletin of engineering geology and the environment, 64(3), 237-245.
- Bakshi, S., Banik, C., & He, Z. (2018). "The impact of heavy metal contamination on soil health". Managing soil health for sustainable agriculture.

- Buchireddy P.R., Bricka R.M., Gent, D.B.,(2009)."Electro-kinetic remediation of wood preservative contaminated soil containing copper, chromium, and arsenic". Journal of Hazardous Materials, 162, 490-497.
- Cai, G. H., Du, Y. J., Liu, S. Y., & Singh, D. N. (2015)."Physical properties, electrical resistivity, and strength characteristics of carbonated silty soil admixed with reactive magnesia". Canadian Geotechnical Journal, 52(11), 1699-1713.
- Dixit R., Malaviya D., Pandiyan K., Singh U. B., Sahu A., Shukla R., ... and Paul D, (2015). "Bioremediation of heavy metals from soil and aquatic environment: an overview of principles and criteria of fundamental processes". Sustainability, 7(2), 2189-2212.
- Ediene, V. F., & Umoetok, S. B. A. (2017). "Concentration of heavy metals in soils at the municipal dumpsite in Calabar metropolis". Asian J Environ Ecol, 3(2), 1-11.
- Faisal, A. A. A. H., & Rashid, I. T. (2015)."Enhancement Solution to Improve Remediation of Soil Contaminated with Lead by Electrical Field". Journal of Engineering, 21(11), 111-129.
- Faisal, A. A., & Hussein, A. A. (2015). "An acidic injection well technique for enhancement of the removal of copper from contaminated soil by electrokinetic remediation process". Separation Science and Technology, 50(16), 2578-2586.
- Fansheng Meng, Xue, H., Wang, Y., Zheng, B., & Wang, J. (2018). "Citric-acid preacidification enhanced electrokinetic remediation for removal of chromium from chromium-residue-contaminated soil". Environmental Technology, 39(3), 356-362.
- Ferrarese, E., (2008). "Electrochemical oxidation of soils contaminated with organic pollutants". Ph.D., Thesis, University of Trento, College of Engineering.
- Haswell, S. J. (1991). Atomic absorption spectrometry.
- Hahladakis, J. N., Latsos, A., & Gidarakos, E. (2016). "Performance of electroremediation in real contaminated sediments using a big cell, periodic voltage and innovative surfactants". Journal of hazardous materials, 320, 376-385.

- Hananingtyas, I., Nuryanty, C. D., Karlinasari, L., Alikodra, H. S., Jayanegara, A., & Sumantri, A. (2022). "The effects of heavy metal exposure in agriculture soil on chlorophyll content of agriculture crops: A meta-analysis approach". In IOP Conference Series: Earth and Environmental Science (Vol. 951, No. 1, p. 012044). IOP Publishing.
- Hassan I., Mohamedelhassanb E. and Yanfula E.K., (2015). "Solar powered electrokinetic remediation of Cu polluted soil using a novel anode Configuration". Electrochimica Acta, Volume 181, Pages 58-67.
- Heister, K., Kleingeld, P. J., Keijzer, T. J., & Loch, J. G. (2005)." A new laboratory set-up for measurements of electrical, hydraulic, and osmotic fluxes in clays". Engineering Geology, 77(3-4), 295-303.
- Hussein A.A., (2012). "Copper removal from the contaminated soils using adsorption and electro-kinetic remediation". M.Sc., Thesis, Baghdad University, College of Engineering.
- Hussein A.A., (2018). "Use of Clean Energy to Remediate Contaminated Soil". Journal of Engineering and Sustainable Development, Issn: 25200917 Volume: 22 Issue: 1 Pages: 12-24.
- Hussein A. A., (2019)." Adsorption of Lead Ions from Aqueous Solution by using Sunflower Husks". International Research Journal of Innovations in Engineering and Technology, 3(8), 7-11.
- Iannelli, R., Masi, M., Ceccarini, A., Ostuni, M. B., Lageman, R., Muntoni, A & Pomi, R. (2015)."Electrokinetic remediation of metal-polluted marine sediments: experimental investigation for plant design". Electrochimica Acta, 181, 146-159.
- Imran, M., Rehim, A., Sarwar, N., & Hussain, S. (2016). "Zinc bioavailability in maize grains in response of phosphorous–zinc interaction". Journal of Plant Nutrition and Soil Science, 179(1), 60-66.
- Iyer, Nalbantoglu, Z. (2001) "An overview of electrokinetic for soil treatment".

- Jayasekera, S. (2008). "An investigation into modification of the engineering properties of salt affected soils using electrokinetics". Dissertation/Thesis, University of Ballarat.

- Karkush M. O., & Ali S. D., (2019). "Effects of copper sulfate contamination on the geotechnical behavior of clayey soils". Journal of GeoEngineering, 14(1), 47-52.
- Khalil, A.H., (2013). "Removal of Cadmium and Phenol from contaminated soil by an upward electro-kinetic process". Ph.D., Thesis, Baghdad University, College of Engineering.
- Khodary, S. M., Fath, H., Negm, A., & Tawfik, A. (2021)." Measuring the engineering properties of landfill leachate-contaminated soil in Egypt". Euro-Mediterranean Journal for Environmental Integration, 6(1), 1-12.
- Kim, H. A., Lee, K. Y., Lee, B. T., Kim, S. O., & Kim, K. W. (2012). "Comparative study of simultaneous removal of As, Cu, and Pb using different combinations of electrokinetics with bioleaching by Acidithiobacillus ferrooxidans". Water research, 46(17), 5591-5599.
- Kim ،S.O., Moon, S.H., Kim, K.W., (2001)." Removal of heavy metals from soils using enhanced electro-kinetic soil processing". Water, Air, and Soil Pollution, 125, 259-272.
- Lata S., Singh P.K. and Samadder S.R., (2014). "Regeneration of adsorbents and recovery of heavy metals: a review". International Journal of Environmental Science and Technology, Volume 12, pages1461–1478.
- Lee, H.S., Lee, K., Kim, S.S., Ko, S.H., (2003). "Effects of buffering capacity and citric acid in electrolyte on electro-kinetic remediation of mine tailing soils". J. Ind. Eng. Chem., 9, 360-365.
- Li, G., Guo, S., Li, S., Zhang, L., & Wang, S. (2012). "Comparison of approaching and fixed anodes for avoiding the ‘focusing’effect during electrokinetic remediation of chromium-contaminated soil". Chemical Engineering Journal, 203, 231-238.
- Lima, A. T., Hofmann, A., Reynolds, D., Ptacek, C. J., Van Cappellen, P., Ottosen, L. M., ... & Sanchez-Hachair, A. (2017). "Environmental electrokinetics for a sustainable subsurface". Chemosphere, 181, 122-133.
- Lone M. I.; He Z. L.; Stoffella P. J.; & Yang X. E; (2008). "Phytoremediation of heavy metal polluted soils and water: progresses

and perspectives". Journal of Zhejiang University Science B, 9(3), 210-220.

- Maria Villen-Guzman , Paz-Garcia, J. M., Rodriguez-Maroto, J. M., Gomez-Lahoz, C., & Garcia-Herruzo, F. (2014). "Acid enhanced electrokinetic remediation of a contaminated soil using constant current density: strong vs. weak acid". Separation Science and Technology, 49(10), 1461-1468.
- Masha Hosseini., Farahbakhsh, M., Savaghebi, G., (2011). "Chelate Agents Enhanced Electro-kinetic Remediation for Removal of Lead and Zinc from a Calcareous Soil". International Conference on Environment Science and Engineering, 8, 208-211.
- Merkx O. K, (2011)." Electrokinetically induced removal of heavy metals from an aged, contaminated sludge".–a laboratory experiment (Master's thesis).
- Mosavat N., Oh, E., Chai, G., (2012). "A Review of electro-kinetic treatment technique for improving the engineering characteristics of low permeable problematic soils". Int. J. of GEOMATE, 2(2), 266-272.
- Muradoglu F.; Gundogdu M.; Ercisli S.; Encu T.; Balta F.; Jaafar H. Z.; & Zia-Ul-Haq M, (2015)." Cadmium toxicity affects chlorophyll a and b content, antioxidant enzyme activities and mineral nutrient accumulation in strawberry". Biological research, 48(1), 1-7.
- 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.
- Nystrøm, G. M. (2001). "Investigations of soil solution during enhanced electrodialytic soil remediation". Rapport BYG DTU R-009: Danmarks Tekniske Universitet.

- Ottosen , L. M., Larsen, T. H., Jensen, P. E., Kirkelund, G. M., Kerrn-Jespersen, H., Tuxen, N., & Hyldegaard, B. H. (2019). "Electrokinetics

applied in remediation of subsurface soil contaminated with chlorinated ethenes"–a review. Chemosphere, 235, 113-125.

- Ottosen, L. M., Cristensen, I. V., Pedersen, A. J., & Villumsen, A. (2005). "Electrodialytic remediation of heavy metal polluted soil". In Environmental Chemistry (pp. 223-233). Springer, Berlin, Heidelberg.
- Paramkusam, B. R., Srivastava, R. K., & Dwivedi, S. B. (2011). "Experimental studies on heavy metal extraction from contaminated soil using ammonium citrate as alkaline chelate during the electrokinetic process". Journal of Hazardous, Toxic, and Radioactive Waste, 15(4), 296-304.
- Peng, C., Almeira, J. O., & Gu, Q. (2013). "Effect of electrode configuration on pH distribution and heavy metal ions migration during soil electrokinetic remediation". Environmental earth sciences, 69(1), 257-265.
- Rasha W. K. (2013). "Electro kinetic remedaition of lead nickel and zinc-contaminated soil". MS.C. Thesis, Baghdad University, College of Engineering.
- Rashid I.T., (2015). "Improve Remediation of Soil Contaminated with Lead and Chromium by Electrical Field Technique". Ph.D., Thesis, Baghdad University, College of Engineering.
- Reddy, K.R., Chinthamreddy, S., 2003."Sequentially enhanced electro – kinetic remediation of heavy metals in low buffering clayey soils". Journal of Geotechnical and Geo Environmental Engineering, 129(3), 263-277.
- Reddy K. R.; & Cameselle; C. (2009)." Electrochemical remediation technologies for polluted soils, sediments and groundwater". John Wiley & Sons.
- Risco C., Rodrigo S., López-Vizcaíno R., Sáez C., Cañizares P., Navarro V. and Rodrigo M.A., (2016). "Electrokinetic flushing with surrounding electrode arrangements for the remediation of soils that are polluted with 2, 4-D: a case study in a pilot plant". Science of The Total Environment, Volumes 545–546, Pages 256-265.
- S. Jayasekera, and S. Hall, "Lime Enhanced Electro kinetic Treatments to Modify the Properties of a Saline-Sodic Soil", Proceedings of International Conference on Problematic Soils, 25-27 May 2005.

- Saeedi M., Jamshidi A., Shariatmadri N. and Falamaki, A., (2009). "An investigation on the efficiency of electro kinetic coupled with carbon active barrier to remediate nickel contaminated clay". Int. J. Environ. Res., 3(4):629-636, Autumn 2009, ISSN: 1735-6865.
- Saeedi, M., Li, L. Y., & MORADI, G. A. (2013). "Effect of alternative electrolytes on enhanced electrokinetic remediation of hexavalent chromium in clayey soil".
- Shen Z.; Chen X.; Jia J.; Qu L.; & Wang W. (2007)." Comparison of electrokinetic soil remediation methods using one fixed anode and approaching anodes". Environmental Pollution, 150(2), 193-199.
- Shen, Z., Zhang, J., Qu, L., Dong, Z., Zheng, S., & Wang, W. (2009). A modified EK method with an I−/I2 lixiviant assisted and approaching cathodes to remedy mercury contaminated field soils. Environmental geology, 57(6), 1399-1407.
- Song Y., Cang L., Xu H., Wu S. and Zhou D., (2019). "Migration and decomplexation of metal-chelate complexes causing metal accumulation phenomenon after chelate-enhanced electro kinetic remediation". Journal of Hazardous Materials, 377, 106–112.
- Thomé, A., Reginatto, C., Vanzetto, G., & Braun, A. B. (2018). "Remediation technologies applied in polluted soils: new perspectives in this field". The International Congress on Environmental Geotechnics (pp. 186-203). Springer, Singapore.
- Tsai J. Y.; Egelman S. Cranor; L. & Acquisti, A. (2011)." The effect of online privacy information on purchasing behavior": An experimental study. Information systems research, 22(2), 254-268.
- Turer D. and Genc A., (2005). "Assessing effect of electrode configuration on the efficiency of electrokinetic remediation by sequential extraction analysis". Journal of Hazardous Materials B119 167–174.

- Virkutyte, J., Sillanpää, M., & Latostenmaa, P. (2002). "Electrokinetic soil remediation—critical overview". Science of the total environment, 289(1-3), 97-121.

- Wan Y., Wang A. and Shen M., (2019). "Restoration of Cadmium Contaminated Soil Using Approaching Anode Method of Polygonal Electrode". Ekoloji 28(107): 1041-1047.
- Wang, H., Liu, T., Feng, S., & Zhang, W. (2017). "Metal removal and associated binding fraction transformation in contaminated river sedimentwashed by different types of agents". PloS one, 12(3), e017457.
- Wang, Y., & Hou, X. (2022). "Electrokinetic Remediation of Cadmium (Cd), Copper (Cu) and Nickel (Ni) Co-contaminated Soil with Oxalic Acid, Acetic Acid or Citric Acid as the Catholyte". Int. J. Electrochem. Sci, 17(220444).
- Wei, X., Guo, S., Wu, B., Li, F., & Li, G. (2017). "Effects of reducing agent and approaching anodes on chromium removal in electrokinetic soil remediation". Frontiers of Environmental Science & Engineering, 10(2), 253-261.
- Wuana, R. A., & Okieimen, F. E. (2011)." Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation". International Scholarly Research Notices, 2011.
- Xu, Y., Fang, Y., Wang, K., Xia, W., & Qian, G. (2022). "Remediation of As/Cr co-contaminated soil by electrokinetic coupled with permeable reactive barrier". Environmental Engineering Research, 27(3).
- Xue, F., Yan, Y., Xia, M., Muhammad, F., Yu, L., Xu, F., & Jiao, B. (2017). "Electro-kinetic remediation of chromium-contaminated soil by a three-dimensional electrode coupled with a permeable reactive barrier". Rsc Advances, 7(86), 54797-54805.
- Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A. R. (2012). "Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil". Chemosphere, 89(11), 1467-1471.

- Yvonne, A. O., Galadima, S. A., & Maryam, S. (2022). "Potential of biochar for clean up of heavy metal contaminated soil and water". African Journal of Environmental Science and Technology, 16(4), 146-154.
- Zhang T., Zou H., Ji M., Li X., Li L. and Tang T., (2014). "Enhanced electrokinetic remediation of lead-contaminated soil by complexing

agents and approaching anodes". Environmental Science and Pollution Research, volume 21, pages3126–3133.

- Zhang, Z., Ren, W., Zhang, J., & Zhu, F. (2021)."Electrokinetic remediation of Pb near the e-waste dismantle site with Fe $(NO3)_3$ as cathode electrolyte". Environmental Technology, 42(6), 884-893.

APPENDIX

APPENDIX-A

Report of Zinc and Chromium Analysis in (AA)

Republic of Iraq
Ministry of Industry and Minerals
corporation for Research
and Industrial Development
Ibn Al-betar Research center

جمهورية العراق
وزارة الصناعة والمعادن
هيأة البحث والتطوير
الصناعي
مركز ابن البيطار

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from	نماذج	Date. 11/5/2022
جامعة بابل-كلية الهندسة	زينة نهر	

NO.	Sample name	Zn ppm	NOTE
1	Initial Soil	8.5	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Zn+DW+FA(S1)	5.8	
	Zn+DW+FA(S2)	6.3	
	Zn+DW+FA(S3)	6.8	
	Zn+DW+FA(S4)	7.225	

Analysit
Hatem H.
Sanaa Shawket
11/5/22

Signatur
Hatem Hussein Rmidh
Head of Section

E:mail: lbn.albetar@ crid.industry.gov.iq

العراق - بغداد - مجمع الجادرية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.1): Report of Zn (II) concentration for EK-1

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from	لقاح	Date. 11/5/2022
جامعة بابل-كلية الهندسة	زيتالفار	

NO.	Sample name	Zn ppm	Note
2	Initial Soil	8.5	تم وزن 1 غرام من المادة وهضمها واكملة الحجم الى 100 مل
	Zn+FA+AA (S1)	4.0346	
	Zn+FA+AA (S2)	5.1856	
	Zn+FA+AA (S3)	5.1115	
	Zn+FA+AA (S4)	5.1444	

Analysit
Hatem H.

Sanaa Shawket
11/5/22

Signatur
Hatem Hussein Rmidh
Head of Section

E:mail: Ibn.albetar@ crid.industry.gov.iq

العراق - بغداد - مجمع الجادرية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.2): Report of Zn (II) concentration for EK-2.

Receiving Date	Name of sample	No. (--)
No.( ) Date 3/7 /2022		
Receiving from	لطاع	Date. 11/5/2022
جامعة بابل-كلية الهندسة	زينة ثامر	

NO.	Sample name	Zn ppm	NOTE
3	Initial Soil	8.5	تم وزن 1 غرام من العلكة وهضمها وتكملة الحجم الى 100 مل
	Zn+AC+FA(S1)	6.375	
	Zn+AC+FA(S2)	6.29	
	Zn+AC+FA(S3)	6.205	
	Zn+AC+FA(S4)	6.18	

Analyst
Hatem H.
Sanaa Shawket

Signatur
Hatem Hussein Rmidh
Head of Section

E:mail: Ibn.albetar@crid.industry.gov.iq
العراق - بغداد - مجمع الجادرية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.3): Report of Zn (II) concentration for EK-3.

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022	تمليح	
Receiving from	زيتالتم	Date. 11/5/2022
جامعة بابل/كلية الهندسة		

NO.	Sample name	Cr ppm	NOTE
4	Initial Soil	2.2	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Cr+DW+FA(S1)	1.459	
	Cr+DW+FA(S2)	1.85	
	Cr+DW+FA(S3)	1.93	
	Cr+DW+FA(S4)	1.95	

Signatur
Hatem Hussein Rmidh
Head of Section

Analysit
Hanin H.
Sanaa Shawket

E:mail: Ibn.albetar@crid.industry.gov.iq

العراق - بغداد - مجمع الدائرية الطبي
web sit : www.crid.industry.gov.iq

Figure (A.4): Report of Cr (III) concentration for EK-4.

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from	غذاع	Date. 11/5/2022
جامعة بابل-كلية الهندسة	زياد ثامر	

NO.	Sample name	Cr ppm	NOTE
5	Initial Soil	2.2	تم وزن 1 غرام من العادة وهضمها وتكملة الحجم الى 100 مل
	Cr+AA+FA(S1)	1.257	
	Cr+AA+FA(S2)	1.29	
	Cr+AA+FA(S3)	1.389	
	Cr+AA+FA(S4)	1.43	

Signatur
Hatem Hussein Rmidh
Head of Section

Analyst
Hatem H. Sanaa Shawket 11/5/22

E:mail: Ibn.albetar@ crid.industry.gov.iq

العراق - بغداد - مجمع الجادرية الطبي
web sit : www.crid.industry.gov.iq

Figure (A.5): Report of Cr (III) concentration for EK-5.

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هيأة البحث والتطوير
الصناعي
مركز بحوث ابن البيطار

Receiving Date No.( ) Date 28/4 /2022	Name of sample	No. (--)
Receiving from جامعة بابل-كلية الهندسة	غضار زيانكر	Date. 5/7/2022

NO.	Sample name	Cr ppm	NOTE
6	Initial Soil	2.2	تم وزن 1 غرام من العادة وهضمها وتكملة الحجم الى 100 مل
	Cr+AC+FA(S1)	1.650	
	Cr+AC+FA(S2)	1.584	
	Cr+AC+FA(S3)	1.540	
	Cr+AC+FA(S4)	1.474	

Analysit

Hatem H. Sanaa Shawket 5/7/22

Signatur
Hatem Hussein Rnidh
Head of Section

E:mail: Ibn.albetar@ crid.industry.gov.iq

العراق - بغداد - مجمع الجادرية الطبي
web sit : www.crid.industry.gov.iq

Figure (A.6): Report of Cr (III) concentration for EK-6.

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and Industrial Development
Iba Al-betar Research center

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وزارة الصناعة والمعادن
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الصناعي
مركز ابو طالب البيطار

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from		Date. 5 /7/2022
جامعة بغداد كلية الهندسة		

NO.	Sample name	Zn ppm	NOTE
7	Initial Soil	8.5	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Zn+DW+AAs(S1)	5.95	
	Zn+DW+AAs(S3)	6.12	
	Zn+DW+AAs(S4)	6.29	

Analyst

Hatem H. Sanaa Shawkat 5/7/22

Sighatur
Hatem Hussein Rmidh
Head of Section

E:mail: Ibn.albetar@crid.industry.gov.iq

العراق - بغداد - مجمع الجادرية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.7): Report of Zn (II) concentration for EK-7.

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from		Date. 5/7/2022
جامعة بابل-كلية الهندسة		

NO.	Sample name	Zn ppm	Note
8	Initial Soil	8.5	تم وزن 1 غرام من العادة وهضمها وتكملة الحجم الى 100 مل
	Zn+AA+AAS(S1)	2.5	
	Zn+AA+AAS(S3)	3.3	
	Zn+AA+AAS(S4)	3.6	

Signatur
Hatem Hussein Rasidh
Head of Section

Analyst
Hatem H. Sonaa Shawket 5/7/22

E:mail: Ibn.albetar@crid.industry.gov.iq
العراق - بغداد - مجمع الجادرية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.8): Report of Zn (II) concentration for EK-8.

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from	نماذج	Date. 5/7/2022
جامعة بابل-كلية الهندسة	زيانكو	

NO.	Sample name	Zn ppm	Note
9	Initial soil	8.5	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Zn+AC+AAs(S1)	5.386	
	Zn+AC+AAs(S3)	6.338	
	Zn+AC+AAs(S4)	6.687	

Analyst
Hatem H.
Sanaa Shawket
5/7/22

Signatur
Hatem Hussein Rnidh
Head of Section

E:mail: Ibn.albetar@crid.industry.gov.iq
العراق - بغداد - مجمع المنارة العلمي
web sit : www.crid.industry.gov.iq

Figure (A.9): Report of Zn (II) concentration for EK-9.

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Ibn Al-betar Research center

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هيأة البحث والتطوير
الصناعي
مركز ابن البيطار

Receiving Date	Name of sample	No. (–)
No.( ) Date 28/4 /2022		
Receiving from	نماذج	Date. 5/7/2022
جامعة بابل-كلية الهندسة	زيا تكر	

NO.	Sample name	Cr ppm	NOTE
10	Initial Soil	2.2	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Cr+DW+AAS(S1)	1.53	
	Cr+DW+AAS(S3)	1.68	
	Cr+DW+AAS(S4)	1.79	

Analyst
Hatem H. Sanaa Shawkat 5/7/22

Signatur
Hatem Hussein Rmidh
Head of Section

E:mail: Ibn.albetar@ crid.industry.gov.iq

العراق - بغداد - مجمع المدارية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.10): Report of Cr(III) concentration for EK-10.

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from	نماذج	Date. 5/7/2022
جامعة بابل-كلية الهندسة	زيادكم	

NO.	Sample name	Cr ppm	NOTE
11	Initial Soil	2.2	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Cr+AA+AAs(S1)	1.01	
	Cr+AA+AAs(S3)	1.26	
	Cr+AA+AAs(S4)	1.277	

Analyst

Hatem H. Sanaa 5/7/22 Sanaa Shawket

Signatur
Hatem Hussein Rnaidh
Head of Section

E:mail: Ibn.albetar@crid.industry.gov.iq

العراق ، بغداد ، مجمع الجادرية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.11): Report of Cr (III) concentration for EK-11.

Receiving Date	Name of sample	No. (–)
No.( ) Date 28/4 /2022		
Receiving from		Date. 5/7/2022
جامعة بابل /كلية الهندسة		

NO.	Sample name	Cr ppm	NOTE
12	Initial Soil	2.2	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Cr+AC+AAs(S1)	1.408	
	Cr+AC+AAs(S3)	1.232	
	Cr+AC+AAs(S4)	1.056	

Analyst

Hatem H. Sanaa 5/7/22 Sanaa Shawket

Signatur
Hatem Hussein Rnidh
Head of Section

E:mail: Ibn.albetar@crid.industry.gov.iq

العراق - بغداد - مجمع الحارية العلمي
web sit : www.crid.industry.gov.iq

Figure (A.12): Report of Cr (III) concentration for EK-12.

Receiving Date	Name of sample	No. (–)
No.( ) Date 28/4 /2022		
Receiving from	نماذج	Date. 5/7/2022
جامعة بابل-كلية الهندسة	زيادة	

NO.	Sample name	Zn ppm	NOTE
13	Initial Soil	8.5	تم وزن 1 غرام من المادة وهضمها وتكملة الحجم الى 100 مل
	Zn+AC+ACS(S1)	6.851	
	Zn+AC+ACS(S2)	5.080	
	Zn+AC+ACS(S3)	3.629	

Analysit

Hatem H. Sanaa Shawket 5/7/22

Signatur
Hatem Hussein Rnidh
Head of Section

E:mail: Ibn.albetar@ crid.industry.gov.iq

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Figure (A.13): Report of Zn (II) concentration for EK-13.

Receiving Date	Name of sample	No. (--)
No.( ) Date 28/4 /2022		
Receiving from	نماذج زيانكو	Date. 5/7/2022
جامعة بابل-كلية الهندسة		

NO.	Sample name	Cr ppm	NOTE
14	Initial Soil	2.2	تم وزن 1 غرام من العلنة وهضمها وتكملة الحجم الى 100 مل
	Cr+AC+ACS(S1)	1.470	
	Cr+AC+ACS(S2)	0.786	
	Cr+AC+ACS(S3)	1.245	

Analyst

Ihtem H. Sanaa Shawket 5/7/22

Signatur
Hatem Hussein Rnaidh
Head of Section

E:mail: Ibn.albetar@ crid.industry.gov.iq

العراق - بغداد - مجمع الجادرية الطبي
web sit : www.crid.industry.gov.iq

Figure (A.14): Report of Cr (III) concentration for EK-14.

الخلاصة

الهدف من هذه الرسالة هو تقييم تأثير اقتراب القطب على هجرة أيونات المعادن من خلال تقنية الحركة الكهربية للتربة الملوثة بالزنك والكروم باستخدام تقنيات الأنودات الثابتة والمتقاربة والتحقق من استخدام المحاليل المختلفة مثل حمض الخليك ((AA) وحامض سترات الامونيوم (AC)) لإزالة الزنك والكروم من تربة الرملية في العملية الكهرو حركية. أجريت أربعة عشر تجربة مختلفة (السلسلة ١، السلسلة ٢، السلسلة ٣،السلسلة ٤ والسلسله٥) على تربة ملوثة بالزنك بتركيز (٨٥٠ملغم / كغم) وتربة ملوثة بالكروم بتركيز(٢٢٠ ملغم /كغم). في التجارب التي أجريت في هذه الدراسة، تم تطبيق تيار كهربائي مستمر بين الأقطاب الكهربائية في (١,٥ فولت / سم) خلال ١٠٠ ساعة لتقنيات الأنودات الثابتة وفولتية ١٤,٦٢٥ لتقنيه الانودات المتحركة.

في التجربة، عند استخدام الماء المقطر كمحلول أنوليت ومحلول كاثوليت لكل من الأنود الثابت والأنود المقترب، أظهرت النتائج أن متوسط كفاءة اختزال الزنك لا يزال منخفضًا إلى حد ما، حيث يقترب من ٢٣,١٦٪ و٢٨٪ على التوالي بالنسبة للزنك. في تجارب الكروم وجد أن نسب الإزالة للقطب الموجب الثابت والأنود المقترب على التوالي كانت ١٨,٣٪ و٢٤,٢٣٪. من ناحية أخرى، فإن استخدام محلول مثل ((1M (AA) يعزز متوسط كفاءة الإزالة؛ على سبيل المثال، يؤدي استخدام 1M AA في تقنية الأنود الثابت لإزالة الزنك يؤدي إلى كفاءة إزالة تبلغ ٤٢,٧١٪، بينما عند اقتراب تقنية الأنود (باستخدام 1M AA) ترتفع كفاءة الإزالة إلى ٦٣,١٠٣٪.

بينما بالكروم عند اضافه (1M AA) تصل كفاءة إزالة لكل من الانودات الثابتة والمتحركة الى ٣٩,٠٢%، ٤٦,٢٥% على التوالي. من ناحية أخرى نلاحظ عند استخدام محلول مختلف اخر (1M AC) في كل من تجارب الكروم والزنك، حيث لوحظ انخفاض متوسط كفاءة الزنك بتقنية الانودات الثابتة والمتحركة حيث كانت ٢٦,٣٢٢% و٢٧,٧٩% على التوالي. بينما بتجارب الكروم نلاحظ ان كفاءة الازالة الانودات الثابتة والمتحركة كانت مساوية الى ٢٩% و٤٤% عل التوالي. وأخيرا في التجارب الأخيرة تم استخدام تقنية تقريب الكاثود باتجاه الانود لكل من الزنك والكروم وتم استخدام محلول سترات الامونيوم (1M AC) حيث كانت نسبة إزالة الزنك والكروم ٣٨,٩٧%، ٤٦,٩٥% على التوالي.