Improved electrokinetic process for capturing heavy metals in contaminated soil

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under the supervision of Professor John L. Zhou and Dr. Ali Altaee

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, ROMINA GHOBADI declare that this thesis, is submitted in fulfilment of the requirements for the award of *PhD*, in the *School of Civil and Environmental Engineering/Faculty of Engineering and Information Technology* at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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As the 1st author, I have published three peer-reviewed articles derived from this thesis:

Romina Ghobadi, Ali Altaee, John L. Zhou, Peter McLean, Sudesh Yadav *“Copper removal from contaminated soil through electrokinetic process with reactive filter media”* **Chemosphere**, 252 (2020): 126607.

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Romina Ghobadi, Ali Altaee, John L. Zhou, Elika Karbassiyazdi, Namuun Ganbat “*Effective remediation of heavy metals in contaminated soil by electrokinetic technology incorporating reactive filter media*”, **Science of the Total Environment**, 794 (2021) 148668.

In addition, I co-authored 2 peer-reviewed publications during PhD Study:

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Namuun Ganbat, Ali Altaee, Uttam Kumar, Andrew Hursthouse, Sudesh Yadav, John Zhou, **Romina Ghobadi** “*Soil remediation techniques from organic and inorganic pollutants: review*”, **Journal of Environmental Management.** Under review.

ABSTRACT

Soil contamination is a worldwide problem affecting human health. Electrokinetic (EK) remediation is a promising electrochemical remediation technology for soil decontamination using low-intensity direct current and resulting in the mobilization of chemical contaminants through electromigration and electroosmosis. EK application in the heavy metals contaminated soil faces with a few obstacles such as high pH distribution and contaminants extraction from the zone near the cathode region. Therefore, this study focused on integrating the EK technique with different reactive filter media (RFM) of activated carbon (AC) and biochar (BC), for the first time, without adding chemicals to facilitate the removal of copper ions from the contaminated kaolinite soil. This study initially selected copper as the heavy metal contaminant due to many reports on soil contamination by copper ions. RFM serves as an adsorbent during the electroosmosis and electromigration processes to facilitate contaminants removal. The performance of these RFMs in the EK system has been examined to select the best in terms of EK performance, regeneration, and contaminant removal. Tests based on EK (control test), EK coupled with AC (EK-AC), and EK combined with BC (EK-BC) were performed under an electric potential of 10 V, and the overall removal efficiency of copper ions decreased as EK-BC > EK-AC > EK. The results show that 27% of copper in the soil was captured by BC, compared with only 10% by AC. Additional EK-BC test performed under a constant current (20.00 mA) revealed that the acid front swept across the soil, resulting in 70.6%-95% copper removal from soil section 4 to section 1 close to the anode region, with more copper accumulation in section 5. Similar to the EK-BC test under a fixed voltage, BC captured 26% of copper in the soil during EK-BC treatment under a constant current, although with higher energy consumption. Moreover, RFM was regenerated by flushing with an acid solution,

achieving 99.3% of the copper recovery in BC and 78.4% in AC. Although the permeability of AC-RFM was higher than that of BC-RFM, the copper contaminant was more easily leached out from the BC-RFM.

Another recyclable RFM called compost (C) was proposed for the first time in this study to be applied in the EK system for copper removal from contaminated kaolinite soil. The feasibility of regeneration of compost was also studied for its reuse. Similar to other RFM, compost placed near the cathode served as an environmentally friendly adsorbent to bind copper ions while buffering the advancement of the alkaline front in the soil. The total copper removal rate increased from 1.03% in EK to 45.65% in EK-C under an electric potential of 10 V. Further experiments conducted by using compost/biochar (C+BC) mixture RFM at different ratios showed total Cu removal efficiency decreasing as EK-100%C > EK-(10%BC+90%C) > EK-(20%BC+80%C) > EK-(30%BC+70%C) > EK. The application of a constant electric current of 20.00 mA further enhanced copper removal to 84.09% in EK-100%C, although it did not show significant enhancement in EK-(BC+C). The compost RFM was regenerated by acid extraction and then reused twice, achieving a total removal of 74.11%. The findings demonstrated compost as a promising and reusable RFM for the efficient removal of copper in contaminated soil.

In addition, compost RFM was incorporated in the EK process for simultaneously treating multi-heavy metals contaminated real soil. Six EK operations were performed to investigate the performance of EK-RFM under different operating conditions such as the electric current, processing time, and the amount of the RFM. The electric current and treatment time demonstrated a significant impact on removing Zn, Cd, and Mn ions, while changing the amount of the RFM had an insignificant impact on heavy metals removal efficiency. The results showed that 51.6% to 72.1% removal of Zn, Cd, and Mn was achieved at 30.00 mA electric current and 14 days of operation. The energy consumption of the EK process was 0.17 kWh

kg^{-1}. The organic matter in the natural soil had a detrimental effect on the mobilization and migration of heavy metals such as Cu and Pb in soil. The results reported in this study should be useful in optimizing the design of the EK-RFM system and extending it to the field-scale applications.

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CHAPTER ONE:

INTRODUCTION

CHAPTER ONE: INTRODUCTION

1.1. Background

1.1.1. Soil pollution

The entire living beings on earth rely on soil for life as it provides essential resources to both humans and nature (Lima et al., 2017). Hence, contamination of the soil is a significant concern for the global environment, and it may result from agricultural, mining, urban, and industrial activities (Cameselle et al., 2013; Gomes et al., 2012). Great efforts have been made to overcome the problems associated with soil pollution. In this regard, many strategies and methods have been developed for mitigating soil contamination (Song et al., 2017). Generally, chemical, physical or biological technologies are used for cleaning contaminated soils. However, no single technology may be applicable for all types of contaminants regarding various site-specific conditions at different contaminated lands (Khan et al., 2004). Traditional remediation techniques have already successfully reduced contamination; however, most of them are time-consuming, relatively expensive, and may be inappropriate for some types of soils, such as fine-grained soils of low permeability (Morillo and Villaverde, 2017; Mosavat et al., 2012; Ren et al., 2014). Electrokinetic (EK) remediation technique stands out as an alternative soil treatment technique, which overcomes the other techniques' shortcomings. The EK is an in-situ remediation approach that applies a low direct-current electric field conducted on the contaminated soil to transport the pollutants towards the side of the system (Zhao et al., 2016). The EK process's application provides low disturbance to the surface when treating subsurface pollutants and strengthening the engineering features of subsurface soils (Mosavat et al., 2012). In recent years, research on electrokinetic remediation has shown the overall environmental and economic benefits from soil remediation as a comparatively new method for both in-situ and ex-situ clean-up of contaminated soils. This technique has been applied for many different purposes, such as removing or separating organic and inorganic contaminants;

leak detection systems and barriers in clay liners; diversions to waste plumes to prevent groundwater contamination; dewatering and consolidation of clay formations; and sub-surface remediation in soil (Apatoczky, 1992).

1.1.2. Adverse effects of heavy metals on the environment

Heavy metals can be defined as metals or metalloids with a density of ≥ 5 g/cm^3 (Yang et al., 2018). These pollutants are a major global concern, extensively released into the environment due to rapid urbanization and industrialization (Mudhoo et al., 2012). Heavy metals such as copper, zinc, cadmium, lead, nickel, chromium, and mercury are frequently detected in soil, which originates from mining activities, battery manufacture, smelting, municipal wastes, petroleum refining, paint manufacture etc. (Mao et al., 2015). Heavy metals are very difficult to be naturally removed from the environment, even at low concentrations, due to their persistence and toxicity in the environment (Ali et al., 2019). They can easily accumulate to highly toxic levels in living tissues and cause various diseases and disorders (Ali et al., 2019; Xu et al., 2017). For instance, cadmium, as one of the most toxic heavy metals, can affect human health with the potential to cause kidney damage, renal disorder, bone fraction, destruction of red blood cells, and high blood pressure (Giannis and Gidarakos, 2005; Mudhoo et al., 2012). Copper is mostly used in electrical and electroplating industries, and its high concentrations become toxic to living organisms. Copper persistence in the environment causes serious toxicological concerns, as it can accumulate in the skin and brain of organisms. Copper can also cause many human health problems such as migraine headaches, anorexia, allergies, childhood hyperactivity, and learning disorders (Apori et al., 2018; Mudhoo et al., 2012). Zinc is considered beneficial for both human bodies and plants, and on the other hand, a toxic environmental element if the concentration exceeds the limits or threshold (Elbana et al., 2018). Zinc can cause non-fatal fume fever and pneumonitis. Besides, high Zn absorption can also lead to subduing Fe and Cu absorption. Zn is employed in a wide range of industries such as smelting, electroplaters, ore processors, mining operations, zinc alloys, galvanizing steel, and iron products, which discharge large amounts of zinc into the global environment (He et al., 2021). Lead is a highly toxic contaminant, released to the environment by anthropogenic activities such as the manufacture of lead-containing products, the mining and smelting of ore, combustion of coal, oil, and waste incineration (Altin and Degirmenci, 2005; Zulfiqar et al., 2017). Lead cannot be easily eliminated in the environment; only its compounds may be transformed to other Pb compounds in the environment (Rouillon et al., 2017). It can deposit mainly in bones, kidneys, brain, and muscles, which may cause some serious disorders, including kidney diseases, anemia, nervous disorders, and even death (Ali et al., 2019; Mudhoo et al., 2012).

In general, heavy metals generate reactive oxygenic species (ROS) in organisms (Belhaj et al., 2016). ROS would cause oxidative stress in organisms, resulting in the generation of various diseases and abnormal conditions. Heavy metals are overall toxic to living organisms (Ali et al., 2019), and therefore, monitoring heavy metal levels in the environment is important for assessing and controlling their pollution (Ali et al., 2019; Belhaj et al., 2016).

1.1.3. Removal technologies of heavy metals from soil

The physical and chemical form of the heavy metal in the contaminated soil significantly affects the proper remediation strategy (Dermont et al., 2008). Therefore, the type and concentration of contamination at the site, as well as the physical properties of the site, should be provided to ensure a precise assessment of site contamination and remedial alternatives (Khan et al., 2004). There are different technologies for the remediation of heavy metals-contaminated soil. Currently, a variety of approaches have been suggested for the remediation of heavy metals contaminated soils, including in-situ and ex-situ remediation approaches. The in-situ expression applies when the contaminants are treated in the contaminated site without excavating the soil (Lima et al., 2017; Song et al., 2017). In contrast, the expression of ex-situ employs when the contaminated soil is removed or excavated from the site or subsurface and transported elsewhere for treatment (Song et al., 2017). The remediation techniques for heavy metal-contaminated soils can be classified under the following approaches: immobilization, isolation, toxicity reduction, physical separation, and extraction (Sabir et al., 2020). However, it may be more effective to combine two or more of these approaches (Dermont et al., 2008; Wuana and Okieimen, 2011). The factors that may affect the practicability and choice of a remediation technique are cost, long-term effectiveness, general acceptance, commercial availability, applicability to high metal concentrations, applicability to mixed wastes (heavy metals and organics), and mobility, toxicity and volume reduction (Abdullahi, 2015). The available remediation technologies for heavy metal-contaminated sites include soil washing, permeable reactive barrier, phytoremediation, and EK.

1.1.4. Removal of heavy metals by EK process

EK is a promising technique for the remediation of heavy metals contaminated soils. A direct electric current is induced to the contaminated soil to remove the contaminants by the mechanisms of electromigration, electroosmosis, and/or electrophoresis (Delgado et al., 2007; Masi and Losito, 2015; Moghadam et al., 2016; Wang et al., 2006). The technique is applicable in fine-grained soils with low permeability (Agnew et al., 2011; Ramirez et al., 2015). However, the efficiency of the technique may be reduced by sorption of heavy metal contaminants on soil particle surfaces and the effects of water electrolysis at the electrodes by generating the hydrogen and hydroxide ions (Cai et al., 2015; Huang et al., 2015; Kaya and Yukselen, 2005; Kornilovich et al., 2005; Ryu et al., 2017). Many studies have been conducted to develop different enhancement techniques that can overcome the EK treatment barriers and will be explained in detail in the following chapters.

1.2. Research Hypothesis

EK soil remediation has been tested at laboratory and field-scale experiments for potential application in soil remediation and treatment (Altaee et al., 2008; Apatoczky, 1992; Bahemmat and Farahbakhsh, 2015; Fu et al., 2017; Iannelli et al., 2015; Kim et al., 2011; Lee et al., 2012, 2009; P.V. Sivapullaiah, B.S.N Prakash, 2015; Paramkusam et al., 2014; Suzuki et al., 2014; Yuan et al., 2016b; Zhao et al., 2016). EK technique has several privileges over conventional soil remediation methods (Kim et al., 2011). The method is applicable for either in-situ and ex-situ treatment of contaminated soils as well as potentially effective in both saturated and unsaturated soils, most successful in the soil with low permeability, which is difficult to remediate by other techniques (Kim et al., 2011; Mosavat et al., 2012), offering the possibility of simultaneously treating both organically and inorganically-contaminated soils. In field application, compared with conventional techniques, EK is easy to set up and operate without disturbing the site activities, potentially cost-effective and relatively offering a short treatment duration (Mosavat et al., 2012; Rosestolato et al., 2015). However, regarding the results of laboratory tests and field applications, the EK remediation technique has several barriers in the heavy metals removal from contaminated soil when applied as a single remediation technique (Acar, Yalcin B, Robert, J. Gale, Akram, N. Alshawabkeh, Robert, E. Marks, Susheel, Puppala, Mark, Bricka, Randy, 1995; Mosavat et al., 2012). When the direct current is imposed across the treated soil, an alkaline pH front is developed near the cathode region, resulting in contaminants precipitation and retarding further contaminants transport and removal. On the other hand, contaminants precipitation in the soil near the cathode requires further treatment to prevent contaminants rebound in the soil.

Current efforts focus on how to improve the efficiency of EK and facilitate its applicability by controlling the pH of the electrolyte; adding enhancement agents such as surfactants, chelating agents, or high molecular polymer; application of a combined system, such as EK-bioremediation, EK-phytoremediation, and EK-Permeable Reactive Barrier (PRB) (Yeung and Gu, 2011; Zhao et al., 2016). However, the choice of an appropriate enhancement technique is significantly important in the EK system in terms of treatment duration, cost, and environmental effect. For example, the enhancement agent's application may affect the soil matrix. Hence, an environmentally friendly reagent should be used in the EK system, and then the electrolyte should be recovered at the end of the EK treatment. Among these enhancement techniques, PRB offers the enrichment or detoxification of the contaminants with a short treatment period and prevent the contamination of the catholyte solution (Zhao et al., 2016). Besides, there is a possibility of regenerating some of the PRB materials by acid leaching. The success of EK treatment, coupled with PRB, significantly depends on the type of PRB materials.

Therefore, the principal hypothesis for this research is that heavy metal contaminants can be effectively removed from the soil by integrating recyclable RFM with a chemical-free EK process. Different filter media are applied in the EK system close to the cathode, where usually the high accumulation of heavy metal ions occurred in the soil due to alkaline pH's advancement to capture heavy metal contaminants and facilitate metal recovery. RFMs' performance and mechanism in the EK process are assessed. In addition, developing a recyclable reactive filter media and its regeneration and reuse is of great importance. Many techniques have been developed to enhance the extraction efficiency of EK remediation in the last decades. Hence, this research aims to develop a recyclable, environmentally friendly reactive filter media to capture heavy metal contaminants and facilitate metal recovery. A comprehensive review of these recent efforts is given in chapter two to provide useful information and facilitate effective applications of these enhancement techniques by researchers in the field of EK remediation of contaminated soil (Yeung and Gu, 2011).

1.3. Research Objectives

This study aims to improve the EK process for capturing heavy metal pollutants in the soil matrix using different RFMs. To achieve the overall aim, this study has set out specific objectives:

i) Review current studies in the literature on soil pollution by heavy metals and technologies to remove the contaminated soil.

ii) Evaluate the performance of EK-RFM for the remediation of contaminated kaolinite soil. Biochar, activated carbon, and compost RMFs will be served to capture the inorganic contaminants in soil. The efficiency of removing inorganic contaminants, such as copper, from kaolin soil with different RFM's and at a constant voltage or electric potential, will be assessed.

iii) To design a novel recyclable RFM for soil remediation by the EK process. The developed RFM is a mixture of compost and biochar that has high adsorption capacity and water permeability. The ratio of compost to biochar should facilitate the recovery of contaminant and RFM reuse to reduce the remediation process's cost. EK-RFM process should subdue the alkaline front's advancement at the cathode to reduce chemical use.

iv) To investigate the performance of EK-RFM for the remediation of natural soil contaminated with a mixture of metal ions. Typically, contaminant removal from real soil is more difficult than kaolin soil because of the high adsorption capacity and interaction between contaminants and natural organic and inorganic soil matters.

Therefore, the present study provided more data and information about the feasibility of removing the contaminant from kaolin through the applications of EK and EK-RFM's. Further experiments were undertaken to treat multi-heavy metals using EK-RFM in the real soil, and post-treatment of RFM for recycling and reuse. Tests were duplicated to confirm the results reproducibility for quality assurance.

1.4. Thesis Outline

This thesis consists of seven chapters as follows:

Chapter 1 presents an introduction to this PhD study, specifically the research problem and technology of heavy metals removal, research hypothesis, and research objectives. The main tasks to achieve the objectives and scope of this research are emphasized in detail. Chapter 1 is the introductory chapter of the thesis and explains the PhD research's background and significance.

Chapter 2, named "literature review", is a review of the literature for the remediation technologies in heavy metals contaminated soil and offers a detailed review of the relevant scientific literature in applying electrokinetic remediation. The factors affecting electrokinetic technology (e.g., soil properties, contaminant types, electrode type, applies voltage) are discussed. Subsequently, the chapter introduces the enhancement techniques and their integration with electrokinetic for removing heavy metals from soil. Chapter 2 concludes with key findings from the literature review and determines the proper research direction.

Chapter 3, named "materials and methodologies", provides information about materials and methodologies used in this study.

Chapter 4, titled “copper removal from contaminated soil through the EK process with reactive filter media” refers to activated carbon and biochar RFM in the EK process for the copper removal from contaminated kaolinite soil.

Chapter 5 explores “enhanced copper removal from contaminated kaolinite soil by the EK process using compost RFM”. This chapter discussed an application of compost in the EK remediation process as an excellent adsorbent for copper-contaminated kaolinite soil with a detailed assessment of sorption mechanisms, RFM characterization, regeneration, and its reuse in the EK process.

Chapter 6 explores “effective remediation of heavy metals in contaminated soil by EK technology incorporating reactive filter media”. This chapter discussed the performance of compost RFM in the EK process for simultaneously heavy metal remediation from natural soil with a detailed assessment of removal mechanisms.

Chapter 7 summarizes significant findings of this work for EK heavy metals removal from soil, and recommendations for future study.

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CHAPTER TWO:

LITERATURE REVIEW

CHAPTER TWO: LITERATURE REVIEW

2.1. Conventional soil remediation techniques

Conventional remediation approaches for contaminated soil rely on a wide variety of physical, chemical, biological, and thermal treatment alternatives (Khalid et al., 2017). Among the conventional soil remediation techniques, the most promising ones are phytoremediation, bioremediation, soil flushing, thermal remediation, and permeable reactive barriers (PRB) (PRC Environmental Management, 1997).

Most of the approaches mentioned above have significant limitations, especially when contaminants are treated in soils of low hydraulic permeability (Lima et al., 2017; Masi et al., 2017a). **Table 2.1** summarizes the main challenges of phytoremediation, bioremediation, soil flushing, thermal remediation, PRB, and EK.

2.1.1. Phytoremediation

Phytoremediation is a cost-effective and environmentally acceptable alternative to conventional remediation technologies, which uses the plants to remediate shallow soils for both heavy metals and organic contaminants (Floris et al., 2017; Lima et al., 2017; Siyar et al., 2020; Yeung and Gu, 2011). Muszyńska and Hanus-Fajerska (2015) stated that about 500 different plant species could accumulate a high amount of toxic metals in their tissues with no toxic effects. Bhargava et al. (2012) and Rascio and Navari-Izzo (2011) revealed *Noccaea caerulescens* as an effective metal hyperaccumulator, which can accumulate high amounts of Cd (1800 mg kg^{-1}) and Zn (39600 mg kg^{-1}) without any damage. Although the technique is of low cost, its application in soil remediation is restricted due to the long remediation time and addressing contaminant typically at the relatively shallow subsurface (i.e., root zone) (Kuppusamy et al., 2017; Lim et al., 2004; Lima et al., 2017; Mao et al., 2016).

2.1.2. Bioremediation

Bioremediation is one of the soil remediation techniques employing microorganisms to break down contaminants and convert them to less harmful forms or immobilize them under proper environmental conditions (Mudhoo et al., 2012; Yeung et al., 2010). Kaksonen et al. (2011) reported that the bioremediation process could successfully solubilize 62% of copper using the bacterial culture of *Leptospirillum ferrooxidans*, *Acidithiobacillus caldus*, *Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans,* and *Sulfobacillus thermotolerans* from copper smelting industry solid waste after 29 days. However, bioremediation has several limitations, such as applying fine-grained soil of low hydraulic conductivity. Bioremediation's favorable outcome would not be achieved without the simultaneous presence of contaminants, microorganisms, electron acceptors, and essential nutrients for the microorganisms to grow (Hou et al., 2020). Furthermore, bioremediation is unsuitable for removing concentrated contaminants that could poison the microorganisms (Hou et al., 2020). Therefore, the individual application of bioremediation in fine-grained soil is costly and mostly ineffective (Apori et al., 2018). It is not easy to provide microorganisms and the desired electron acceptors or nutrients to the pollutants in this type of soil to its low permeability (PRC Environmental Management, 1997). For this reason, it is recommended for application with the other remediation techniques.

2.1.3. Soil flushing

Soil flushing is one of the most popular conventional in-situ soil remediation techniques, extracting the contaminants from the soil with water or other suitable aqueous solutions (Surriya et al., 2014). This remediation technique is carried out by passing the extraction fluid through in-place soils by applying an injection or infiltration process (Khan et al., 2004). Soil flushing is most applicable for inorganics, but it is suitable for treating some organic compounds at less cost-effective than alternative technologies. This technique is applicable to a limited number of metals that are soluble in water. Moreover, the technology cannot be successfully applied when treated in low permeability soils (PRC Environmental Management, 1997; Sturges et al., 1991).

2.1.4. Thermal

Thermal soil remediation is a technology most suitable for treating organic contaminants by subjecting soil to high temperatures (Kuppusamy et al., 2017; O'Brien et al., 2018). This approach is typically dedicated to the soil that has been contaminated with hydrocarbon compounds such as oil or other petroleum products. The process is performed by baking the soil, causing contaminants to evaporate (Lim et al., 2016; O'Brien et al., 2018). This technology only removes specific types of contaminants, and it is not suitable for inorganic contaminants (e.g., heavy metals). Additionally, it requires a high energy cost, making the technique inappropriate (Gill et al., 2014; Gong et al., 2018; Lima et al., 2017).

2.1.5. Permeable reactive barrier (PRB)

PRB is an in-situ remediation technology previously applied only to treat groundwater contaminated with organic chemicals and heavy metals (Han et al., 2010; Huang et al., 2015). This innovative and cost-effective technique employs an engineered zone of reactive materials installed in an aquifer to prevent contamination transport in the aquifer by capturing the contaminants (Yuan and Chiang, 2007). The design and choice of the reactive material filled in PRBs are crucial to achieving the remediation target and a more extended life service before breakthrough (Naidu and Brike, 2007). The treatment media in PRBs varies according to the type of target contaminants and may include different kinds of materials such as zero-valent iron, activated carbon, and activated bamboo charcoal (Blowes et al., 2000; Di Natale et al., 2008). Most of the installed PRBs have high hydraulic conductivity to allow groundwater flows through the barrier with no additional energy input (Benner et al., 1997; Kamolpornwijit et al., 2003). Natale et al. (2008) investigated the reliability of an activated carbon PRB in cadmium extraction from a contaminated shallow aquifer. Their results demonstrated the long-term efficiency of AC-PRB by reducing river pollution for several months. Liu et al. (2015) studied the application of natural pyrite as an effective reactive medium for treating Cr-contaminated groundwater (Liu et al., 2015). The granular zero-valent iron as PRBs has been widely used for years with success for the organic and inorganics' treatment (Galdames et al., 2017). The effectiveness of this technique was also successfully proven in the heavy metals-contaminated soil by Galdames et al. (2017), where a zero-valent iron as a PRB medium was applied for in-situ immobilisation of Cr and As. The advantages of PRB, including no chemicals, no additional energy, low cost in operation and maintenance, high remediation efficiency, and low risk to the environment, make this technology of interest in soil remediation applications (Li et al., 2011; Ren et al., 2014). Unfortunately, the efficiency of the technique is limited to the reactive lifetime of the barriers.

2.2. Overview of EK soil remediation

EK soil remediation is a relatively new and cost-effective physiochemical technique involving contaminant desorption, transport, capture, and removal from the soils with low permeability by applying a low-level DC through electrodes in a saturated contaminated soil (Acar et al., 1993; Khalid et al., 2017). The low DC applied to the wet soil in practice, causing contaminated pore water to flow towards the cathode (Apatoczky, 1992). EK remediation is also known as EK soil processing, electro-reclamation, electromigration, or electrochemical decontamination. This technique can be employed to remove metals, some types of organic wastes, and radionuclides from either saturated or unsaturated soils, slurries, and sediments (Fu et al., 2017;

Moghadam et al., 2016; Peppicelli et al., 2018). **Figure 2.1** shows a fundamental concept of in-situ electrokinetic extraction of contaminants in the soil.

The applications of EK technology started in the 19th century; Acar and Alshawabkeh (1993), and Yeung and Mitchell (1993) have fundamentally studied this technology in soil remediation. After that, many studies have been published following an experimental approach. Several feasibility studies have been carried out to prove the efficiency of the technology relying on various parameters, such as the electrical conditions (e.g., constant current, constant voltage or pulse current), the soil physicochemical characteristics, and the target contaminant (e.g., inorganic or organic contaminant) (Garcia, 2012; Kornilovich et al., 2005; Sun et al., 2019). EK remediation has been widely applied for removing heavy metals from fine-grained soils in many bench-scale studies and is considered as a promising in-situ remediation strategy for the simultaneous extraction of multi-heavy metals from soil (Acar et al., 1993; Acar and Alshawabkeh, 1993; Altin and Degirmenci, 2005; Yuan et al., 2016b).

Nowadays, most researchers focus on the experimental works associated with the development of the so-called enhanced EK techniques to improve the selective removal of a target contaminant, reducing energy consumption and diminishing the side effects on the treated porous media (Falciglia et al., 2016; Garcia, 2012; He et al., 2021; Mohamadi et al., 2019). A better understanding of the chemistry associated with conduction phenomena under electrical currents would be required (Acar et al., 1993). The feasibility and efficiency of the EK technology have been widely demonstrated in bench-scale studies and limited pilot-scale studies.

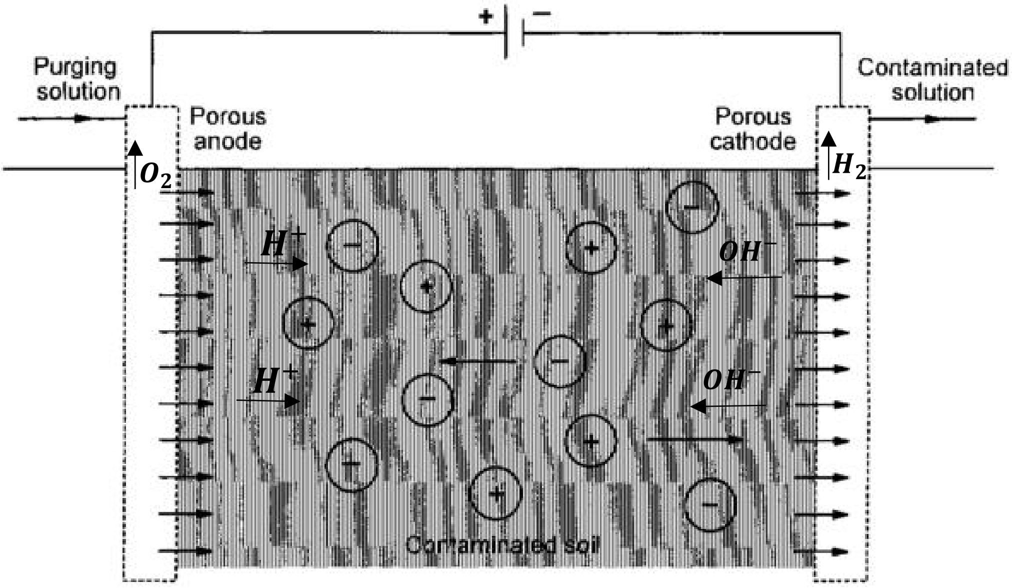

Figure 2.1. Concept of in-situ EK remediation of contaminants (Alshawabkeh et al., 1999).

Table 2.1. Summary of the main application challenges of conventional soil remediation techniques (Lima et al., 2017; O'Brien et al., 2018; Ren et al., 2014; Sturges et al., 1991; Yeung et al., 2010; Yeung and Gu, 2011).

	Phytoremediation	**Bioremediation**	**PRB**	**Soil Flushing**	**Thermal**	**EK**
Advantage	- Cost-effective - Environmentally friendly - Suitable for both inorganic and organic contaminants	- Cost-effective - Less disruption of the contaminated environment	- Cost-effective - Environmentally friendly - Suitable for both inorganic and organic contaminants - No additional chemical and energy	- Cost-effective	- Effective removal of Non-Aqueous Phase Liquid (NAPL) source zones in soil	- Cost-effective - Suitable for both inorganic and organic contaminants - Sub-surface remediation in soil
Disadvantage	- Long remediation time - Address contaminant mainly at the relatively shallow subsurface	- Long remediation time for some compounds - Affects biodegradable compounds where degradation products may be more persistent or toxic than parent compounds	- Limited reactive lifetime of barriers - Reactive barriers require to be delivered to contaminant zone	- Less cost effective in organic contaminants - Difficult to treat in low permeability or heterogeneous soils	- High energy expenditure and potential difficulties due to surface infrastructure requirements. - Not suitable for heavy metal contaminants	- pH dependent - Necessity to apply enhancing technique

2.3. Transport mechanism of EK process

The transport mechanism occurring in the soil-water system by applying the electrical field is divided into electroosmosis, electromigration, electrophoresis, and electrolysis (Gill et al., 2014; Yan et al., 2018). However, heavy metals removal from the soil in the EK treatment is achieved by two main transport processes, i.e., electromigration and electroosmosis (Acar and Alshawabkeh, 1993; X. Li et al., 2020; Masi et al., 2017b). The combination of these mechanisms results in EK extraction's applicability (Alshawabkeh et al., 1999; Iannelli et al., 2015; Kim et al., 2002). In general, the mechanisms of sorption/desorption, precipitation, and dissolution synchronously control the heavy metal contaminant movement in the soil during the EK process (Yuan and Chiang, 2007).

Electroosmosis: Most clay minerals surface is negatively charged. When an electric current is applied in wet soil, the pore water cations close to the soil surface start moving toward the cathode (Yuan et al., 2009). The movement of pore water is correlated to the voltage gradient. The phenomenon which transporting water from anode to cathode is called electroosmosis (Gidudu and Chirwa, 2020; Masi et al., 2017a).

Electromigration: Electromigration means transporting ions in the soil pore water to the opposite electrode (Yang et al., 2014). Therefore, the electromigration's direction is related to the charge of the ion (Kim et al., 2001). Metal ions with negative charges (such as As as arsenate or arsenite) migrate to the anode while metals present as cationic species (e.g., Cd) migrate to the cathode by electromigration (Yang et al., 2014).

Electrophoresis: By conducting the electric current, charged soil particles in the suspended colloidal soil solution move to the opposite electrode (Mosavat et al., 2012). This phenomenon is defined as electrophoresis.

Electrolysis: Electrolysis occurs by applying electric current as follows reactions,

$$\text{At anode: } 2H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad (2.1)$$

$$\text{At cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2.2)$$

When an electrical potential is applied in the EK system, the hydrogen ions are generated at the anode under water electrolysis and move towards the cathode, while at the cathode, the hydroxyl ions produced migrate towards the anode electrode (Fu et al., 2017; Y. Liu et al., 2016; Yeung and Gu, 2011). The generation of H^+ ions provides an acidic pH condition in the soil specimen near the anode, which can favor the dissolution of the heavy metals and transport them towards the cathode electrode (Hassan et al., 2015; Kim et al., 2002). In contrast, an alkaline front is created through the production of OH^- ions close to the cathode. The advance of the alkaline front into the soil specimen from the cathode end allows to a pH jumping, leading to the immobilization of heavy metals (Zulfiqar et al., 2017). At high pH values, an occurrence of soil alkalization may cause species precipitation inside the soil, consequently retarding contaminant transport (Huweg, 2013; Kim et al., 2002).

2.4. Factors affecting EK technology

The applicability of EK technology depends on different parameters such as soil properties, contaminant species, electrode type and applied voltage (Kim et al., 2002; Lim et al., 2016; Vocciante et al., 2017).

2.4.1. Soil properties

Soil properties such as soil type, sorption capacity, buffering capacity, pH of the pore water, soil pH and electrical conductivity can considerably affect the electrokinetic treatment (Jensen et al., 2007). Saturated soils of high moisture content and low activity provide the most desirable conditions for contaminants' transportation by electro-osmotic and electro-migration (P.V. Sivapullaiah, B.S.N Prakash, 2015). Buffering capacity and sorption capacity are related to the type of clay minerals and their contents in the soil. High activity soils containing clay minerals (e.g., montmorillonite, Illite, and impure kaolinite), reveal high acid/base buffer capacity and consequently need enhancement agents to make contaminants soluble before they move through the subsurface and to be removed. Soils with high clay minerals content typically carry negative charges, and they can strongly retain the positive species (e.g., heavy metals) as a result of ionic interactions (Alcántara et al., 2012). Therefore, the high sorption capacity of the clayey soil for positive species would further intensify the problem by hindering contaminant movement (Sivapullaiah and Prakash, 2015). The pore water and soil pH can largely influence the valence, solubility, and sorption of contaminant ions (Kim et al., 2002).

Understanding the soil's electrical conductivity (EC) is important, which can significantly affect the performance of the EK process. Generally, EC is described as the ability of a material to transmit an electrical current and is generally expressed in units of milli Siemens per meter ($\mathrm{mS\ m^{-1}}$) (Grisso et al., 2009; Seifi et al., 2010). The electrical conductivity of soils varies depending on the moisture content of the soil and the type and concentration of ions existing in the soil. The soil EC typically ranges between 10 and 500 $\mathrm{mS\ m^{-1}}$ for uncontaminated clayey soils and 0.1 and 5 $\mathrm{mS\ m^{-1}}$ for sand and gravels soils (Samouëlian et al., 2005). The electric current generated from the imposed electrical field is strongly affected by soil conductivity. Therefore, the difference in the various soils' electrical conductivity results in a variation in the electrical field applied during the EK experiments.

2.4.2. Contaminant type

The EK process efficiency depends not only on the soil's physical and chemical properties but also on the type of contaminants, concentration, and distribution (Garcia, 2012; Lim et al., 2016; Vocciante et al., 2017; Yeung, 2011). Thus, experimental and theoretical feasibility studies have been widely performed to determine which type of contaminants can be mobilised and which enhancement techniques would be applied in the EK process for that specific target contaminant (Bahemmat and Farahbakhsh, 2015; López-Vizcaíno et al., 2017).

Generally, in the EK system, the target contaminants must be in a soluble condition to be transported by electroosmosis and/or electromigration. For example, in alkaline conditions, insoluble metal hydroxides would be precipitated at the cathode. By precipitation of the heavy metals at the cathode, the technique's efficiency is reduced (Garcia, 2012).

Cauwenberghe (1997) suggested a classification of the contaminants, which could be treated by EK processes as follows:

- Heavy metals (cadmium, lead, chromium, mercury, copper, nickel, zinc)
- Anions (sulfates, nitrates)
- Radioactive species (Sr90, Cs137, Ur, Co60)
- Cyanides
- Petroleum hydrocarbons (diesel fuel, gasoline, kerosene, and lubricating oils)
- Dense non-aqueous phase liquids (DNAPLs)
- Polycyclic aromatic hydrocarbons (PAH)
- Explosives
- Halogenated hydrocarbons (TCE)
- Nonhalogenated organic pollutants (BTEX)
- Mixed organic/inorganic contaminants

2.4.3. Electrode type

Electrodes are the electrical conductors used to carry electric current into a given location. Materials, shapes, and configurations of the electrodes are critical in the EK process, while they considerably influence the efficiency of the process, installation cost, and operation time (Kim et al., 2014). The electrodes are used in different forms such as rods, plates, tubes, or wires and can be made of metals or non-metallic substances (Lee et al., 2012). In terms of electrode materials, inexpensive, inert with less corrosion, low resistance, and least voltage drop at the soil-electrode interface are the most desired electrokinetic applications (Huweg, 2013; Mosavat et al., 2012). The most suitable electrodes applied for research purposes consist of graphite, platinum, gold, and silver. Simultaneously, it is more practical for pilot studies to use much cheaper ones, even though reliable, such as titanium, stainless steel, or even plastic electrodes (Virkutyte et al., 2002). Recently, conductive materials such as graphite, stainless steel, copper, zinc, and titanium coated with a mixed metal oxide are of interest because of their high electrical conductivity and easy installation (Chen et al., 2002). The efficiency of different electrode materials in removing different contaminants in the EK process has been remarkably studied (Lee et al., 2012, 2009; Suzuki et al., 2014; Yuan et al., 2016b).

Suzuki et al. (2014) designed different bench-scale experiments to investigate the influence of three different electrode materials, including platinum-coated titanium (Pt/Ti), iridium dioxide-coated titanium (IrO_2/Ti), and graphite on the lead-contaminated kaolinite remediation efficiency. Their results were based on the change in the current density with time for each electrode material. According to the experimental results, the graphite electrodes revealed a significant decrease in the current density over time than the other electrodes. This decrease may be derived from the production of hydrogen or oxygen gases through water electrolysis at the electrodes' surface and the accumulation of these gases on the porous graphite electrodes (Suzuki et al., 2014). The Pt/Ti electrode showed no decrease in the current density with time and preserved its initial range to a large extent. Thus, the study suggested that the transport of ionic compounds would be more efficient with the Pt/Ti electrode than graphite and IrO_2/Ti electrodes.

Lee et al. (2009) applied a boron-doped diamond (BDD) electrode in the EK remediation process of organic contaminants. The proposed electrode was made of a diamond thin film with boron doping and characterized by its higher conductivity and a wide potential window. The study showed that applying the BDD electrode could elevate the electrochemical oxidation of organic contaminants, which generate different oxidants such as OH radicals. Moreover, the BDD electrode indicated higher resisting corrosion, which could offer the EK remediation process a longer lifetime.

The effect of cathode materials on the EK remediation efficiencies has not been well studied so far; however, it is a critical factor determining the construction cost of the EK remediation process. Therefore, Yuan et al. (2016b) conducted several laboratory EK tests by applying three types of electrode materials as the cathode to compare their efficiency on the EK process, including carbon nanotube covered polyethylene terephthalate yarns (PET-CNT), Pt/Ti, and graphite. Their results indicated that the PET-CNT as cathode could produce higher electric current and electro-osmotic flow than graphite or Pt/Ti, which directly results in the lower soil pH and consequently improving the removal efficiencies of heavy metals. It may be explained by the higher specific surface area and also electrochemical activity of CNT in PET-CNT compared to the other electrode materials. However, the PET-CNT operation had higher electrical energy consumption than that in the Pt/Ti and graphite, and it was cheaper than Pt/Ti electrode but more costly than the graphite electrode.

Electrode material affects the electrolysis reactions at both the cathode and anode. Hence, electrode material effect on salt extraction was studied by comparing different materials as anodes such as dimensionally stable anode, Pt, Si/BDD, and Fe electrode (by Lee et al. (2012)). Compared to other insoluble anodes, Fe could achieve a higher electrical conductivity reduction because of generating more electroosmosis flow and, as a result, higher SO_4^{2-} removal. Although Fe is more economical than the other electrodes, it has a short lifetime as a soluble electrode, and it releases Fe^{2+}which can easily produce iron oxides and be precipitated in the soil and electrolyte reservoir and may alter soil colour. Accordingly, to achieve a successful application of the EK system, a suitable electrode material should be chosen to consider the removal efficiency factors (Lee et al., 2012).

2.4.4. Electric voltage

To design the EK system, the application of a sufficient voltage gradient is of importance. Hence, the researchers worked on finding the optimized voltage gradient for the EK processes.

In lab-scale investigations, the low voltage is typically applied at the start of the EK process. Gradually increasing to a maximum over a period when the current is maintained constant, or a predetermined voltage is employed from the beginning and kept steady to the entire duration of the treatment process (Huweg, 2013). Casgrande (1949) reported that the voltage gradient should be enforced on the soil, not more than 50 $V\,m^{-1}$ to prevent energy losses and soil heating. The high voltage gradient application may affect soil's physical and chemical properties, hence reducing the electric current and electroosmotic permeability, leading to an inefficient EK process (Cheng et al., 2016; Huweg, 2013). In the EK applications, the electric current is defined as charged particles' movement through an electrical circuit (Suzuki et al., 2014). The decrease in the electric current during the EK treatment can be related to increased total electric resistance. In the EK system, when a constant voltage is applied across the soil, the resulting current flow will drop over time due to the formation of a high electric resistivity zone, which can be explained as a result of ions removal and precipitation close to the cathode region (Huweg, 2013). Yuan et al. (2016b) revealed several reasons that resulted in the current reduction: 1) the electromigration transported the ions in the soil towards the electrode compartments; 2) metal ions precipitation due to increased soil pH near the cathode, decreasing the EC. Yuan et al. (2016b) also reported that the electroosmosis flow is dependent on the electric current.

2.5. Enhancement techniques and integration with EK

As reviewed by many researchers, the application of EK remediation as a single technique is not often sufficient to treat the contaminated soil in many cases. Thus, the method is enhanced by integrating the EK with other remediation technologies or chemical processes to achieve better results (Lim et al., 2004; Lima et al., 2017; Lohner et al., 2008; Tian et al., 2017; Yeung and Gu, 2011; Zhao et al., 2016). Yeung and Gu (2011) comprehensively reviewed the techniques developed to increase the removal efficiency of EK remediation in the contaminated soil over the years and classified these techniques into three groups: (1) techniques that solubilize contaminants and maintain them in a mobile chemical state by using complexing agents, chelators, surfactants, oxidizing/reducing agents and cation solutions; (2) techniques that control soil pH within a range of values favoring the EK application such as electrolyte conditioning and use of ion exchange membrane; and (3) remediation techniques including oxidation/reduction, bioremediation, phytoremediation, ultrasonication and permeable reactive barrier that can be combined with EK technique to breakdown, or transform the contaminants sequentially or simultaneously. Nevertheless, the first two groups are interrelated somehow by keeping contaminants soluble during the EK process.

2.5.1. EK using enhancement agents

The recent enhanced techniques integrate specific extractant agents with the EK system to react with the target contaminant to control pH changes and increase pollutants solubility to facilitate the EK process. This type of enhanced technique significantly improves the efficiency of the process and provides selective removal of the target contaminants, and hinders undesirable impacts on the treated soil (Garcia, 2012). In general, the application of an enhancement agent in an EK system will extend the ionic conductivity of treated soil, resulting in an increase in the electric current across the soil specimen. Thus, the treatment time of an enhanced EK process would be longer than the unenhanced process (Altaee et al., 2008).

Some enhancement agents include chelating agents, complexing agents, surfactants, cosolvents, oxidizing/reducing agents, and cation solutions (Masi and Losito, 2015; Yeung, 2011). However, selecting an agent is crucial in the EK process, and some factors should be considered in choosing an appropriate enhancement agent (Fu et al., 2017). It is essential that the agents do not generate insoluble salts with the contaminant within the different pH values range during the process. However, forming soluble complexes with the contaminant can be effectively transported by imposing a direct-current electric field. Moreover, they should not produce toxic residues in the treated soil (Yeung, 2011).

Paramkusam et al. (2014) investigated the efficiency of different desorbing agents during the EK process on cadmium and copper's sorption/desorption behavior on clayey soil. The results presented a higher removal for both Cu and Cd while ammonium citrate (1 M) was employed as a desorbing agent in the EK process.

The application of enhancement agents in the EK remediation system has not always been favored since some laboratory tests were unsuccessful (Tian et al., 2017). The potential of an EK remediation process using mixtures of eco-friendly enhancing agents (rhamnolipids, saponin, and citric acid) was evaluated for the first time by Tian et al. (2017) to remove simultaneous metal including Cd, Cr, Cu, Pb, Zn and PAH/PCB from harbor sediment. Their experimental results demonstrated that the mixture of the agents could not successfully remove the high amounts of metals (4.4–15.8%) and only a slightly better removal of PAH and PCB (29.2% and 38.2%, respectively). Due to aged contamination, a high buffering capacity, a very low hydraulic permeability, reduced environment, and high organic matter content, the harbor sediment was highly resistant to the mobilization and transport of metal and organics (Tian et al., 2017). Therefore, the efficiency of the technique did not considerably increase.

2.5.2. EK coupled with bioremediation

Individual application of bioremediation in fine-grained soil is costly and mostly ineffective. It is not easy to provide microorganisms and the desired electron acceptors or nutrients to the contaminants in this soil type due to its low permeability (Gill et al., 2014). EK-enhanced bioremediation (EK-BIO) is recalled to overcome these limitations, integrating bioremediation in the EK process by using the microorganisms or transferring the contaminants to the microorganisms by EK flow processes (Yeung and Gu, 2011). In practice, electro-osmosis or electrophoresis mechanisms are applied to mobilise bacteria, while electromigration is addressed to carry nutrients in low porous materials (Lima et al., 2017). Some lab-scale studies have been developed to demonstrate the success of EK-BIO in low permeability soils.

Lee and Kim (2010) employed the EK-enhanced bioremediation by injecting *A. thiooxidans* (sulphur-oxidising bacteria) into shooting range soil contaminated with multiple-metals such as Pb, Cu, and Zn. The bioleaching treatment enhanced the removal efficiencies of Zn and Cu by applying an electrical field. However, there was precipitation of $PbSO_4$ as a by-product of sulphur oxidation, and the subsequent addition of EDTA hindered the problem.

2.5.3. EK coupled with phytoremediation

Combination of EK with phytoremediation can mobilise and redistribute contaminants in-situ, thus enhancing their transport to the plant roots and improving plant growth by mobilising nutrients into the root zone (Lima et al., 2017; Siyar et al., 2020). In the EK-Phytoremediation process, electromigration helps transport ions and contaminants to the root zone, while the imposed electrical field may provide ideal uptake conditions for the plant (Bi et al., 2011).

Cang et al. (2011) applied the low-intensity direct current on the growth of Indian mustard (*B. juncea*) multiple-metals contaminated soil in pot experiments for 35 days. According to their experimental results, the efficiency of plant uptake of metals was enhanced by combing the EK with phytoremediation. They reported that the electrical gradient was the most important factor influencing the plant growth, soil properties, and metal concentrations in the soil and plant. Lim et al. (2004) reported the integration of EK with phytoremediation of lead removal from the soil in a bench-scale experiment. They studied the efficiency of Indian mustard (*Brassica juncea*) grown in the contaminated soil for accumulating high tissue concentration of Pb by applying an electric field around the plants and adding EDTA into the soil. They concluded that experimental studies presented the best results with implementing an electrical field in the phytoremediation process.

2.5.4. EK coupled with PRB

A wide range of experimental studies has been recently conducted to integrate the application of PRB with the EK technique to facilitate the removal of contaminants from the soil during the EK remediation (Cang et al., 2009; Ma et al., 2010; Ren et al., 2014; Yuan et al., 2009; Yuan and Chiang, 2007; Zhao et al., 2016).

When a PRB is combined with electrochemical remediation, the transport of contaminants through the barrier is provided by the electroosmotic flow of soil pore fluid, electromigration of charged species, and electrophoresis of charged particulates (Cang et al., 2009). The reactive barrier serves as an adsorbent of the contaminant during the electroosmosis and electromigration process. One of the significances of the EK-PRB approach is reducing contamination concentration in the catholyte and anolyte solutions. Therefore, there is no need to recycle the electrolyte solution (Huang et al., 2015). The sorption attributes to most solid particle surfaces, and the degradation reactions of many contaminants strongly depend on the pH. Therefore, the pH gradient generated by the EK remediation process in the PRB may impact the sorption and degradation mechanisms of the reactive media in the PRB (Han et al., 2010). When a PRB is applied in the EK remediation system to improve the EK remediation efficiencies of organic, inorganic, or mixed contaminants, some aspects must be considered, such as the type, cost, and lifetime of reactive media (Zhao et al., 2016).

Degradation, adsorption, and precipitation in the PRB system depend on the reactive material's characteristics based on the target contaminants. The treatment media in PRBs implemented with EK may include different kinds of adsorbent materials such as zero-valent iron, activated carbon, activated bamboo charcoal, atomising slag (Sweetman et al., 2017). Among all PRBs, the zero-valent iron is the most common reactive material due to its low cost. However, the lifetime of ZVI can be reduced because of the contamination coating the surface of the ZVI particles, preventing flow through the barrier because of this build-up. It may also be due to the formation of iron oxides on the surface of ZVI, which prevents the reaction on Fe^0. Additionally, iron reactivity can be decreased if exposed to silica or natural organic matter (Ren et al., 2014).

An application of ZVI as a PRB in EK remediation of Cr-contaminated soil has been investigated by Cang et al. (2009). The results revealed that the electrochemical remediation coupled with a ZVI-PRB could achieve a maximum removal efficiency of Cr equal to 72%. The amount of Cr in the anolyte and catholyte was smaller when EK was combined with a ZVI.

The feasibility of integrating EK remediation with PRB on As removal from the soil was studied by Yuan and Chiang (2007). In their study, PRB was composed of ZVI and FeOOH. By applying PRB in the EK system, the removal efficiency of As was increased by

60–120%. Yuan et al. (2009) also investigated the removal mechanism of As by EK-PRB. The reactive barrier used in their study was made of carbon nanotube coated with cobalt (CNT-Co). The experimental results indicated that the EK remediation integrated with a PRB made of CNT-Co was not effective in removing. There was only an increase of 35% to 62% in the removal efficiency of As.

Zhao et al. (2016) investigated the application of activated carbon as a PRB combined with an EK system to remediate copper contaminated kaolin. Their experimental results presented that the EK-PRB test had a slightly higher soil pH than the EK test without PRB. It may be resulted due to the adsorption of some of the hydroxide ions produced at the cathode by activated carbon. Moreover, the electrical conductivity was found to be at a higher level in the EK than the EK-PRB test, which the lower soil pH may cause in the EK experiment. They reported that the PRB filled with activated carbon had great adsorption capacity for copper, and better removal would be achieved for those with higher copper concentrations. In addition, the main advantage of PRB was reducing electrolyte pollution. However, the feasibility of regeneration of PRB was not investigated in their study.

2.6. Conclusion and research gaps

Soil contaminated with heavy metals calls for applying remediation technologies that accomplish heavy metals removal with the least possible destruction to the environment or ecological systems. Conventional ex-situ remediation processes can be successful in the immobilization of heavy metals in soils; however, these methods are often found costly for their high-energy consumption. Besides, the soil cannot be used again for its normal uses. In addition, there may be a risk of future mobilization of heavy metals after such treatments (e.g., solidification and stabilization). Consequently, in-situ technologies for heavy metals removal from contaminated soil are highly demanded to treating a mixture of heavy metals.

From the literature review, in-situ soil washing and soil flushing with a strong chelating agent were possible remediating alternatives for heavy metal contaminated soils, which releases heavy metal cations from the functional groups on the surface of soil particles. Nevertheless, some concerns such as the high reagents consumption, the lack of proper strategy to efficiently treat the washing effluent, and additionally the extreme soil nutrient loss after washing, retarding the application of this technology. The application of these technologies is only limited to coarse soils. Phytoremediation was another alternative with large energy efficiency to eliminate the heavy metal contamination with negligible damages to the soil, offering its agricultural uses after the treatment. However, the extremely long treatment time with the low remediation rate restricts it only to remote areas applications, and the accumulation of heavy metals in biomass may result in secondary contamination. The application of high-surface-area sorbent was another choice of treatment to reduce the mobility of heavy metal cations. However, the major drawbacks, such as the slow capture speed and low adsorption capacity, were addressed because of its physicochemical adsorption nature. Long-term monitoring was also required for the stability of immobilized heavy metals. The mentioned technologies remove or accumulate heavy metal ions with their oxidation states not changed. Nevertheless, the most compact and immobilized conditions of heavy metals are found to be in the solid forms as charge-neutral metals or metal alloys. Hence, the main aim of the remediation process should be to reduce heavy metal cations to zero-valent metallic forms while separating them from the soil matrix. It would improve not only the remediation capacity but also makes heavy metal recovery possible.

Among various remediation techniques, the EK technique offers the most practical system for reducing heavy metal ions as well as distinguishing heavy metals from nutrient elements based on their reduction potentials. Previous studies in the application of the EK process for removing heavy metals contaminated soil have reported a major obstacle occurring during the EK remediation process, which was caused by the heavy metals' precipitation in the area of high pH. This pH jumping has become a limiting factor for removing heavy metals from the soil by the EK process. To overcome this limitation, the EK process was coupled with complexing agents. However, previous studies demonstrated that strong acids could change some soil characteristics such as electrical conductivity and pH and increase the remediation cost due to the recovery of the electrolyte after EK treatment. Besides, some complexing agents would not be recommended to extract heavy metals due to their unsuccessful applications in full-scale EK operation. The EK process was also combined with bioremediation. Although the technique is one of the most environmentally friendly remediating choices to extract heavy metals from the soil, it is relatively inexpensive, and it may take a long remediation time.

To overcome the limitations of existing enhancement approaches in the EK process, PRBs have been used since shown better performance compared with the conventional enhanced EK process. However, their application would be restricted due to their cost, availability, and especially life cycle. Besides, PRBs may not be able to prevent the advancement of the alkaline front, and hence their application was always combined with chemical reagents. As a result, such EK treatment will not be a cost-effective process. Therefore, to enhance the EK process for heavy metal removal, it is essential to use the reactive media that are environmentally friendly, reusable, and likely have the potential of buffering alkaline pH near the cathode and hence the advancement of an alkaline front in the soil.

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CHAPTER THREE:

MATERIALS AND METHODS

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3.1. Materials

Copper sulphate ($CuSO_4$) with a purity > 99 % was purchased from Sigma-Aldrich, Australia. Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$) (> 97%), and zinc nitrate hexahydrate ($N_2O_6Zn.6H_2O$) (98%) were also purchased from Sigma-Aldrich, Australia. In this study, commercial kaolinite and natural soil were used for the enhanced EK remediation of heavy metals. Commercial kaolinite (clay mineral) in the form of a fine white powder obtained from the N-Essential Co. Ltd (Australia) was used as a model soil in this study. Its characteristics are summarised in **Table 3.1**. The application of heavy metal spiked simple model soils such as kaolin was useful to study the fundamentals of the technology; however, their behavior was entirely different from that in the real soils. Therefore, natural soil was collected from surface soil (10–20 cm depth) in Northwest Sydney, Australia (latitude 33.79° S, longitude 151.03° E). After removing debris, visible pieces of roots, and stones, the specimen was first air-dried and then passed through a 0.60 mm sieve (Yuan et al., 2017). The characteristics of collected natural soil before preparation were provided in **Table 3.2**.

Granular activated carbon (GAC) purchased from James Cummings and Sons Pty Ltd, Australia, was applied as an adsorbent for the copper removed by the EK process. Biochar (BC) was obtained from Karr Group Co, USA and was also investigated as an RFM in the EK system. Compost (Searles 10 L, Organic Compost) as another RFM alternative was purchased from Bunnings Warehouse Ltd (Australia). HCl and HNO_3 were of analytical grade and used as the concentrated acid solutions for the RFM regeneration purposes.

Table 3.1. Chemical and physical properties of kaolinite clay soil.

Soil characteristics	Value
Particles size analysis (%)	
Clay (%)	67.5
Silt (%)	30.5
Sand (%)	2
Permeability (m s^{-1})	5.7×10^{-10}
Organic matter (%)	Negligible
Initial soil pH	5.44±0.04
Initial electrical conductivity (mS cm^{-1})	0.50±0.011
Initial copper concentration (mg kg^{-1})	1000±20

Table 3.2. Key characteristics and heavy metal content of the natural soil before and after spiking.

Characteristics	**Before spiking**	**Post spiking**
Particles size (%)		
Sand	20.6	20.6
Silt	65.8	65.8
Clay	13.6	13.6
Organic matter content (%)	1.2	1.1
pH	5.5±0.3	4.3±0.1
Electrical conductivity (µS cm^{-1})	31.4±0.2	260±23
Elemental composition (%)		
O	51.2	56.2
C	12.1	10.5
Si	23.3	22.4
Al	6.9	5.8
Fe	2.7	2.3
Other	3.8	2.8
Heavy metal concentration (mg kg^{-1})		
Cu	185±14	545±21

Pb	214.5±22.5	561±28
Zn	311±12	585±34
Zr	243.5±12.5	243.5±12.5
Cr	41.5±10.5	41.5±10.5
Ni	12.5±2.5	12.5±2.5
Mn	288±5	288±5
Cd	Negligible	552±30

3.2. Methods

3.2.1. Preparation of heavy metal-spiked kaolinite soil

This study initially selected copper as the heavy metal contaminant due to many reports on soil contamination by copper ions (Boiteau et al., 2011; Hadri et al., 2012), which requires remediation. Copper-contaminated kaolinite soil was prepared by thoroughly mixing 1 kg of kaolinite with 1000 mL of an aqueous solution containing 1000 mg L^{-1}. To prepare a stock solution of 1000 mg L^{-1}, Cu^{2+}, 2.52 g of copper sulphate was weighed and dissolved in 1000 mL of distilled water. The Cu solution was stirred on a magnetic stirrer for 20 min, then added to the soil and mixed thoroughly with a stainless spatula. The contaminated soil was stored for 72 h to allow for copper adsorption by the soil to occur and reach equilibrium (Altaee et al., 2008). The saturated soil was packed into the EK cell in layers and compacted uniformly using a hand compactor.

3.2.2. Preparation of multi-heavy metals contaminated real soil

After collecting the soil, the debris, visible pieces of roots, and stones were carefully removed. The specimen was first air-dried and then passed through a 0.60 mm sieve (Yuan et al., 2017). Heavy metal concentrations of the collected natural soil were < 300 $mg\,kg^{-1}$ (**Table 3.2**). Heavy metals contaminated natural soil was prepared by spiking $Cu(NO_3)_2$, $Cd(NO_3)_2$,

$Pb(NO_3)_2$, and $Zn(NO_3)_2$ to achieve the target concentration of 500 mg kg^{-1} for Cu, Cd, Pb and Zn (Bahemmat et al., 2016; Ma et al., 2010). Briefly, the given amounts of heavy metals nitrate salts were dissolved in deionized water. Afterwards, the collected soil was homogeneously mixed with the prepared heavy metals solution in a soil-to-solution ratio (m/V) of 1:1, shaken in a jar test at a speed of 100 rpm for 72 hours to ensure the adsorption of heavy metals. Again, the obtained contaminated soil was air-dried for 48 h (Fu et al., 2017). A total of 1.4 kg of contaminated soil was mixed with a measured amount of deionized water to get the target water content (34%) and then placed in the experiment apparatus using a tamper (Ma et al., 2010; Yuan et al., 2017).

3.2.3. Preparation of RFM

In this study, different types of reactive filter media, including granular activated carbon (25 g), biochar (25 g), and compost (70 g) were used in the separated EK tests to enhance the EK remediation process for the copper contaminated kaolinite soil. RFM was used in the EK system as supplied to fully pack the RFM cell in EK between soil and cathode compartments. In addition, a novel recyclable RFM was designed for soil remediation to increase the RFM adsorption capacity by thoroughly mixing the compost with biochar (BC+C) at different ratios while maintaining the total amount of RFM at 70 g. The RFM blends were applied in a series of EK-RFM operations to examine the feasibility of copper extraction from kaolinite soil. The detailed properties of the RFMs are shown in **Table 3.3**. The measured amount of compost (90 g–120 g) was filled into the RFM section for the EK remediation of multi-heavy metals contaminated real soil.

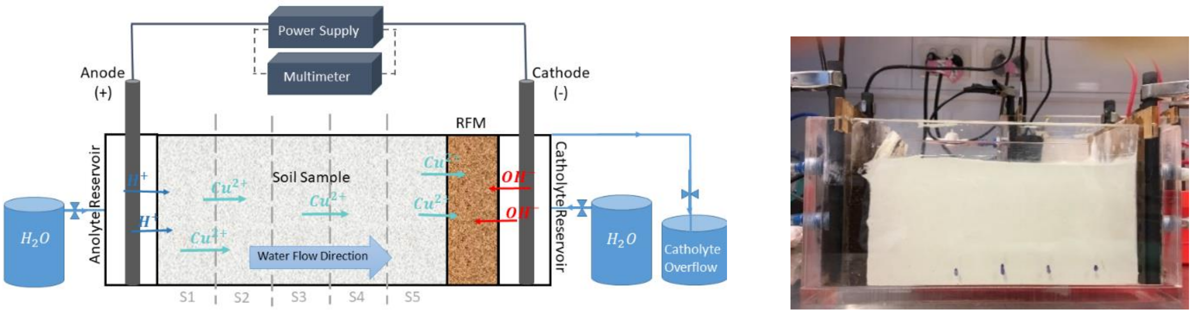
Table 3.3. Physicochemical characteristics of RFMs.

Properties	Activated carbon	Biochar	Compost
Particle size distribution (%)			
d > 2 mm	0	2.59	21.50
1 mm < d < 2 mm	71.63	14.51	21.70
d < 1 mm	28.37	82.89	56.80
Permeability (m s^{-1})	1.11×10^{-3}	0.17×10^{-3}	0.72×10^{-3}
Organic matter (%)	89.20	98.36	43.09
Surface area (m^2 g^{-1})	845.036	114.05	0.78
pH	8.2±0.15	8.95±0.05	5.13±0.20
Electrical conductivity (mS cm^{-1})	2.4	0.11	1.11
Metals ion concentration (mg kg^{-1})			
Cu	N/A	9	135
Cd	15	21	12
Zn	52	35	122
Pb	6	3	8
Elemental composition (%)			
O	9.28	11.60	50.45
C	89.23	87.23	35.02
N	N/A	N/A	7.78
Si	N/A	0.37	4.76
Al	0.54	N/A	1.50
Other	0.95	0.80	0.49

3.2.4. EK reactor setup

A schematic diagram of the EK experimental apparatus and the EK cell used in this study is shown in **Figure 3.1**. The EK experiments were conducted in a 23 cm × 8 cm × 11 cm reactor, made of plexiglass material to facilitate visual observation. This reactor consisted of three compartments: two electrode compartments placed at each end of the sample compartment and the contaminated soil compartment. On both sides, two graphite rod electrodes (15 cm × 1 cm) were connected to a DC bench power supply (EA-PS 3016-10B, EA Electro-Automatik) to apply the electric current, which was recorded hourly using a current meter (Keithley 175 Autoranging multimeter). The graphite electrodes were purchased from Graphite Australia Pty

Ltd. Two cellulose filter papers (pore size 5-13 µm, LLG Labware), supported by a perforated plexiglass plate, were placed between the soil and the electrode compartments to prevent soil particles penetrating into the electrolyte cells. RFM was loaded into the soil compartment near the cathode, and a filter paper was also placed between RFM and the soil to separate them at the end of the experiment. Distilled water was used as the anolyte and catholyte solution, respectively. Distilled water was periodically added to the anolyte compartment to replenish water losses due to the electroosmotic flow and water electrolysis.



(a) (b)

Figure 3.1. (a) Schematic diagram of the EK apparatus; (b) front view of the EK apparatus.

3.2.5. Regeneration and reuse of RFM

For the regeneration of activated carbon and biochar, a plastic column packed with used RFM was flushed using a concentrated acid (HNO_3) solution with a pH of 1.5. A peristaltic pump circulated the acid solution for 5 h at 5 mL min^{-1} flow rate to facilitate the recovery process. At the end of the leaching process, RFM was flushed with deionized water to neutralize the pH to normal conditions before reuse. After leaching, samples of RFM were tested for the copper concentration.

For the regeneration of compost RFM, the compost was removed from the EK reactor and mixed with a known amount of concentrated HCl acid solution in a 250-mL Erlenmeyer flask (Alcántara et al., 2012). The flask was then placed in an orbital shaker incubator

(Thermoline Scientific) to shake at 250 rpm and room temperature for 24 h. After that, the sample was centrifuged to separate the compost from the acid solution, and the compost was washed with deionized water to adjust the pH to its original condition. Then, the sample of the compost RFM was dried and ground (Rouillon et al., 2017) for the copper concentration measurement before reuse. The compost was recycled twice after being used in the EK-RFM system to evaluate its copper removal during reuse.

3.2.6. Removal efficiency

The efficiency of the EK treatments was evaluated by calculating copper removal efficiency in each soil section using Eq. (3.1) (Y. Liu et al., 2016; Ortiz-soto et al., 2019):

$$Removal\ efficiency_i = ((m_{i,initial} - m_{i,final})/m_{i,initial}) * 100\% \qquad (3.1)$$

where $m_{i,initial}$ is the initial metal concentration (mg kg^{-1}) in section i before treatment, and $m_{i,final}$ is the residual metal (mg kg^{-1}) in section i after EK treatment. The negative value indicates that metal ions are accumulated in that section.

Total heavy metal removal from the soil sample is an important parameter, indicating the overall EK treatments performance, which is determined from Eq. (3.2) (Ortiz-soto et al., 2019):

$$Total\ heavy\ metal\ removal = ((m_{initial} - m_{final})/m_{initial}) * 100\% \qquad (3.2)$$

where $m_{initial}$ is the initial heavy metal mass (mg) before treatment, and m_{final} is the final residual heavy metal mass (mg) after treatment, in the whole soil sample.

3.2.7. Power consumption

The overall cost of the EK remediation is mainly affected by the cost of fabrication, installation of electrodes, electric energy, remediation enhancements (if used), labour, and other fixed costs (Gidudu and Chirwa, 2020; Yuan et al., 2017). Among these economic factors, electric energy expenditure is the most important factor; however, the electric energy consumption is crucially controlled by many components, including contamination conditions, soil features, and electrode configuration during the EK remediation process (Yuan et al., 2017). For instance, the electrical conductivity increases in soils with high ionic strength, which may result in wasting more electric energy due to dissolving and carrying macroelements out of the soil (Jeon et al., 2015). In this study, the specific energy consumption (SEC) as a dominant factor for the total cost of the EK remediation was calculated according to Eq. (3.3) (Y. Liu et al., 2016).

$$\mathrm{E_u} = \frac{10^{-3}}{\mathrm{V_s}} \int \mathrm{V\,I\,dt} \tag{3.3}$$

where $\mathrm{E_u}$ is the specific power consumption (kWh $\mathrm{kg^{-1}}$), I is the electric current (A), V the applied voltage (V), t the experimental time (h) and Vs the total amount of soil treated (kg).

3.2.8. Analytical methods

At the end of the EK experiments, the soil specimen was evenly cut into five regions (S1-S5) from the anode to the cathode end. Each soil region was tested for pH, EC, and heavy metal content analysis. The pH and EC of RFMs and kaolinite soil before and after the EK treatments were determined using a multimeter (model Hach HQ40d) by providing slurries with dry soil to water ratio of 1:5 (w/v) (Altaee et al., 2008). The pH and EC of the real soil before and after the EK treatments were also measured by the same multimeter, with a soil-water volume ratio of 1:2 (Xu et al., 2019). Heavy metal concentrations in either soil and RFM were determined by a portable X-ray fluorescence (pXRF) analyzer (M series), from Olympus Corporation, based on the procedure described by Parsons et al. (2013). The advantages of pXRF compared to the more widely used analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) are the limited preparation required for solid samples, non-destructive analysis, decreased production of hazardous waste, low start-up and running costs, increased total speed and throughput, and comparable measurement quality (Kilbride et al., 2006; Parsons et al., 2013; Radu and Diamond, 2009). Based on the triplicate analyses of the soil samples spiked with 10−1500 $\mathrm{mg\,kg^{-1}}$ Cu by both ICP-MS and pXRF, the results show that the difference between the two analytical methods was $\leqslant$ 8%, demonstrating the reliability of pXRF analyses. Samples of the contaminated soil and RFM were first dried, pulverized using a mortar to be in the form of loose powders, and then filled in the XRF sample cups for heavy metal concentration analysis (Rouillon et al., 2017; Rouillon and Taylor, 2016). The procedure for the elemental analysis of heavy metals was conducted by Vanta software inserted in the XRF instrument, which is regularly calibrated. Standard reference materials (NIST 2710) were used as calibration verification checks (Peralta et al., 2020), with a bias (systematic error) of <3%. All the analysis was performed in triplicate, and the result was calculated as the average (Ma et al., 2010). The functional groups of the soil were detected using a Fourier transform infrared (FTIR) spectrometer on a Miracle-10: Shimadzu Spectrometer before and after EK-RFM application. Energy-dispersive X-ray spectroscopy (EDS) in conjunction with scanning electron microscopy (SEM) was taken for detecting the soil and RFM elemental composition by Zeiss Evo-SEM with an acceleration voltage of 15 kV for EDS collection. The zeta potential values of the RFM were measured using a Nano-ZS Zeta-seizer (Model ZEN3600) from Malvern Panalytical before and after the EK treatment. The specific surface area was determined using Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherms and the Barrett-Joyner-Halenda (BJH) method, respectively, by using a Micromeritics 3-FlexTM surface characterization analyzer at 77 K.

Faculty of Engineering and Information Technology

CHAPTER FOUR:

COPPER REMOVAL FROM CONTAMINATED SOIL THROUGH ELECTROKINETIC PROCESS WITH REACTIVE FILTER MEDIA

CHAPTER FOUR: COPPER REMOVAL FROM CONTAMINATED SOIL THROUGH EK PROCESS WITH RFM

This chapter has been constructed from the following publication:

Romina Ghobadi, Ali Altaee, John L. Zhou, Peter McLean, Sudesh Yadav *“Copper removal from contaminated soil through electrokinetic process with reactive filter media”* **Chemosphere**, 252 (2020): 126607.

4.1. Introduction

Soil provides essential resources to both humans and nature (Lima et al., 2017), and soil contamination is a globally significant concern, which may result from a variety of agricultural, industrial, and other human activities (Belhaj et al., 2016; Bi et al., 2011; Cameselle et al., 2013; Gomes et al., 2012; Nguyen et al., 2019). Heavy metals are widely detected in soil and are of great risk to the environment and public health due to their toxicity and persistence (Nguyen et al., 2019; Yuan et al., 2016a). Great efforts have been made to overcome the problems associated with soil pollution by developing different strategies and methods (Song et al., 2017). EK remediation stands out as an alternative technique that overcomes the shortcomings in the other decontamination techniques, such as applicability for the low-cost and on-site treatment of low-permeability soils (Agnew et al., 2011). EK soil remediation has been tested under laboratory and field conditions for potential soil remediation and treatment (Fu et al., 2017; Hassan et al., 2015; Iannelli et al., 2015; Kim et al., 2011; P.V. Sivapullaiah, B.S.N Prakash, 2015; Zhao et al., 2016). Regarding the results of laboratory tests and field applications, the EK remediation technique has several barriers when applied as a single remediation process (Peng et al., 2011). When the direct current is imposed across the treated soil, an alkaline pH front is developed near the cathode region, resulting in contaminants precipitation and retarding further contaminants transport and removal. On the other hand, contaminants precipitation in the soil near the cathode requires further treatment to prevent contaminants from the rebound in the soil.

Progress has been made to enhance the extraction efficiency of EK remediation in the last decades (Lim et al., 2004; Lima et al., 2017; Lohner et al., 2008; Yeung, 2011; Yeung and Gu, 2011; Zhao et al., 2016). The current efforts focus on improving the efficiency of the EK process and facilitating its applicability by adding enhancement agent such as surfactants and chelating agents to enhance the contaminant mobility, or acids/bases solution to control the pH of the electrolyte, and application of a combined system such as EK-bioremediation, EK-phytoremediation, and EK-PRB (J. Li et al., 2020; Lim et al., 2004; Lohner et al., 2008; Yeung and Gu, 2011). However, the choice of an appropriate enhancement technique is significantly important in the EK system in terms of treatment duration, cost, and environmental impact. For example, the application of the enhancement agent may affect the soil matrix; then, the electrolyte ought to be recouped at the end of the EK treatment (Lim et al., 2016; Yeung, 2011). The application of enhancement agents in the EK remediation system has not always been favoured since some laboratory tests were unsuccessful (Tian et al., 2017). The capability of an EK remediation process utilizing blends of eco-friendly improving agents (e.g., rhamnolipids, saponin, citric acid) was evaluated for the first time by Tian et al. (2017) to simultaneously remove contaminants including Cd, Cr, Cu, Pb, Zn and PAH/PCB from harbor sediments. Their experimental results demonstrated that the mixture of the agents could only remove small quantities of metals (4.4–15.8%) and only a slightly better removal of PAH (29.2%) and PCB (38.2%). Among these enhancement techniques, PRB offers the enrichment or detoxification of the contaminants with a short treatment period and prevents the contamination of the catholyte solution (Zhao et al., 2016). A range of experimental studies has been recently conducted to integrate PRB application with EK to improve contaminants removal from the soil during the EK remediation (Cang et al., 2009; Ma et al., 2010; Ren et al., 2014; Yuan et al., 2009; Yuan and Chiang, 2007; Zhao et al., 2016). When a PRB is combined with electrochemical remediation, the transport of contaminants through the barrier is provided by the electroosmotic flow of soil pore fluid, electromigration of charged species, and electrophoresis of charged particulates. The reactive barrier becomes an adsorbent for the contaminants during the electroosmosis and electromigration process. One of the significances of the EK-PRB approach is the reduction of contamination concentration in the catholyte and anolyte solutions (Zhao et al., 2016), therefore eliminating the need for their recycling. The sorption and degradation reactions of many contaminants are pH-dependent; hence the pH gradient generated by the EK remediation process may affect the sorption and degradation mechanism in PRB (Yeung and Gu, 2011). When a PRB is applied in the EK remediation system to improve its remediation efficiencies of organic, inorganic, or mixed contaminants, consideration should be given to factors such as the type, cost, and particularly the lifetime of reactive media, which would limit its applications. The treatment media in PRBs implemented with EK may include different kinds of adsorbent materials such as zero-valent iron, activated carbon, and activated bamboo charcoal (Cang et al., 2009; Ma et al., 2010; Ren et al., 2014; Yuan et al., 2009; Yuan and Chiang, 2007; Zhao et al., 2016). Among all PRBs, ZVI is the most popular reactive material due to its low cost (Cang et al., 2009). However, the lifetime of ZVI is short because of the contamination coating the surface of the ZVI particles, preventing flow through the barrier (Cang et al., 2009). Additionally, iron reactivity can be decreased if exposed to silica or natural organic matter (Cang et al., 2009; Ren et al., 2014). In an investigation into the application of ZVI as a PRB in EK remediation of Cr-contaminated soil, Cang et al. (2009) reported that the electrochemical remediation coupled with a ZVI-PRB could achieve 72% removal efficiency of Cr, and the amount of Cr in the anolyte and catholyte was smaller when EK was combined with ZVI.

The application of AC as RFM in the EK system was evaluated in the copper-contaminated kaolinite soil. AC is widely used as an adsorbent material in both water and soil treatment as it has shown the high performance of contaminants removal (Ahmed et al., 2015; Ando et al., 2010; Bhatnagar et al., 2013; Brändli et al., 2008). Due to its high surface area, AC removes metal contaminants from the soil through surface adsorption (Üçer et al., 2006). Despite the advantages of AC, there are also concerns such as the high production costs and availability of sufficient amounts of suitable AC forms (Ahmed et al., 2015; Alhashimi and Aktas, 2017). Accordingly, intensive research uses alternative carbon material, especially biochar, for contaminant removal (Ahmed et al., 2015; Alhashimi and Aktas, 2017; Beesley et al., 2010). Alhashimi and Aktas (2017) reported that BC has lower energy demand and global warming potential impact than AC. In recent years, BC has been successfully applied to reduce the mobility of heavy metals in soil because of its affinity for heavy metals, low cost, and availability (Alhashimi and Aktas, 2017; Beesley et al., 2010; Khalid et al., 2017; Zeng et al., 2015). BC has some significant features such as higher porosity, high surface area, variable charge, and functional groups, and when added to the soil, can change the soil properties (Anawar et al., 2015; Beesley et al., 2010). As a result, these features can enhance soil water-holding capacity, pH, surface sorption capacity, cation exchange capacity (CEC), and base saturation (Anawar et al., 2015; Beesley et al., 2010).

In the EK process, the extraction of heavy metal ions precipitated in the soil near the cathode region complicates the remediation process due to the low permeability of most contaminated soils. Studies on the impact of RFM on the performance of the EK process for metal removal from the soil are scarce. This study investigated the performance of the EK process for copper removal using AC and BC as RFM. BC has a high affinity for heavy metal adsorption, and there is no study yet comparing the impact of the type of RFM on the efficiency of heavy metal removal in the EK process. The impact of AC and BC as RFM on the removal of heavy metals from soil and the energy requirements for the EK treatment were investigated and compared with the conventional EK process (without RFM). This study selected copper as the heavy metal contaminant due to many reports on soil contamination by copper ions (Boiteau et al., 2011; Hadri et al., 2012), which requires remediation. Furthermore, AC and BC RFMs have the potential of buffering alkaline pH near the cathode and hence the advancement of an alkaline front in the soil. RFM is loaded close to the cathode zone to trap copper ions precipitated in the soil near the cathode. The high permeability of AC and BC will facilitate the extraction of copper ions at the end of the EK process, while AC and BC RFMs will be recycled and reused. Both AC and BC are cost-effective and permeable and have good adsorption capacity for heavy metals; hence, they can provide long-term services as they can be regenerated by acid leaching. This study will provide valuable knowledge of the performance of RFM in the EK system while comparing their performance in terms of removal efficiency and regeneration potential.

4.2. Material and Methods

4.2.1. Materials and soil preparation

Detailed descriptions of the materials, soil preparation, and the apparatus used in the EK experiments are found in **Chapter 3**. AC and BC RFM were used in two separate EK remediation processes under the same experimental conditions to investigate the feasibility of copper removal from the kaolinite soil. In each experiment, a measured amount of RFM was placed in the soil compartment close to the cathode to trap the copper ions and buffer the advancement of the soil's alkaline front. The chemical and physical properties of the soil and RFM used in this study are presented in **Chapter 3** (**Table 3.1 and 3.3)**. Briefly, 25 g of GAC was evaluated as an adsorbent for the copper removed by the EK process. At the end of the EK experiment, precipitated copper ions were leached out of AC RFM by flushing with an acid pH solution before reuse to reduce the treatment cost. BC (25 g) was packed in the EK cell near the cathode to capture copper ions. Similar to the soil pH measurement procedure, the pH of AC and BC was determined to be slightly alkaline at 8.2 and 8.95, respectively, which is suitable for the precipitation of copper ions (**Chapter 3, Table 3.3**). The permeability of the RFMs was measured by the constant head flow permeability test, which was recommended for the coarse-grained soils with regard to AC and BC particle sizes (**Chapter 3, Table 3.3**).

4.2.2. EK test design

Four sets of EK experiments were conducted to investigate copper removal from the contaminated kaolinite soil (**Table 4.1**). A constant voltage (10 V) was applied across the electrodes in all tests, except in Exp. 4, which was performed under a constant current of 20.00 mA. The experiments were stopped after seven days when the electric current across the soil specimen diminished, and the electroosmotic flow was decreased.

Exp. 1 was the conventional EK experiment on spiked kaolinite with 1000 mg kg^{-1} copper concentration. Exp. 2 and Exp. 3 were carried out to investigate the effect of RFM, AC and BC, respectively, on the electrokinetic removal of copper from the kaolinite soil. Exp. 4 was implemented to investigate the performance of EK-RFM under a constant electrical current of 20.00 mA.

As described in **Chapter 3** (**Section 3.2.6**), aqueous solutions from the anode and cathode compartments and the electrode assemblies were collected at the end of the experiments. Then, the soil specimen was divided into five equal sections, and each section was preserved in plastic bags. Each soil section was then homogenized, and samples were taken for pH, EC, and copper concentration measurements.

Table 4.1. Summary of the experimental conditions.

Experiment	Type	RFM	Applied constant Voltage (V)	Applied constant Current (mA)	Cu ($mg\ kg^{-1}$)	Treatment duration (d)
Exp. 1	EK	-	10	6.20-15.00	1000	7
Exp. 2	EK-AC	Activated carbon	10	2.51-7.90	1000	7
Exp. 3	EK-BC	Biochar	10	3.20-14.90	1000	7
Exp. 4	EK-BC	Biochar	12.46-35.22	20.00	1000	7

4.3. Results and discussion

4.3.1. Electrical current

During the electrokinetic treatment, electrical current through soil cell is strongly correlated with the content of free ions; hence, electrical current is an essential factor affecting the efficiency of contaminants transmission through soil (Zhou et al., 2017; Zhu et al., 2016). The change of electric current over time in Exp. 1 to Exp. 3 is shown in **Figure 4.1a**. Generally, in the EK system, the electric current initially increased to a maximum value within a short time due to the solubilisation and movement of ions in the soil towards the cathode compartment (Ammami et al., 2015). Then, the electric current gradually reduced as a result of metal ions precipitation close to the cathode zone or in the high soil pH (Ammami et al., 2015; Bahemmat et al., 2016; Zhu et al., 2016). With increasing electric current, the higher copper removal was achieved by the EK test. The electrical current was low at the beginning of the EK experiments since it takes time for anolyte and catholyte to enter the contaminated soil and for contaminant ions to dissolve and desorb from the soil (Zhou et al., 2017). The electrical current in the EK and EK-BC experiments was higher than that in the EK-AC test. In the EK experiment, the electric current reached the peak (15.00 mA) after 24 h but started decreasing dramatically thereafter due to the depletion in the migration of copper ions in soil-pore fluid and the precipitation of $Cu(OH)_2$ at the cathode region. The electrical current reached 7.21 mA after 168 h at the end of the EK treatment. The electric current in the EK-BC reached a maximum amount of 14.90 mA after 48 h, then dropped to 6.79 mA at the end of the EK process. However, in this experiment, the electric current remained higher for a longer period compared to that of the EK test. The reason may be attributed to the adsorption of hydroxide ions generated at the cathode reaction by BC, which promoted the transport of the acid front in the soil. This caused solubilisation and movement of copper ions in the soil and increased the electric current in the EK-BC test. The average electric current was similar between the EK-BC (11.33 mA) and EK (11.30 mA) processes. The electric current in the EK-AC test was relatively low, with the average and maximum electric current of 5.52 mA and 7.90 mA, respectively, which would adversely affect the removal of copper ions in the soil.

4.3.2. Soil pH

Soil pH has a significant impact on the environmental behaviour of heavy metals in soil. A low pH environment can improve the dissolution of heavy metals and remove contaminated soil (Yuan et al., 2016a). Chemical reactions during the EK process would cause a substantial change in soil pH and result in contaminant dissolution or precipitation (Cameselle et al., 2013). The distribution of pH across the soil from anode to cathode (sections 1 to 5) after the remediation experiments is shown in **Figure 4.1b**. It is clear that the EK process changed the soil pH. In general, the soil pH after EK treatment was low in sections close to the anode side due to hydronium ions transport across the soil, but gradually increased in the soil sections close to the cathode as a result of hydroxide ions (OH^-) migration in the soil from the cathode to the anode (Fu et al., 2017; Yuan et al., 2016a). The reduction in pH favoured the removal of the contaminants because of the production of H^+ ions from water electrolysis at the surface of the anode ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) (Masi et al., 2017b; Zhao et al., 2016). An increase in the soil pH in the sections near the cathode was due to the advancement of OH^- generated through water electrolysis at the cathode ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) and affected the pH distribution across the soil. As observed in **Figure 4.1b**, the pH profile from section 1 to section 5 in the EK-BC test was lower than that of the EK and EK-AC experiments, especially in the soil sections close to the cathode region (sections 3 to 5), which would favour copper removal by EK-BC. It was probably caused by the interaction between BC and hydroxide ions in the soil near the cathode. EK-AC test generally showed higher soil pH in sections 1 to 4 (except section 5), compared to those of the EK and EK-BC experiments. Higher pH across the soil sections confirmed that AC in the EK system did not assist in removing copper ions from the soil sections close to the anode side. However, the soil pH in section 5 was lower in the EK-AC than in the EK, resulting in less copper precipitation in the soil close to the cathode (**Figure 4.2**). It seems that both RFMs could trap contaminants by lowering the soil pH close to the cathode. However, AC RFM unfavourably served during the EK process for copper removal in most soil sections compared to the EK and EK-BC (**Figure 4.2b**). **Figure 4.1b** shows that the soil pH with the value above the initial pH of the soil (pH 5.44) would cause contaminant precipitation in the soil during the EK treatment, as observed in section 5 in all EK tests with or without RFM. EK treatment also affected the pH of RFMs, especially BC, which dramatically increased from 8.95 to 11.07 while the pH of AC changed from 8.2 to 9.34.

4.3.3. Electrical conductivity of soil

After seven days of EK treatment, the soil EC of different sections presented a decreasing trend from the anode to the cathode (**Figure 4.1c**). In general, soil EC results were consistent with those of soil pH, demonstrating that the content of free ions in the soil near the anode region was higher than that close to the cathode. The reason would be that the acid condition facilitated the dissolution of ions in the soil, as demonstrated in **Figure 4.1c**. The soil conductivity of the EK-AC was the lowest because of copper precipitation in the soil at an early stage of the EK process and hence reduced the soil EC. Additionally, acid and alkaline fronts met closer to the anode in the EK process when AC was applied as an RFM. EK-BC showed more electrical conductivity because of more copper solubilisation due to the migration of acid front closer to the anode and hence solubilizing more copper ions. The soil EC in the EK-BC test was higher than that of the EK and the EK-AC systems, because of the lower soil pH in the EK-BC, which caused the higher dissolution of copper ions in the soil.

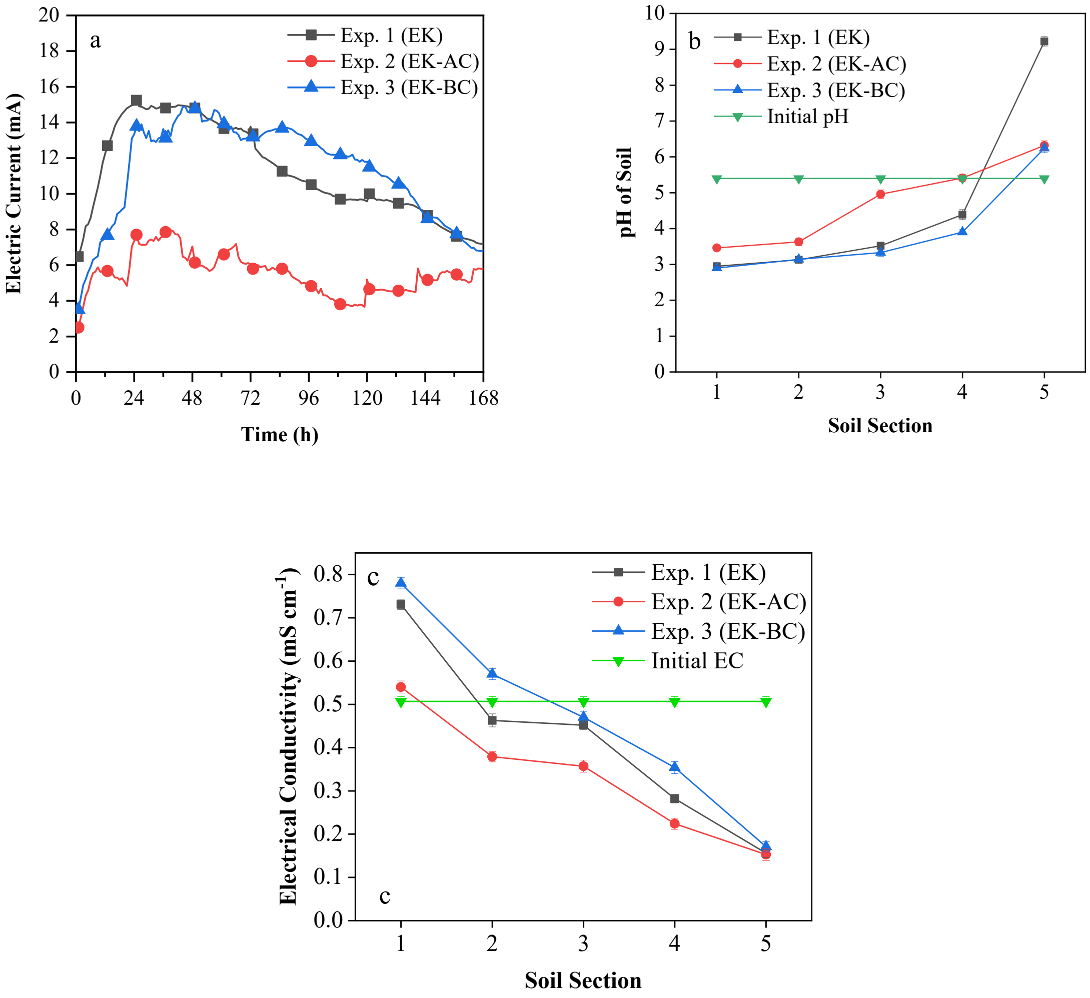


Figure 4.1. (a) Change of electric current during the EK treatments (with a constant applied voltage); (b) pH of different soil sections (normalized distance from anode to cathode) after the EK operations; (c) EC of different soil sections (normalized distance from anode to cathode) after the EK operations.

4.3.4. Removal of copper from soil

Figure 4.2a shows the distribution of residual copper in the soil after remediation. Copper distribution in the soil follows the soil pH profile, which is very acidic close to the anode side and continuously increased towards the cathode, where it is slightly alkaline (**Figure 4.1b**). For the EK and EK-BC, copper concentrations were found to be lower than the initial concentration of copper in the soil, particularly in the sections close to the anode (sections 1 to 4) (**Figure 4.2a**). Most copper ions were accumulated in section 5, close to the cathode region through precipitation as $Cu(OH)_2$ due to the high soil pH.

The residual concentrations of Cu in the soil sections, especially in sections 3 to 5 for the EK with BC RFM (Exp. 3) were significantly lower than those of the EK and EK-AC tests. Cu transport rate toward the cathode was enhanced in the EK-BC compared to the EK and the EK-AC. This is probably due to the lower soil pH (**Figure 4.1**) in the EK-BC, which enhanced the efficiency of the EK process and copper removal. In the EK-BC experiment, the concentration of Cu decreased rapidly from the initial concentration (1000 mg kg^{-1}) to about 100 mg kg^{-1} in section 1, gradually increased to about 500 mg kg^{-1} in section 4, and reached 2490 mg kg^{-1} in section 5. For the EK-AC test, copper concentrations were lower than the initial concentration in sections 1 and 2, ranged between 230 mg kg^{-1} and 650 mg kg^{-1}, and showed no significant changes in section 3 to section 4 compared with the initial Cu concentration. The results indicate that copper concentration in the soil was not affected when the soil pH was around the initial pH of the soil (**Figure 4.1b**). Compared to the EK experiment, the integration of AC RFM in the EK system decreased Cu concentration, mainly in section 5, which adversely affected the Cu transport rate in the other soil sections toward the cathode. In the EK only process, the content of copper close to the anode was low, ranging from about 100 mg kg^{-1} to 220 mg kg^{-1} in sections 1 to 2, which is similar to that in the EK-BC. Then it reached approximately 950 mg kg^{-1} in section 4 and drastically increased to around 3250 mg kg^{-1} in section 5 while getting close to the cathode because of the high pH in the region. The removal efficiency was calculated by Eq. (3.1). As shown in **Figure 4.3b**, in soil sections 1 to 4, the copper removal ranges from 92% to 47% in the EK-BC system, while it changes from 92% to 6.5% for the EK experiment. Hence, the application of BC in the EK system has not only affected the Cu removal in section 5 but considerably in sections 3 and 4. For the EK-AC test, the Cu removal percentage was 78% in section 1, then decreased to almost zero in sections 3 and 4. High pH in section 5 resulted in the negative removal of Cu there for the EK experiments. However, the negative removal in that section for the EK-AC test was less due to the low Cu transport rate through the soil. Hence, less free Cu ions were transported across the soil from the anode to the cathode during the EK-AC treatment. **Table 4.2** shows the mass balance and overall Cu removal in the EK experiments. The overall copper removal in the EK-AC and the EK-BC was 10% and 27%, respectively, higher than that in the EK test. The application of BC represented the highest removal in the EK system without adding chemicals. The soil pH was expected to be responsible for the different removal efficiencies of copper in the EK treatments. According to the mass balance, the best performance was obtained when BC was loaded in the EK cell near the cathode compartment (Exp. 3).

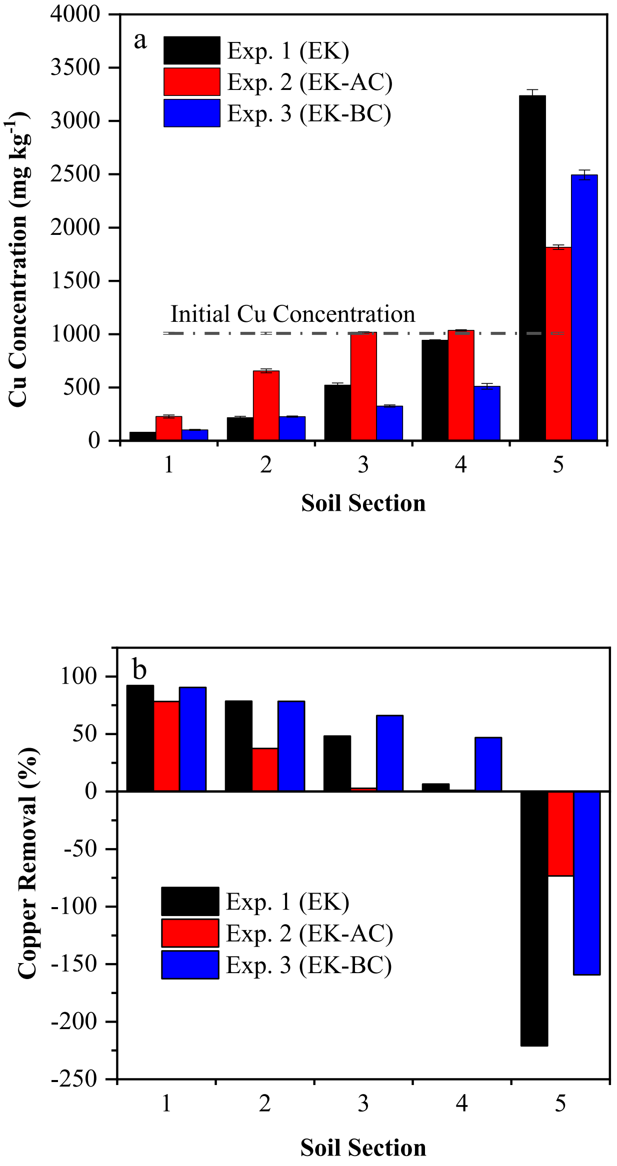


Figure 4.2. (a): Copper concentration through the soil sections (from anode to cathode) after EK Operation; (b): Efficiency of copper removal through the soil sections.

Table 4.2. Mass balance and removal efficiency of copper in the EK experiments.

Experiments	Initial Cu in soil (g)	Residual Cu in treated soil (g)	Cu mass in RFM (g)	Cu mass in electrolyte solution (g)	Cu mass in soil pore water (g)	Mass balance (%)	Cu removal (%)
Exp. 1	1.01	1	-	0	0.008	99.80	1
Exp. 2	1.02	0.92	0.053	0	0.007	96.08	10
Exp. 3	0.98	0.71	0.21	0	0.005	94.39	27

4.3.5. Characterisation of RFMs

The surface characteristics of RFMs, which were examined by SEM coupled with EDS (**Figure 4.3**), clearly confirmed the presence of copper on BC and AC after the EK treatment. The percentage of copper in BC was higher than that in AC RFM. EDS results showed that the Cu content was 0.38% in BC and only 0.10% in AC, indicating that the removal of copper in the EK treatment with BC RFM was higher than that in using AC RFM. Also, the zeta potential measurements of the RFMs before and after EK experiments illustrated that the zeta potential of BC was more negative than AC before EK treatment (**Figure 4.4**), suggesting more negative charges being available in BC than in AC. Therefore, BC can potentially adsorb larger amounts of the positively charged heavy metal cations than AC. FTIR spectra are widely used to provide valuable information on the functional properties of BC and AC (Ahmed et al., 2017; Lu et al., 2013). Both BC and AC before and after EK treatment presented approximately the same spectra. However, stronger bands have been observed in BC, before and after EK treatment, compared to those in AC-EK operation, demonstrating the great potential of EK-BC for copper removal. The FTIR spectra from BC and AC after EK treatment (**Figure 4.5**) showed a peak in the region 3600-3700, related to OH stretching. A strong band at approximately 1002.5 cm^{-1} is presented in EK-BC spectra attributed to copper absorption.

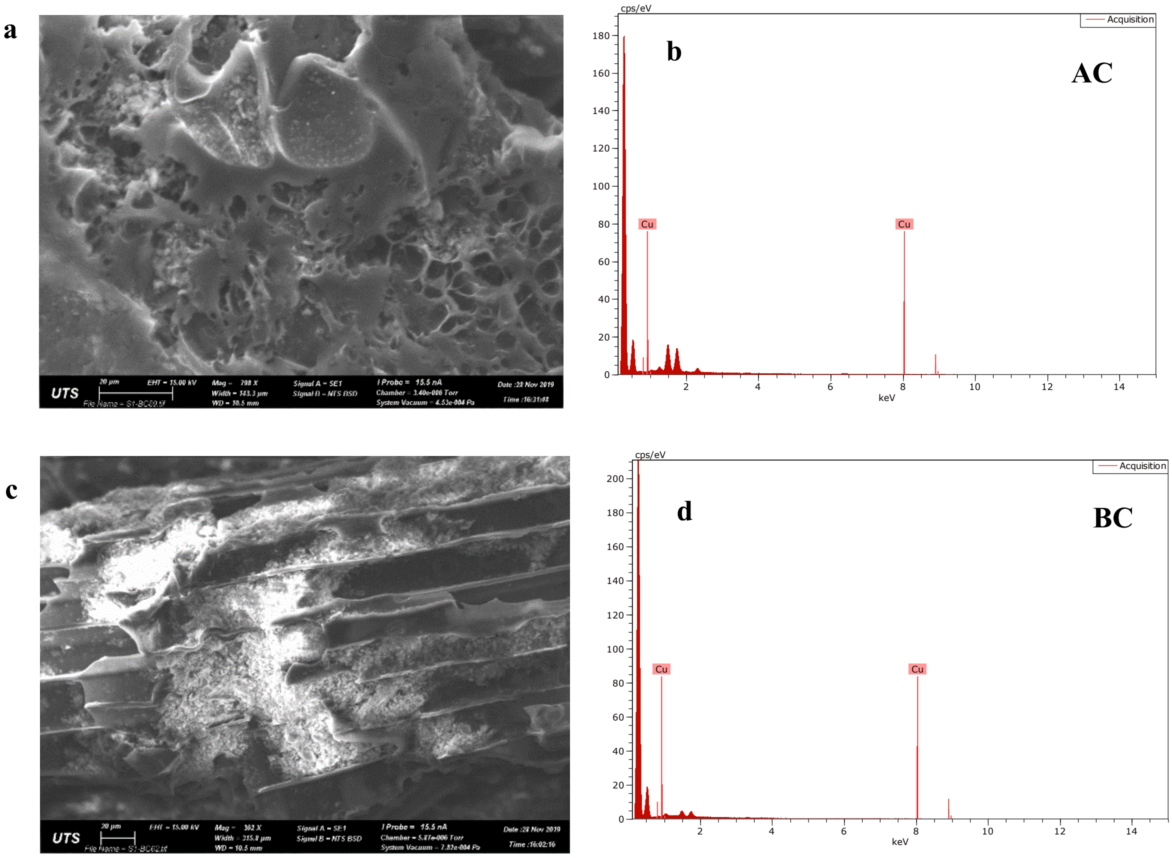


Figure 4.3. SEM images and EDS of (a, b) activated carbon and (c, d) biochar after EK treatment.

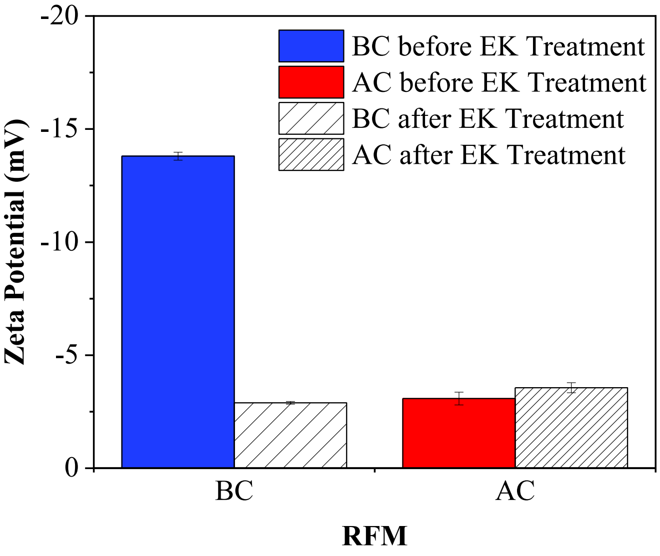


Figure 4.4. Zeta potential of BC and AC before and after EK experiments.

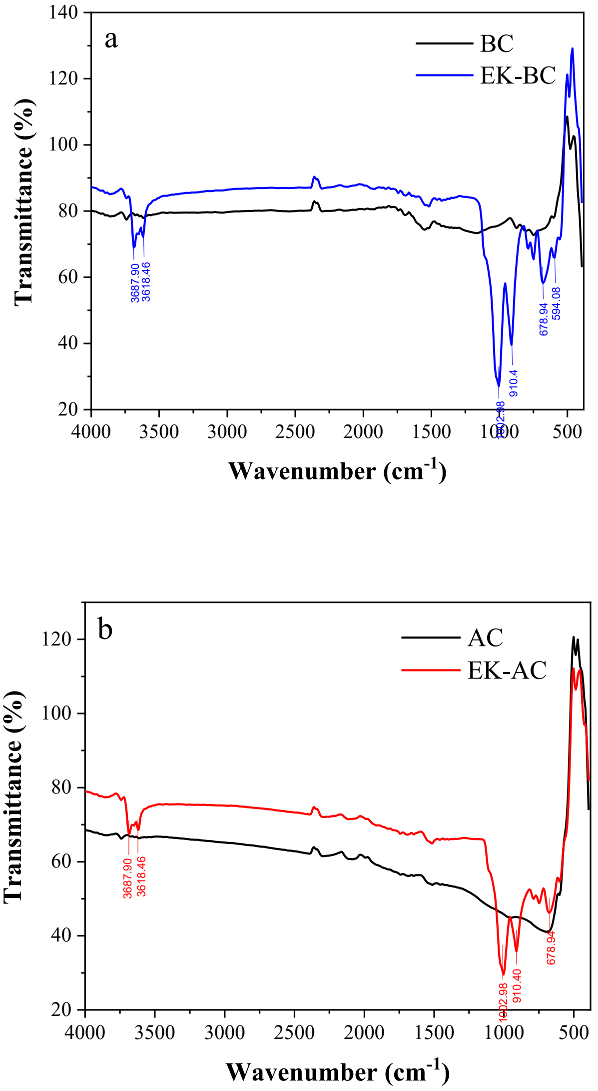


Figure 4.5. Fourier transform infrared (FTIR) spectra of (a) BC before and after EK treatment (EK-BC); (b) AC before and after EK treatment (EK-AC).

4.3.6. Performance of EK-RFM under constant current

Since the EK treatment with BC RFM exhibited a higher copper removal efficiency in the contaminated kaolinite soil, further EK-BC experiments were carried out under a constant current of 20 mA to explore for treatment improvement. Copper concentrations in sections 1 to 4 significantly reduced, ranging from 50 mg kg^{-1} to 294 mg kg^{-1}, and the majority of copper was precipitated in section 5. Moreover, 26% of Cu was captured by BC. Approximately

70.6%-95.0% of copper removal was successfully achieved from sections 4 to 1 at an electric current of 20 mA. The reason is due to a high electric current, which promoted water electrolysis reaction at the anode and generated more hydronium ions that migrated across the soil and facilitated the removal of copper ions from the soil. **Figure 4.6** shows that soil pH was acidic, except in section 5, which was higher than the initial soil pH (5.44). This alkaline pH retarded copper ions dissolution and resulted in significant copper precipitation in section 5 close to the cathode compartment. It is concluded that maintaining a constant electric current in the EK-BC operation could significantly enhance copper removal in the first four soil sections close to the anode but did not decrease copper accumulation in section 5.

In addition, the energy consumption Eu (Wh m^{-3}), which is a major factor affecting the total cost of the EK remediation (Masi et al., 2017b; Yuan et al., 2017), was calculated by Eq. (3.3) (W. S. Kim et al., 2012). The energy consumption per unit volume of soil in the EK experiments (**Figure 4.7**) shows that the EK-AC approach was the least demanding, and the EK-BC (constant current) was the most demanding. Low energy consumption observed in the case of EK-AC would be due to less ion migration through the soil sections 1 to 4, which was compatible with the results shown in **Figure 4.1**. The EK and EK-BC experiments carried out under a constant voltage required almost the same power consumption value, at 10.78 and 10.81 kWh m^{-3}, respectively. Of all tests, the EK-BC under a constant electrical current consumed the highest energy amount (43.5 kWh m^{-3}). At a constant electric current, high concentrations of dissolved ions would be transferred through the system, particularly through the soil sections 1 to 4, which in turn increased the rate of electrolysis reactions at the electrodes by sustaining the electric current and thus producing the increased energy expenditure in this experiment. Such a high energy consumption may limit its practical application compared with fixed voltage tests since there was no significant difference in overall Cu removal efficiency. However, using the solar cell-based power supply for EK remediation treatments will reduce energy consumption compared with traditional power supply (Jeon et al., 2015; Zhou et al., 2017).

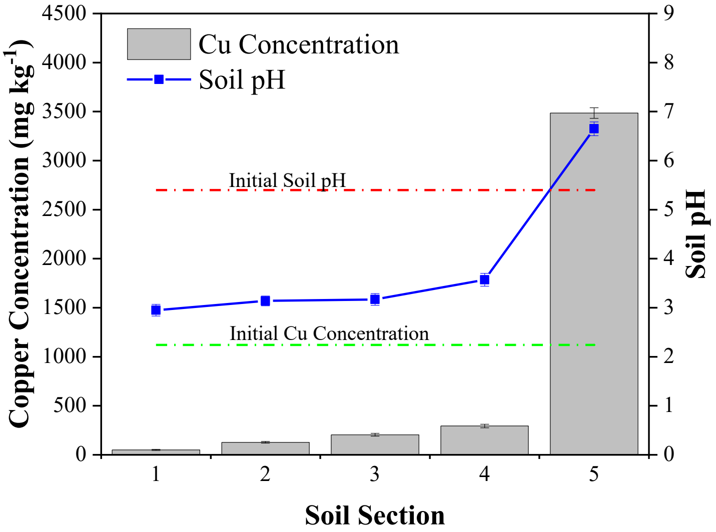


Figure 4.6. Residual copper concentration and pH of the soil through the soil sections from anode to cathode after EK-BC under constant current operation.

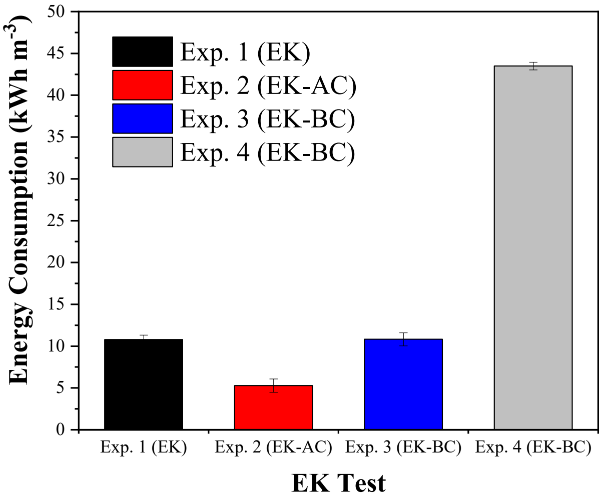


Figure 4.7. Energy consumption per unit volume of soil treated by EK.

4.3.7. Regeneration of RFM

In order to be practicable, the regeneration of RFM is essential. After leaching, samples of RFM were tested for the copper concentration by the XRF analyser. Moreover, the permeability of the RFMs was measured by performing a constant head permeability test, and the result (**Chapter 3, Table 3.3**) demonstrated a high permeability of AC. However, XRF results suggested a higher copper recovery by BC at 99.3% than by AC at 78.4%. Therefore, the findings favour BC for the regeneration process to be reused as RFM for future EK experiments.

4.4. Conclusions

This study investigated the remediation of Cu-contaminated soil with integrated EK-RFM treatment. The removal efficiency of Cu increased with the application of RFM, which trapped copper. The overall removal efficiency of the EK process decreased as EK-BC > EK-AC > EK. BC adsorption of copper facilitated Cu removal in all soil sections while applying AC as RFM improved Cu removal only in soil section 5 near the cathode. Integration of AC with EK technique increased soil pH in most soil sections, except section 5, and reduced the electric current through the soil. This reduced the rate of copper removal in the majority of soil sections in the EK-AC system. However, AC RFM adsorbed a considerable amount of Cu in soil section 5 due to interactions between AC and hydroxide ions near the cathode. SEM-EDS results confirmed the presence of copper on BC and AC after EK treatment, whereas the percentage of copper in BC was higher than that in AC. In addition, the more negative charges available in BC than in AC could offer a higher copper removal from contaminated kaolinite soil in the EK-BC treatment. BC could be easily recovered by acid leaching after EK treatment; however, it has lower permeability compared to AC. The application of a fixed electric current in the EK-BC process significantly enhanced the removal rate of copper in the soil, especially in sections 1 to 4, by lowering the soil pH. However, its high energy consumption may be a constraint in its wide application. It is concluded that BC is a better RFM than AC in terms of EK performance, Cu removal and regeneration. As the EK-RFM process has many advantages, including short treatment duration, easy installation, efficient contaminant removal, no chemical addition, and feasibility of regeneration, it is a good technique for future sustainable soil remediation.

Faculty of Engineering and Information Technology

CHAPTER FIVE:

ENHANCED COPPER REMOVAL FROM CONTAMINATED KAOLINITE SOIL BY EK PROCESS USING COMPOST RFM

CHAPTER FIVE: ENHANCED COPPER REMOVAL FROM CONTAMINATED KAOLINITE SOIL BY EK PROCESS USING COMPOST RFM

This chapter has been constructed from the following publication:

Romina Ghobadi, Ali Altaee, John L. Zhou, Peter McLean, Namuun Ganbat, Donghao Li "*Enhanced copper removal from contaminated kaolinite soil by electrokinetic process using compost reactive filter media*", **J. Hazard. Mater.** 402 (2021) 123891.

5.1. Introduction

Soil contamination by heavy metals is a global environmental issue and may cause serious environmental risk and potential harm to human and living organisms (Y. Liu et al., 2016; Yuan et al., 2016b). For example, soil samples from a former wood impregnation site north of Copenhagen, Denmark, contained 1662 mg kg^{-1} of copper among a suite of heavy metals (Frick et al., 2019). Similarly, as high as 800 mg kg^{-1} of copper was detected in soils from vineyards in France (Fagnano et al., 2020). Therefore, remediation technologies that ensure the removal of heavy metals with the least damage to the soil environment are urgently sought. EK treatment is an emerging technique for heavy metals removal from soils, especially those with low permeability, which are usually difficult to be treated (Hassan et al., 2015; Iannelli et al., 2015; Sun et al., 2019; Yuan et al., 2017), by imposing a small electric field between electrodes installed in the contaminated soil (López-Vizcaíno et al., 2017; Peppicelli et al., 2018; Yuan et al., 2017). Heavy metals are typically extracted from soil mainly by electromigration mechanism during the EK remediation treatment. The removal of heavy metal contaminants from the soil in the EK process is significantly pH-dependent. An alkaline front is developed and responsible for the precipitation of heavy metal ions close to the cathode. This alkaline condition would lead to the heavy metals' sorption on soil particle surfaces and/or their precipitation in the soil pores, which may make the heavy metals immobile temporarily and difficult to remove (Yeung, 2011). The application of EK remediation can only remove mobile heavy metals from soil sections near the anode so that heavy metals precipitate in the soil close to the cathode zone, where base and acid fronts meet. Therefore, there is an increasing demand to develop enhanced EK techniques, which can mitigate the advancement of the alkaline front by providing the desired soil pH for heavy metals removal (Yuan et al., 2016b). A low pH condition would enhance the removal of heavy metals from the contaminated soils, by improving desorption of the majority of heavy metals from the surface of the soil (Al-Shahrani and Roberts, 2005). In laboratory EK experiments, the catholyte compartment was treated by applying an enhancement agent such as surfactants, chelating agents (Hahladakis et al., 2014; Kaya and Yukselen, 2005), or acids/bases (Al-Shahrani and Roberts, 2005; Iannelli et al., 2015; Suzuki et al., 2013) to increase the contaminant mobility or to adjust the pH. Bahemmat et al. (2016) investigated the use of fulvic and humic acids as chelating agents as well as the effects of catholyte conditioning to improve EK remediation efficiency in highly heavy metals contaminated soil. They indicated that both humic substances and catholyte conditioning with 0.1 N HNO_3 enhanced the remediation efficiency of heavy metals by two to three times after 20 days, compared to the conventional EK treatment. Yuan et al. (2016b) proposed an enhanced EK remediation using citric acid and $CaCl_2$ for the removal of heavy metals from a contaminated kaolinite soil. They reported an improved remediation process compared to other agents (e.g., HCl) in terms of metal removal, power consumption and environmental risk. In studying two different conditioning electrolytes (polyaspartic acid, citric acid) for EK remediation of industrial chromium waste, Fu et al. (2017) showed that citric acid was merely effective for total Cr removal. Moreover, energy expenditure was increased in EK remediation by adding the enhancement agents because of water electrolysis, heat loss, and ions transport compared to deionized water as the electrolytes (Fu et al., 2017). Iannelli et al. (2015) investigated the effect of conditioning agents such as citric acid, oxalic acid, ascorbic acid, HCl, HNO_3, H_2SO_4, and EDTA for the extraction of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) from marine sediments. They reported that although sulphuric acid enhanced the removal efficiency, it produced significant sulphates precipitation in the solid material and catholyte. In addition, HCl acid was the most effective for the metals; however, significant chlorine gas was produced at the anode that required further gas treatment (Iannelli et al., 2015). The review demonstrated that although strong acids could overcome the major drawback of the EK process by preventing the advancement of the alkaline front in soil, they would increase the power consumption and treatment duration (Al-Shahrani and Roberts, 2005). Moreover, some soil properties such as pH and electrical conductivity may be altered by the addition of the enhancement agent (Bahemmat et al., 2016). Additionally, the electrolyte should ideally be recovered after EK treatment, which will otherwise increase the remediation cost (Lim et al., 2016; Yeung, 2011). Some enhancement agents may not be practical for the removal of heavy metals (Tian et al., 2017), and their application in full-scale EK remediation may often be unsuccessful (Iannelli et al., 2015; Tian et al., 2017). Besides the enhancement agents, there are hybrid techniques to extract the heavy metals, such as EK-phytoremediation (Bi et al., 2011; Cang et al., 2011), EK-bioremediation (Lee and Kim, 2010), and EK remediation coupled with a permeable reactive barrier (Xue et al., 2017; Yuan and Chiang, 2007). However, among these combined techniques, PRB can facilitate the removal of heavy metals with a short operation period and prevents the contamination of the catholyte solution (Ghobadi et al., 2020; Yuan and Chiang, 2007), which make the technique cost-effective. PRB serves as an adsorbent during the electromigration and electroosmosis process to trap the metal ions transported from the contaminated soil.

To overcome the limitations of existing approaches using chemical agents in the EK process, PRBs made of activated carbon, activated bamboo charcoal, and zero-valent iron (Ma et al., 2010; Ren et al., 2014; Xue et al., 2017; Yuan and Chiang, 2007) have been used, which have shown better performance compared with the conventional EK process. However, their application would be restricted due to their cost, availability, and especially life cycle. Besides, PRBs may not be able to prevent the advancement of the alkaline front, and hence their application was always combined with chemical reagents. As a result, such EK treatment will not be a cost-effective process (Chang and Cheng, 2006; Ma et al., 2010). Therefore, this study aims to use environmental-friendly reactive filter media to improve Cu removal from contaminated kaolinite soil. Copper was used as the target contaminant because of its ubiquitous occurrence in the soil environment. Specifically, the first objective is to apply compost as a novel and recyclable RFM near the cathode to buffer the alkaline front and to capture copper ions. Compost is widely applied to treat the contaminated soil and groundwater due to its low-cost and adsorption capacity of humic substances (Farrell and Jones, 2010; Hermana and Nurhayati, 2010; Tandy et al., 2009); however, no compost application in the EK process has been reported yet. The application of compost RFM in the EK process presents several advantages. First, compost is rich in organic matter and nutrients and often used to improve soil fertility and quality (Masi and Losito, 2015). It is of low cost and environmentally friendly. The humic substances and iron oxides in compost can form stable complexes with heavy metal ions, helping in their metal uptake from contaminated soil (Clemente and Bernal, 2006). Additionally, the potential regeneration and reuse of compost RFM were evaluated for copper removal. The second objective is to use a mixture of biochar and compost at different ratios as a novel RFM in the EK-RFM system. Similar to compost, biochar is widely used as a soil conditioner and has shown a high capacity for heavy metals adsorption from the contaminated soil (Alhashimi and Aktas, 2017; Beesley et al., 2010). The performance of biochar filter media in the EK process has been investigated in the previous chapter (**Chapter 4**) while improving copper extraction from the contaminated kaolinite soil (Ghobadi et al., 2020). The potential drawbacks of compost and biochar are their highly complex composition and relatively small particle size; hence both need to be packed in RFM to prevent their loss into the soil. In addition, their efficiency in Cu removal has to be determined. The findings would provide further insights into the best RFM for the effective removal of heavy metals from soil using EK remediation technology.

5.2. Material and Methods

5.2.1. Materials, soil preparation and analysis

Detailed descriptions about the materials, soil preparation, EK apparatus, and analysis are found in **Chapter 3**. The chemical and physical characteristics of the commercial kaolinite soil and the RFM, used in this study, were reported in **Table 3.1** and **3.3**. The copper-contaminated kaolinite soil was loaded into the EK cell after 72 h equilibrium. All the tests were performed with an initial moisture content of 100%. The compost (70 g) was fully packed into the EK RFM cell between soil and cathode compartments.

In this chapter, a novel recyclable RFM was also designed for soil remediation by mixing the compost with biochar at different ratios to increase the RFM adsorption capacity. The previous experimental results have proved biochar as a potential RFM to enhance copper extraction from contaminated kaolinite soil in the EK system (Ghobadi et al., 2020). However, the performance of EK–BC required further improvement. Therefore, commercial biochar used in our previous study (Ghobadi et al., 2020), was mixed with the compost at different ratios while maintaining the same total amount of RFM at 70 g in all experiments. The RFM blends were applied in a series of EK-RFM operations to examine the feasibility of copper extraction from kaolinite soil.

The morphological and chemical composition of compost RFM were determined by using EDX, in conjunction with SEM. A Nano-ZS Zeta-seizer was used to measure the zeta potential of the compost before and after treatment. In addition, FTIR analyses were performed to characterize surface functional groups for both treated and untreated RFMs.

5.2.2. EK experimental design

Ten EK experiments were carried out at room temperature, without pH control, for a treatment time of seven days to evaluate copper extraction from the contaminated kaolinite soil. The experimental conditions are summarized in **Table 5.**1. A fixed voltage of 10 V was imposed on the saturated soil in Exp-01 to Exp-06, while Exp-07 to Exp-10 were conducted under a fixed electric current (20.00 mA).

Exp-01 was the conventional EK treatment and performed as a reference (unenhanced) experiment to investigate copper extraction using deionized water as the electrolyte. Exp-02 was implemented to investigate the effect of compost RFM on the EK removal of copper from the kaolinite soil. To design a novel recyclable RFM, a series of EK-RFM experiments (Exp-03 to Exp-05) were performed by mixing compost with biochar in different ratios to increase the RFM adsorption capacity for copper removal. An additional EK-RFM test (Exp-06) was also run by loading biochar (100%BC) in the RFM compartment to compare the performance of RFMs in the EK-RFM process. The weight of RFM for all EK-RFM tests was 70 g.

Exp-07 and Exp-08 were performed using EK-C and EK-(BC+C), respectively, under a fixed electrical current (20.00 mA). To examine the regeneration of compost RFM and the performance of the recycled compost RFM in the EK process, after Exp-07, compost RFM was recovered by acid solvent extraction technique, and reused in new EK-C treatment (Exp-09, Exp-10) in two cycles.

After seven days, the DC source was disconnected, and the set-up was disassembled. At the end of each test, the soil sample was cut into five equal sections, S1 to S5, from the anode to cathode. Each slice was oven-dried and analyzed for pH, electrical conductivity and copper content. All data were inputted into OriginPro (v 9.6), and an ANOVA test was conducted with a significance level of 0.05 to differentiate between the EK treatments.

Table 5.1. Experimental condition of different EK experiments.

Exp. no.	Experiment type	RFM	Constant voltage (V)	Constant current (mA)	Cu (mg kg^{-1})	Operation time (d)
Exp-01	EK	N/A	10		1000	7
Exp-02	EK-100%C	Compost	10		1000	7
Exp-03	EK-(10%BC+90%C)	Biochar+Compost	10		1000	7
Exp-04	EK-(20%BC+80%C)	Biochar+Compost	10		1000	7
Exp-05	EK-(30%BC+70%C)	Biochar+Compost	10		1000	7
Exp-06	EK-100%BC	Biochar	10		1000	7
Exp-07	EK-100%C	Compost		20.00	1000	7
Exp-08	EK-(10%BC+90%C)	Biochar+Compost		20.00	1000	7
Exp-09	EK-RC	Recycled Compost		20.00	1000	7
Exp-10	EK-RC	Recycled Compost		20.00	1000	7

5.3. Results and discussion

5.3.1. Performance of EK-C in copper removal

5.3.1.1. Profiles of electric current, soil pH and electrical conductivity

Figure 5.1a presents the change of electric current with time, under a constant applied voltage of 10V, for the EK-C as well as the conventional EK experiment. Generally, in the EK remediation of the heavy metal-contaminated soil, the electric current increased firstly, then reached its highest value after a certain time due to the accelerated generation of the acid front at the anode, leading to the solubilization of copper ions and their migration through the soil in the direction of the cathode (Ghobadi et al., 2020; Zhou et al., 2017). Afterwards, the electric current slowly decreased and stabilized at a low constant value, which could be attributed to reducing mobile ions in the soil (Fu et al., 2017; Ghobadi et al., 2020; Hahladakis et al., 2016). The alkaline pH would explain the continuous decrease of the electric current at the cathode side. The development of the alkaline front into the soil resulted in the precipitation of metals and fewer ions available for the electric charge transportation (Figueroa et al., 2016). Besides, the decrease in the content of mobile ions in the soil refers to the movement and extraction of free metals (Fu et al., 2017). The pattern of current change in time in the EK-C experiment is very similar to that in the previous study (Ghobadi et al., 2020) (**Figure 5.1a**). The average electric current for the EK-C test (11.42 mA) was slightly higher than that in the EK treatment (11.30 mA). The higher electric current would result in a higher metal contaminant removal (**Figure 5.2**), and it was due to the presence of compost filter media in the EK system, which buffered the advance of hydroxide ions generated at the cathode reaction, promoting the transport of the acid front in the soil. In the EK-C experiment, the electric current was at a low value of 5.50 mA in the beginning, and then reached a maximum value of 18.49 mA within a day. After that, it dramatically dropped to 10.64 mA over 72 h and remained almost stable at 8.65 mA by the end of the experiment. The sharp fall may be associated with the early precipitation of copper ions in the soil. The highest value of electric current in the EK experiment without compost RFM was 14.97 mA. As shown in **Figure 5.1a**, the EK-C test also showed a higher electric current at the end of the experiment in comparison with that of the EK without RFM. This could be explained by the continuous adsorption of OH^- produced at the cathode reaction by the compost, promoting the advancement of the acid front in the soil and hence maintaining the electric current at a higher level. The available form of heavy metals in the soil is significantly pH-dependent. Hence, a low pH environment can enhance the heavy metals dissolution and the degree of their removal from the contaminated soil (Hahladakis et al., 2016; Yeung and Gu, 2011). When inducing the electric field during the EK process, the soil pH would change due to the chemical reactions that occurred in the EK system (Cameselle et al., 2013; Habibul et al., 2016). Specifically, the application of the electrical field causes the oxidation of water at the surface of the anode, which causes a reduction in pH due to the production of H^+ ions. Hence, an acid front is electrogenerated at the anode region favoring the dissolution of the heavy metals migrated towards the cathode (Figueroa et al., 2016; Habibul et al., 2016; Masi et al., 2017b). Simultaneously, an increase in the soil pH near the cathode side is derived from the furtherance of OH^- created by the reduction of water at the cathode surface (Habibul et al., 2016). These changes in pH would lead to dissolution or precipitation of heavy metal contaminants across the soil.

Figure 5.1b presents the soil pH profile in different soil sections from the anode to cathode (S1-S5) at the end of EK experiments. Compared to the pure EK treatment, the EK-C remarkably presented a lower soil pH, due the compost RFM adsorbed the hydroxide ions produced at the cathode migrating towards the anode. Lower pH in the soil near the cathode region would cause less Cu precipitation in S5, and consequently, copper removal would be achieved in a reasonable degree. In the EK-C test, the soil was acidic through S1 to S4, ranging between pH 2.92 and pH 3.35, which favored copper removal in those sections. Soil pH in S5 near the cathode region was only 5.70, slightly above the initial soil pH, compared to pH 9.29 in the EK test without RFM. Compost RFM could successfully lower the soil pH in the soil sections close to the cathode side, from pH 4.36 to pH 3.35 in S4 and from pH 9.29 to pH 5.70 in S5, which is usually high, at alkali condition, when there is no pH control or RFM in the EK experiment. The high pH area near the cathode in the conventional EK caused massive precipitation of $Cu(OH)_2$ (Hassan et al., 2015; Pazos et al., 2006), which blocked the pore fluid and made copper removal difficult during the treatment.

Figure 5.1b also shows the electrical conductivity of soil sections (S1-S5) after the EK treatments. The soil EC values in the EK-C experiment were higher than that in the EK test without compost RFM. This tendency was following the change of electrical current and soil pH, as explained above. The soil's electrical conductivity in the conventional EK treatment represented a decreasing trend from anode towards cathode; however, the behavior was inconsistent in the EK-C as the EC increased in S5 near the cathode. In the conventional EK test, the hydroxide ions moved from the cathode area into the soil and reacted with copper ions in soil pore fluid to form $Cu(OH)_2$ precipitation (Hassan et al., 2015; Pazos et al., 2006). As a result, the EC of soil decreased near the cathode area. In contrast, the presence of compost RFM in the EK-C treatment could successfully reduce the formation of copper hydroxide in S5 near the cathode, which resulted in higher soil EC in S5. In general, compared with other types of RFM such as activated carbon and biochar, which were investigated in our previous work (Ghobadi et al., 2020), compost had the greatest capacity in the EK-RFM process in buffering soil pH as well as presenting higher soil EC (**Figure 5.1b**).

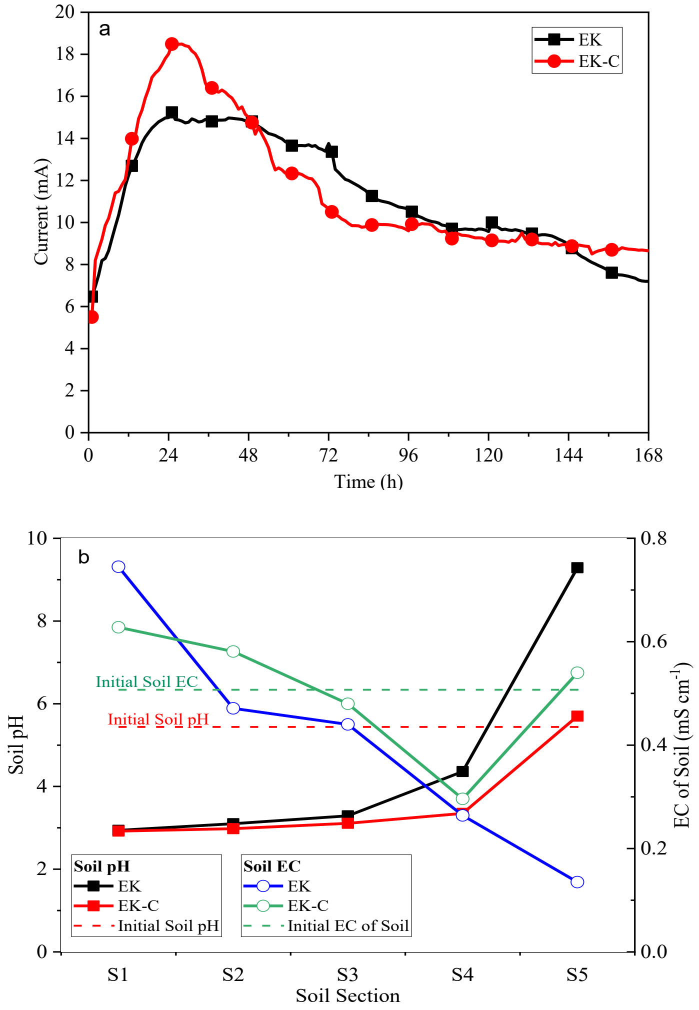


Figure 5.1. (a) Variation of electric current during seven days of EK operations under a constant voltage; (b) profiles of pH and electric conductivity in soil sections (from anode to cathode) after the experiments.

5.3.1.2. Copper extraction from soil

Metal ions during EK treatment are mainly transported through electroosmosis and electromigration processes (Yang et al., 2014). Generally, the ionic species move towards the opposite-charged electrode (Rezaee et al., 2019) as anticipated, hence copper cations electromigrated from anode to cathode (**Figure 5.2a**). The advancement of the acid front at anode resulted in the dissolution of Cu into the pore solution as Cu^{2+} ions were then transported towards the cathode. However, the electromigration of Cu^{2+} was retarded by the alkaline pH front at the cathode, which caused Cu accumulation in the soil section near the cathode (S5).

In general, the results of Cu^{2+} concentration in the soil were consistent with those of electric current, soil pH, and soil electric conductivity. After EK-C remediation, the final copper content in the soil was lower than the initial ones. According to **Figure 5.2**, EK-C operation was found to be more successful in removing copper from the kaolinite soil compared to the conventional EK test. In the EK-C experiment, the copper concentration declined enormously from the initial content (1000 mg kg^{-1}) to 105 mg kg^{-1} in S1, and then gradually raised to about 496 mg kg^{-1} in S4. Copper precipitation has been significantly decreased in S5 close to the cathode compartment (1441 mg kg^{-1}) due to lower soil pH in EK-C (**Figure 5.1b**), compared to that of the EK without RFM, which are significantly different among each other ($P < 0.05$). It can be observed from **Figure 5.2a** that more than half of copper usually accumulated in S5 during the conventional EK test was successfully trapped by compost RFM in the EK-C treatment. Moreover, copper concentration in other sections has been considerably reduced, particularly in S4, which can be ascribed to the decreasing soil pH in the EK-C operation (**Figure 5.1b**). The efficiency of the EK treatments was also evaluated by calculating copper removal efficiency in each soil section using Eq. (3.1) and presented in **Figure 5.2b**. The negative value indicates that copper is accumulated in that section. EK-C and conventional EK operations represented almost similar performance in Cu removal in S3-S1, ranging from 54.10% to 91.02% (**Figure 5.2b**). However, the percentage of Cu removal in S4 (47.79%) and S5 (-51.68%) for the EK-C was significantly higher than that in the EK without RFM, at 8.69% and -222.20%, respectively, which are statistically significantly different ($P < 0.05$). Total copper removal from the soil sample is an important parameter, indicating the overall EK treatments performance, which is determined from Eq. (3.2) (Ortiz-soto et al., 2019). Under a constant voltage of 10 V, the highest total copper removal of 45.65% was achieved by the EK-C test (**Table 5.2**). This removal rate was substantially higher than the EK coupled with other types of RFM such as AC (10%) and BC (27%) under the same experimental conditions

(Ghobadi et al., 2020). In contrast, total copper removal was only 1.03% in the conventional EK test due to the massive copper accumulation in S5 (close to the cathode zone). Comparing these results and those from previous work (Ghobadi et al., 2020) confirms that compost RFM has the highest adsorption capacity for copper without adding chemicals, preventing additional pollution by the electrolytes and their further treatment.

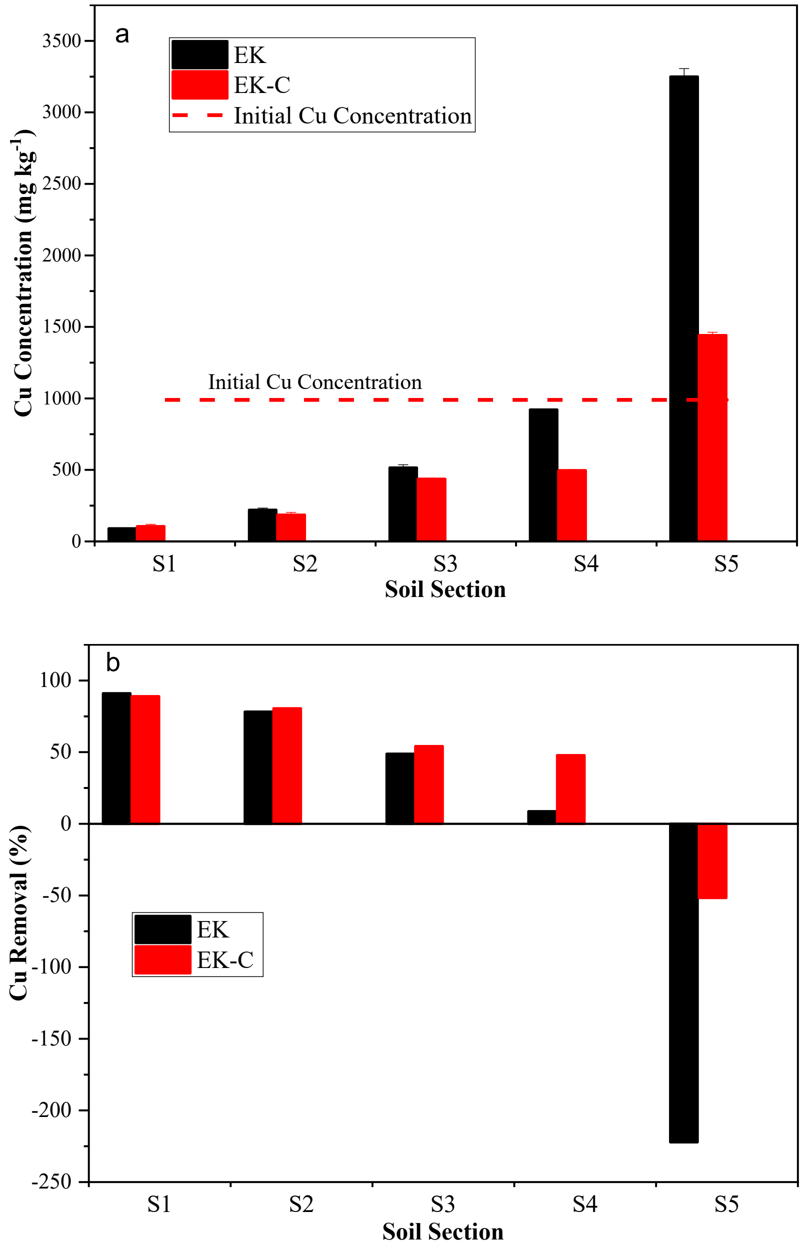


Figure 5.2. (a) Residual copper and (b) efficiency of copper removal in soil sections S1-S5 after EK and EK-C experiments.

5.3.2. Performance of EK-(BC+C) in copper removal

Figure 5.3 presents copper concentration, copper removal efficiency, and soil pH in the soil sections from the anode to the cathode for the EK-(BC+C) experiments at the different biochar-compost ratios. For comparison, the results of the EK-100%C test and EK-100%BC treatment were also displayed in **Figure 5.3**. In general, the removal efficiency of the EK-(BC+C) increased with the increasing percentage of compost in the RFM mixture, particularly in the soil portions near the cathode area (**Figure 5.3b**), while decreasing the copper concentration (**Figure 5.3a**). Adding biochar to compost RFM increased the soil pH during the EK-RFM treatment, especially in the areas close to the cathode zone (S5) (**Figure 5.3c**). It would retard the impact of humic substances in compost in lowering soil pH and binding metal ions from the contaminated soil. Total copper removal of the EK-(BC + C) experiments was following a declining order: EK-(10%BC + 90%C) > EK-(20%BC + 80%C) > EK-(30%BC + 70%C), at 31.01%, 19.94% and 7.67%, respectively (**Table 5.2**). In the case of EK-100%BC, 26.83% of copper was removed during the treatment. All RFMs reduced the availability of copper in the soil during the EK-RFM process, of which 100%C presented the greatest capacity for that. The reason could be that compost was capable of buffering the alkaline soil pH close to the cathode region, which enhanced the efficiency of RFM in copper removal.

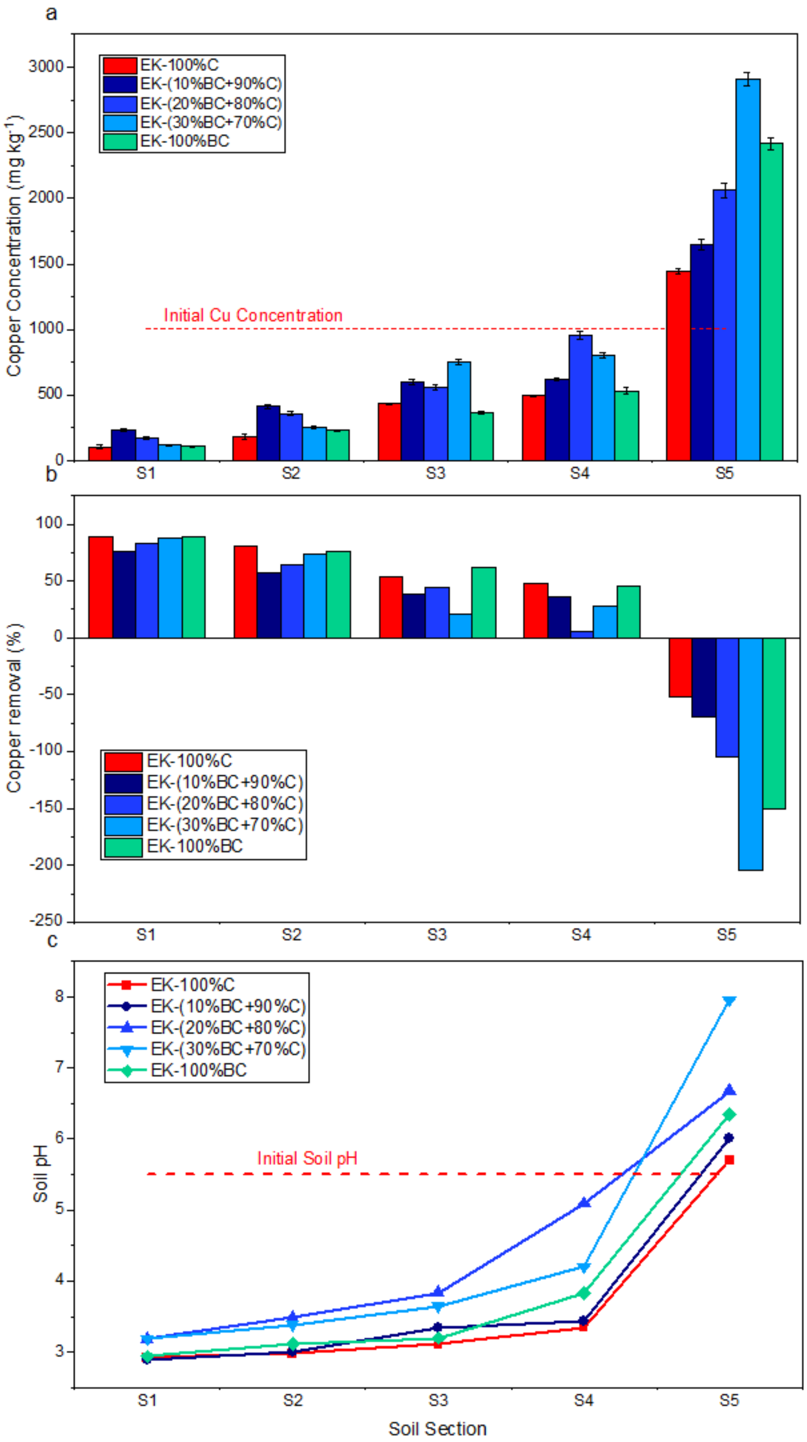


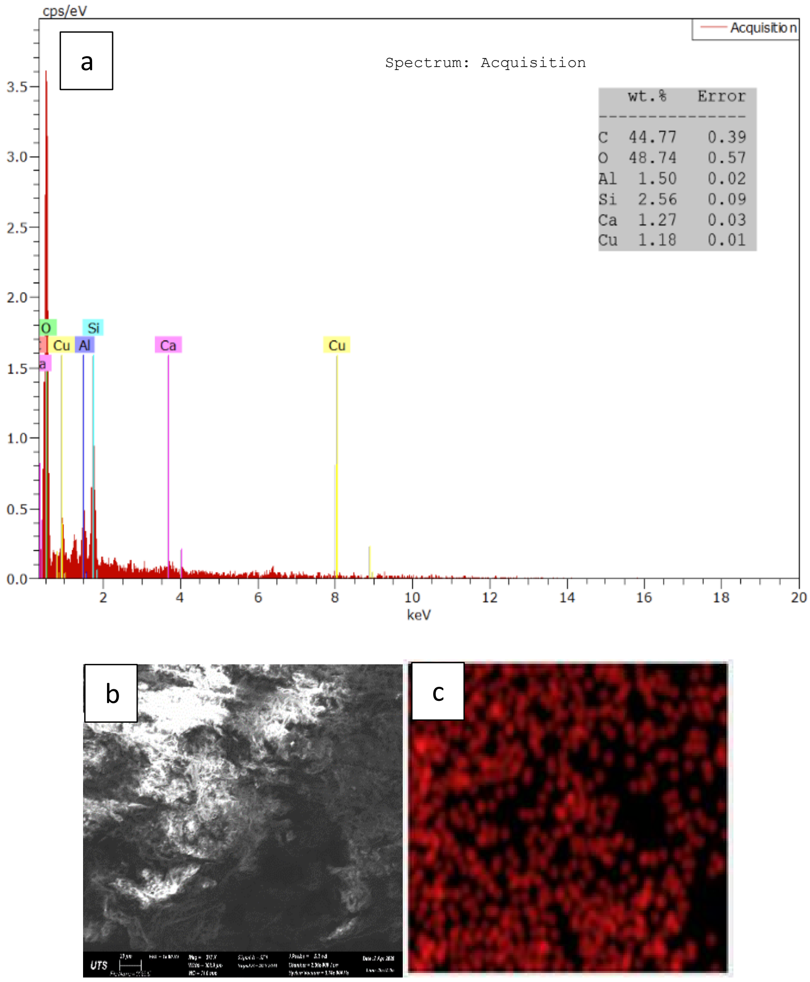
Figure 5.3. (a) Copper concentration, (b) removal efficiency of copper, and (c) pH profile across the soil sections at the end of EK treatment.

5.3.3. Characterization of compost RFM

To validate the results presented above, the compost RFM samples were taken after the EK treatment for further characterization to understand their behavior better. EDS-SEM (**Figure 5.4**) was used to confirm the capacity of compost RFM in trapping Cu ions from the contaminated soil in the EK process. **Figure 5.4b** shows a typical selected area for EDS mapping measurement. The EDS analysis indicates that the sample contains a Cu element, which is homogeneously distributed in the compost RFM sample (**Figure 5.4c**). Besides, the survey spectrum again confirms the presence of Cu in compost samples after EK treatment (**Figure 5.4a**). The EK phenomena significantly affected the zeta potential of the compost RFM, which increased from −6.39 mV to −0.77 mV after the EK treatment (**Figure 5.5a**). This increase is probably due to the interaction between compost particles and free Cu ions. The adsorption of the positively charged heavy metal cations existing in the soil decreases the negative charge of compost particles; therefore, zeta potential becomes less negative.

The FTIR spectra were applied as an analytical technique for providing valuable information on the functional characteristics of compost and biochar RFM before and after EK operation (**Figure 5.5b**). Although the characteristic peaks of the main organic components are present in both spectra before and after EK treatment, significant differences can be observed, such as the appearance or disappearance of peaks in the EK treated compost sample when compared to the compost before the EK treatment. The FTIR spectrum of RFMs displayed a band centred at approximately 1630 cm^{-1}, which can be ascribed to the C—O stretching, mainly in the carboxyl groups (Hotová et al., 2020). A strong band at 1030 cm^{-1} which was observed only in the spectrum of compost RFM could be related to the C–O–C bond in polysaccharides; however, the peak increased after EK treatment which can be attributed to copper adsorption. O–H stretch occurred as a very broad peak at 3000−3500 cm^{-1} in the FTIR spectrum of the compost. The intensity of this band increased in the spectrum of the treated compost, which can contribute to the capacity of the compost in buffering soil pH during the EK process. Comparison of chemical composition (**Table 3.3**) and the FTIR spectra of compost and biochar RFMs after EK treatment indicated that the oxygen-containing functional group could be involved in the copper ions adsorption by the compost RFM in the EK–C treatment.

In general, the adsorption of Cu in compost which contains a wide variety of organic compounds, would involve several mechanisms such as (1) Cu ions exchange with Ca^{2+}, Mg^{2+} and other cations in the compost, leading to co-precipitation; (2) the surface and inner-sphere complexation of Cu ions with different functional groups in compost e.g., hydroxyl groups in mineral oxides and humic materials; and (3) the physical adsorption of Cu ions on compost through Van der Waals forces. According to the experimental results, it was found that compost RFM had the greatest efficiency of adsorbing Cu, compared to the mixture of biochar/compost and biochar itself. This can be attributed to the higher oxygen content and surface functional groups in the compost, compared to biochar, which can adsorb Cu ions.



	wt.%	Error
C	44.77	0.39
O	48.74	0.57
Al	1.50	0.02
Si	2.56	0.09
Ca	1.27	0.03
Cu	1.18	0.01

Figure 5.4. (a) EDS analysis and spectrum of compost, (b) SEM image showing EDS analysis area, and (c) EDS map showing detection of copper (red). Scale bars: 20 µm.

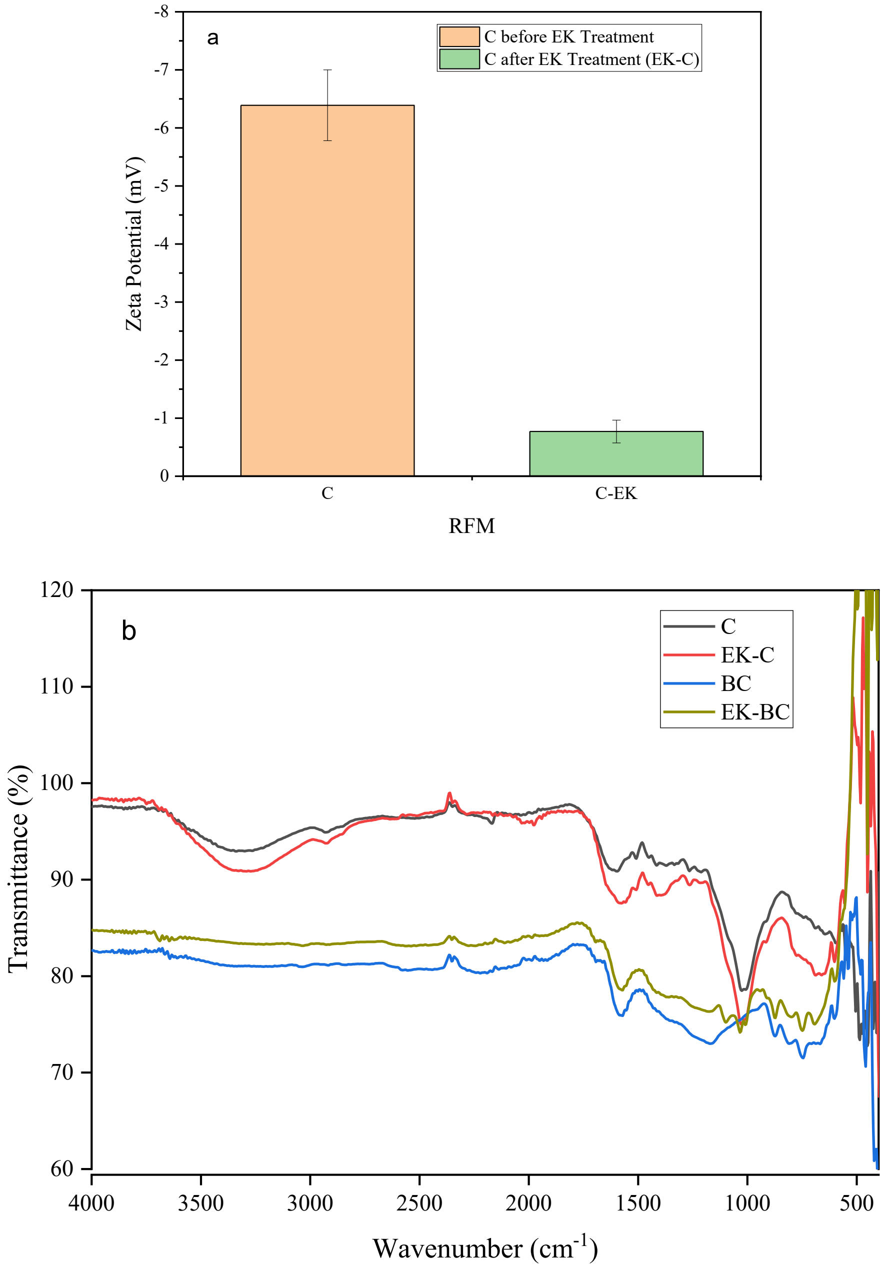


Figure 5.5. (a) Zeta potential of compost before and after EK operations; (b) FTIR spectra of compost and biochar before and after EK operations.

5.3.4. Performance of EK-RFM under a constant current

To further enhance the EK process in contaminant removal, additional EK-C treatment was carried out with the application of a constant electric current at 20.00 mA. Maintaining electric current instead of voltage at a constant value successfully enhanced the total copper removal from 45.65% to 84.09% in the EK-C treatment (**Table 5.2**). The 20.00 mA is slightly higher than the maximum current of 18.49 mA observed under constant voltage, but the difference is relatively insignificant. The improved performance under a constant electric current can be explained by the increased rate of Cu ion transport by accelerating the acid front movement. Copper concentration dramatically declined from the initial concentration of 1000 mg kg^{-1} to 41.50 mg kg^{-1} in S1, and then slowly rose to about 315.50 mg kg^{-1} in S5 (**Figure 5.6b**). The soil pH distribution, which was consistent with the copper removal results (**Figure 5.6b**), represented an acidic environment throughout the soil, ranging between pH 2.28 and pH 3.06 (much lower than initial soil pH 5.44). The soil pH in S5 was 3.06 at which copper ions will be solubilized and removed from the soil. To evaluate the performance of EK with BC and C mixture as RFM under a constant electric current of 20.00 mA, Exp-08 was conducted and the results are displayed in **Figure 5.6c**. The total Cu removal increased from 31.01%–48.51% in the EK-(10%BC + 90%C) at the constant electric current (**Table 5.2**), which was significantly lower than the EK-100%C results under the same condition. It appears that maintaining the electric current at a fixed level could not lower the pH in S5, which caused the copper accumulation in that section, although it was effective in lowering soil pH in S1-S4. The reason may be the presence of the biochar in the RFM mixture, which could slightly reduce the electric conductivity of the soil and increase soil pH near the cathode (S5) (**Figure 5.6**). It would reduce the impact of humic substances of compost in lowering soil pH and binding metal ions from the contaminated soil. Additionally, the average voltage during EK-(10%BC + 90% C) treatment was 24.62 V, which was higher than that during EK-(100% C) at 20.45 V, suggesting lower power consumption using compost RFM. Considering the remediation efficiency, energy consumption per unit volume E_u (Wh m^{-3}) was calculated according to Eq. (3.3) (Hahladakis et al., 2016). As shown in **Figure 5.7**, EK-(BC+C) operations generated less total copper removal than EK-100%C but offered higher total Cu removal than conventional EK treatment.

The EK remediation treatments, either with or without compost RFM, consumed similar electrical energy, but the total copper removal in the EK remediation coupled with compost RFM was nearly 45 times that in conventional EK remediation (**Table 5.2**). The application of constant electric current in the EK-C treatment outstandingly improved the total copper removal to 84.09% compared with that under constant voltage (45.65%), although at the same dramatically increased the energy consumption from 10.90 kWh m^{-3} to 39.07 kWh m^{-3}. With renewable energy, especially solar power under rapid research and development, the practicability of this technique is expected to be extended. EK-(BC+C) application under a constant current would be limited due to its high-energy consumption demand and no significant improvement in removal rate compared with the EK-C under the same condition.

Mass balance and total extraction of copper after the EK operations were calculated and presented in **Table 5.2**. All experiments demonstrated an excellent mass balance of 95.89%–103.63%. The results indicated the success of different EK operations for copper removal, whether under a constant electric current or a constant electric voltage.

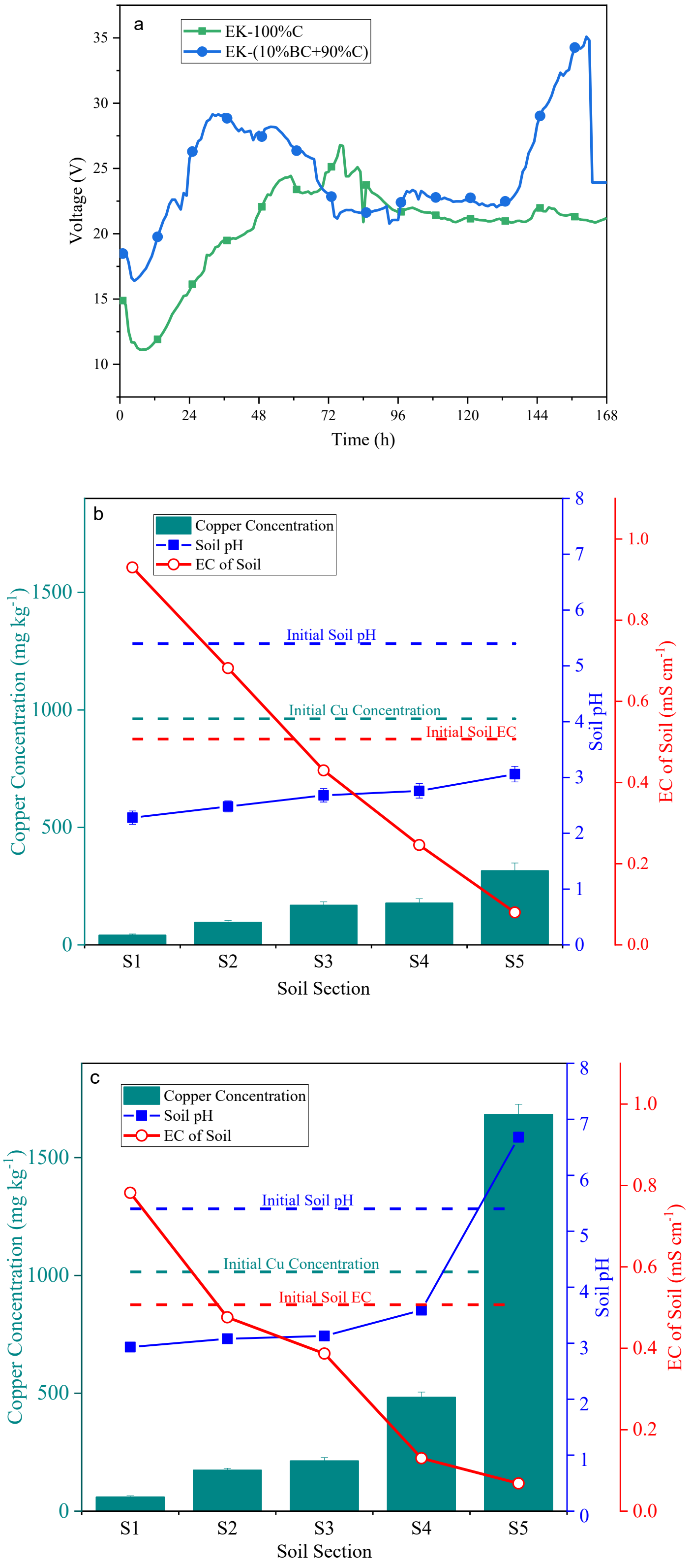


Figure 5.6. (a) Variation of voltage over time for EK-100%C and EK-(10%BC+90%C) treatments under a constant current; Copper concentration, pH and electric conductivity in soil sections after (b) EK-100%C and (c) EK-(10%BC+90%C) treatment under a constant current.

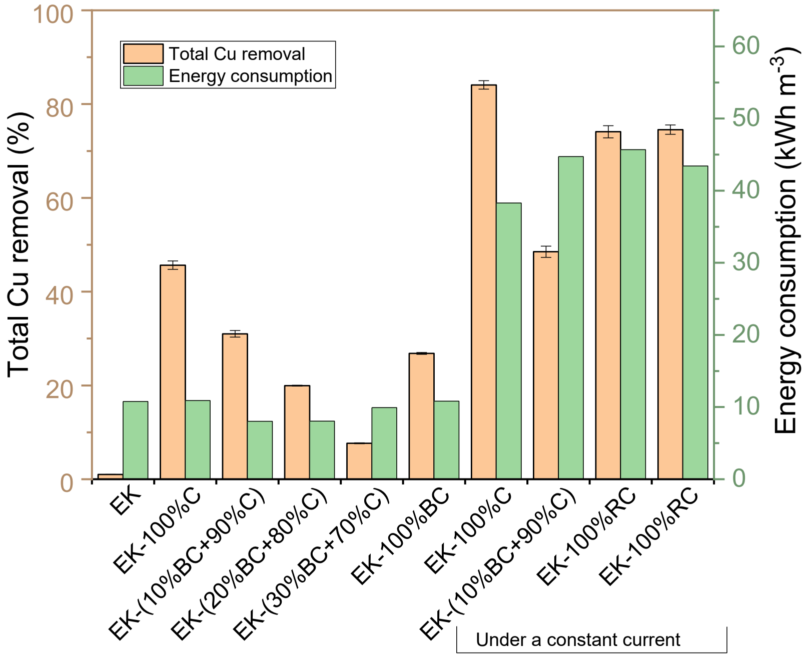


Figure 5.7. Comparison of total copper removal and associated power consumption per unit volume of soil during different EK treatments.

Table 5.2. Mass balance and total copper removal in the EK tests.

Exp. no.	Initial Cu in soil (mg)	Residual Cu in soil (mg)	Cu in RFM (mg)	Electrolyte/pore water Cu (mg)	Mass balance (%)	Total removal of Cu (%)
Exp-01	1010	999.60	N/A	8	99.76	1.03±0.02
Exp-02	980	532.60	405.30	10	96.72	45.65±0.90
Exp-03	1020	703.60	353.50	0	103.63	31.01±0.70
Exp-04	1025	820.60	213.50	3	101.18	19.94±0.11
Exp-05	1025	946.40	105	0	102.57	7.67±0.09
Exp-06	999	731	220	7	95.89	26.83±0.20
Exp-07	1005	159.90	840	0	99.49	84.09±0.90
Exp-08	1015	522.60	455	0	96.31	48.51±1.20
Exp-09	1005	260.20	730	8	99.32	74.11±1.30
Exp-10	995	253.20	737	3	99.82	74.55±1.01

5.3.5. Regeneration and reuse of compost RFM

The regeneration of RFM is of importance as it can reduce the EK operation cost and minimize further waste management problems. Furthermore, it would be interesting to assess whether such regenerated RFM can still be effective in the EK-RFM system for different cycles. In this study, compost RFM was regenerated by acid extraction, with approximately 85% of Cu in RFM being removed. In addition, about 35 g of compost remained after the regeneration process, representing a mass loss of 50%. The compost was recycled twice after being used in the EK- RFM system to evaluate its copper removal during reuse. Since 50% of compost was lost during each regeneration process, additional fresh compost was adequately mixed with the recycled compost to maintain 70 g before reuse. Additional EK-C experiments by maintaining 20.00 mA of electric current (Exp-09) were carried out using the recycled compost. After the EK process, the soil was removed from the cell for analysis, and the RFM was taken out for regeneration purposes. The same procedure was performed to extract copper from the RFM and then reused in further EK-C tests (Exp-10). The experimental results revealed that the total Cu removal rate decreased by nearly 10% (from 84.09%– 74.11%) in both experiments (**Table 5.2**). The copper removal efficiency reduced slightly in S4 and considerably in S5 (**Figure 5.8**). The reason may be that the compost likely lost the humic substances to some extent when extracted with the acid solution, which affected the performance of compost RFM in copper sorption during the EK treatment. Nevertheless, the regenerated compost is still effective, showing high copper removal efficiency compared to the conventional EK process.

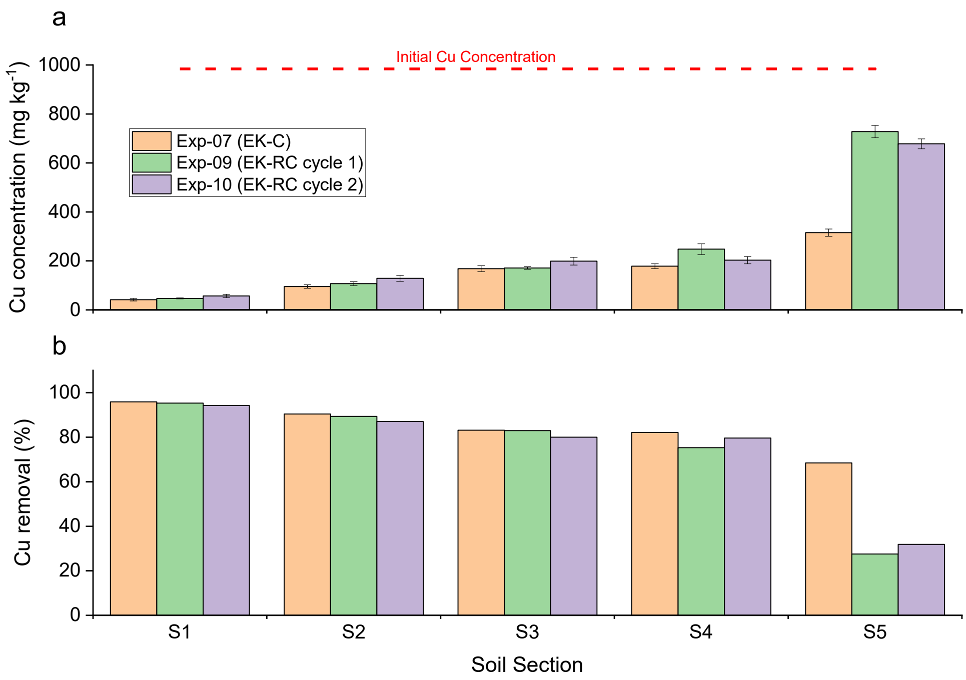


Figure 5.8. (a) Cu concentration and (b) Cu removal efficiency across the soil sections after the EK experiments coupled with the recycled compost RFM.

5.4. Conclusions

This study evaluated EK remediation of copper-contaminated kaolinite soil in conjunction with compost or compost-biochar mixture as novel RFM. In the test trials under a constant voltage, the total removal of copper was increased significantly from 1.03% in the EK treatment to 45.65% in the EK-compost RFM treatment. The key advantages of compost EK-RFM over other EK processes include its great capacity to buffering the alkaline soil pH near the cathode zone where the high copper accumulation occurred and eliminating the need for chemical agents that may cause damage to the soil environment and increase the treatment cost. The results demonstrated that mixing biochar with compost in the RFM did not improve the removal of copper ions in the soil during the EK-RFM operation. The total removal of copper ions by the EK treatment decreased in the order of EK-100%C > EK-(10%BC + 90%C) > EK-(20%BC + 80%C) > EK-(30%BC + 70%C) > EK. The application of a constant electric current in the EK-100%C treatment further improved copper extraction in the soil to 84.09%, although increasing energy consumption. Furthermore, compost was regenerated and reused in the EK process, although the total Cu removal decreased from 84.09%–74.11%. The findings confirm compost as a promising green RFM which enhances heavy metals removal in the EK process, especially under a constant electric current, by generating a low pH environment through the soil.

Faculty of Engineering and Information Technology

CHAPTER SIX:

EFFECTIVE REMEDIATION OF HEAVY METALS IN CONTAMINATED SOIL BY EK TECHNOLOGY INCORPORATING RFM

CHAPTER SIX: EFFECTIVE REMEDIATION OF HEAVY METALS IN CONTAMINATED SOIL BY EK TECHNOLOGY INCORPORATING RFM

This chapter has been constructed from the following publication:

Romina Ghobadi, Ali Altaee, John L. Zhou, Elika Karbassiyazdi, Namuun Ganbat "*Effective remediation of heavy metals in contaminated soil by electrokinetic technology incorporating reactive filter media*", **Science of the Total Environment**, 794 (2021) 148668.

6.1. Introduction

Anthropogenic activities such as mining (Yuan et al., 2016b), transportation (Mohsen et al., 2018), and poor management of municipal and industrial wastes (Nguyen et al., 2019; Xu et al., 2019) generate serious soil pollution with multiple heavy metals such as lead, cadmium, zinc, and copper. The widespread soil contamination with heavy metals calls for remediation technologies that accomplish heavy metals removal with the least possible destruction or disturbance to the surrounding environment or ecological systems (Figueroa et al., 2016; Gong et al., 2018; Xu et al., 2019; Yuan et al., 2016b). Most soil remediation technologies involve off-site treatment processes and have been successful in the immobilization of heavy metals in soils, although the transport cost and the potential to cause additional contamination during transit can be a significant issue. In addition, such methods, for instance, vitrification or solidification and stabilization, are found costly for their high-energy consumption. Besides, the soil cannot be used again for its normal uses (Gong et al., 2018; Tokunaga and Hakuta, 2002). Furthermore, there is a risk of future mobilization of heavy metals after treatments such as solidification and stabilization (Dermont et al., 2008; Figueroa et al., 2016; Gong et al., 2018; Tokunaga and Hakuta, 2002). Consequently, in situ technologies for heavy metals removal from contaminated soil are highly beneficial and desirable for treating a mixture of heavy metals. Among various in situ remediation technologies, the electrochemical methods offer the most practical system for the removal of heavy metal cations from the contaminated soil (Acar et al., 1993; Acar and Alshawabkeh, 1993; Giannis and Gidarakos, 2005; Y. Liu et al., 2016; Xu et al., 2019). Despite a large number of studies on the EK process in soil remediation, only a few studies investigated soil remediation from a mixture of heavy metals (Bahemmat et al., 2016; Giannis et al., 2009; H. Kim et al., 2012; Yuan et al., 2016b). The latter example resembles the field situation in which contaminated soil is often caused by a mixture of heavy metals rather than a single metal ion.

An assisting agent, citric acid plus calcium chloride (CA + $CaCl_2$), was investigated by Yuan et al. (2016b) to simultaneously remove multi-heavy metals (Zn, Cd, Ni, Cu, and Pb) from contaminated kaolin. The initial heavy metal concentrations were between 41.6 mg kg^{-1} and 293.7 mg kg^{-1} in dry kaolinite soil. The removal efficiencies of Zn, Ni, Cd, Cu, and Pb were 99%, 98.9%, 98.2%, 95.2%, and 86.2%, respectively, with the energy consumption of 124.8 kWh m^{-3} after 72 h operation. Yuan et al. (2016a) also evaluated the effect of a novel material, i.e., carbon nanotube covered polyethylene terephthalate yarns (PET-CNT), as a cathode electrode on simultaneous EK remediation of multi-heavy metals (Cu, Cd, Pb, Ni, and Zn) contaminated kaolin. PET-CNT cathode was found to significantly increase the electric current and electroosmotic flow, reduce soil pH, and as a result, enhance heavy metals extraction efficiencies. Their observations demonstrated that the order of heavy metal removal efficiency decreased as Ni > Cd > Zn > Cu > Pb, indicating that Ni, Cd, and Zn were generally relatively easy to extract, whereas Cu and Pb were found to be more difficult to remove. After 72 h of the EK treatment, the highest removal efficiency was for Ni (90.7%), and the least was for Pb (19.2%). The removal efficiencies of Cd, Zn, and Cu were reported at 89.7%, 88.7%, and 63.6%, respectively (Yuan et al., 2016a).

Up to now, EK research has been mostly conducted for the heavy metals spiked kaolinite soil, and few studies have been conducted regarding the transport and removal of multiple heavy metals during EK remediation in natural soil. The application of contaminant spiked model soils (such as kaolin) is useful to study the fundamentals of the technology (Han et al., 2010; Ghobadi et al., 2020; 2021); however, contaminant behavior is different from that observed for the real soils (Villen-Guzman et al., 2015). Hence, research with natural soils is required since spiked kaolinite could be remediated faster than complex soils (Jensen et al., 2007). Generally, the high organic matter content in the natural soil can capture and retain heavy metals, which can make the solubilization and mobility of the heavy metals rather difficult (Altin and Degirmenci, 2005; Figueroa et al., 2016). Yang et al. (2014) studied the transport of multi-heavy metals (e.g., Cu, Zn, Pb, and As) from paddy soil within 28 days of EK operation. Their work was mainly focused on the transport behavior of heavy metals in the natural soil, the relationships between the heavy metal fractionation and extraction mechanisms, and the effects of electrolyte conditioning in the EK process. They described electroosmosis and electromigration as the main transport mechanisms during the first two weeks and then electromigration during the later weeks. Besides, the electrolyte conditioning (e.g., NaOH, H_3PO_4, and Na_2SO_4) during the EK process resulted in the precipitation of heavy metal hydroxides, sulphates, and phosphates in the soil. The removal efficiencies were 31.1%-54.7% for As, 27.3%-44.4% for Cu, -4.3%-68.9% for Zn, and -7.1%-3.9% for Pb. They concluded that the heavy metal fractionation and distribution would change during the EK operation due to a number of physicochemical processes such as adsorption, complexation, and precipitation/dissolution. Yuan et al. (2017) also applied their previously proposed novel assisting agent to simultaneously remove multi-heavy metals (Zn, Cd, Ni, Cu, and Pb) from contaminated black soil (containing organic matter of 2.4%). The operation was carried out for a longer duration (705 h) with the same potential gradient. The removal efficiencies of heavy metals were higher than 80%, with an energy consumption of 132.7 kWh m^{-3}. Giannis et al. (2009) reported a chelating agent-assisted electrokinetic removal of multi-heavy metals such as cadmium, copper, and lead from contaminated real soil. Their experimental results demonstrated that the removal efficiency of Cd, Cu, and Pb ranged between 65–95%, 15–60%, and < 20%, respectively. An EK combined with the enhancing agents was conducted by Bahemmat et al. (2016) using a real soil contaminated with multi-heavy metals including Co, Cd, Pb, Ni, Mn, and Zn. Their observations proved that both humic substances (e.g., humic and fulvic acids) and catholyte conditioning (0.1 N HNO_3) could enhance remediation efficiency by approximately 2–3 times after 20 days EK operation. They stated that the transportation of free heavy metal cations and positively charged complexed heavy metals toward the cathode end was induced by electromigration. Different designs of EK remediation, including the integration of bioremediation, were applied to simultaneously remove mixed metals of As, Pb, and Cu from contaminated paddy soils by Kim et al. (2012). They found that the individual EK and sequential Bio-EK were not effective for soils contaminated with mixed metals. The sequential Bio-EK with *A. ferrooxidans* led to enhanced removal of As by 25% but dramatically decreased the removal of Pb by 10.6%. Their experimental results also demonstrated that the integrated Bio-EK with inoculation of *A. ferrooxidans* into the electrolyte improved the extraction of the mixed metals with less power consumption after 20 days, compared to those in single EK and sequential Bio-EK.

In the literature, for the simultaneous extraction of multi-heavy metals from the contaminated soil, the EK process was conducted by mainly coupling with complexing agents such as EDTA, humic acid, nitric acid, citric acid (Bahemmat et al., 2016; Bahemmat and Farahbakhsh, 2015; Falciglia et al., 2016; Giannis et al., 2009) or combining with other remediation techniques such as bioremediation (H. Kim et al., 2012). Although enhancing agents have been widely used in the EK process for the simultaneous extraction of multi-heavy metals, laboratory-scale studies demonstrated the adverse effects of strong acids on some soil characteristics such as electrical conductivity and pH after treatment (Gong et al., 2018; Mao et al., 2015) and increased the remediation cost due to the recovery of the electrolyte after EK treatment. Besides, some enhancement agents would not be recommended to extract heavy metals due to their unsuccessful applications in full-scale EK operations (Giannis et al., 2009; Gong et al., 2018; Iannelli et al., 2015). For instance, Tian et al. (2017) stated that the combination of citric acid and biosurfactant (e.g., saponin) as enhancing agents would not be practical for the simultaneous removal of heavy metals (Cr, Cd, Pb, Zn, and Cu) by the EK process, with the low removal rates of 4.4%-15.8%. Besides, Bio-EK remediation, as one of the most environmentally friendly remediating choices to extract heavy metals from the soil, may take a long remediation time (Gong et al., 2018), although it is relatively inexpensive. Simultaneous extraction of heavy metals has also been investigated by the EK remediation coupled with PRB; however, its application for the multi-heavy metals contaminated natural soil was relatively rare. An innovative EK remediation system combined with PRB was proposed by Yuan and Chiang (2007) for the removal of arsenic from As-spiked real soil. The soil collected from farmland had a texture of silt loam with an organic matter content of 0.35%. EK experiments were conducted using PRB media of Fe^0 and FeOOH over five days. Arsenic removal in EK-PRB was successfully enhanced by 1.6–2.2 times than that in EK without PRB media. Yuan and Chiang (2007) confirmed that among the electrochemical removal mechanisms, electromigration was dominant over electroosmotic flow. According to their observations, surface adsorption was considered as the key removal mechanism under the acid environment near the anode side, and precipitation was the main removal under an alkaline environment near the cathode side. In addition, their experimental results proved that the surface adsorption/precipitation on PRB media was more effective than the EK process for As removal in the EK-PRB system. An enhanced EK-PRB was reported by He et al. (2021) as a promising technology for the remediation of heavy metals (Zn and Cd) contaminated real soils. A new sheet PRB with good adsorption capacity was prepared by synthesizing sodium alginate/polyvinyl alcohol/attapulgite. They also investigated the impact of pre-treatment of citric acid and *Shewanella oneidensis* (MR-1) on the removal efficiency of Cd and Zn from the soil during EK-PRB. Their results showed that the removal efficiencies of Zn and Cd increased to 58% and 53%, respectively, after 8 days of EK-PRB remediation. They stated that the addition of both complexing agents and microbes resulted in the highest electric current, reduction of pH, and the more negative soil zeta potential. They found that the percentages of exchangeable and carbonate fractions were reduced after enhanced EK-PRB, as they can readily migrate in the soils. In addition, an increase in Fe-Mn oxidation and residual fractions was observed, which were found to be difficult to migrate in the soils. Although the performance of EK-PRB was successful, the proper selection of reactive materials was challenging as they were difficult to reuse (Gong et al., 2018; Wang et al., 2021).

The EK process has been recently enhanced by integrating with a recyclable environmentally friendly reactive filter media (EK-RFM) such as compost, biochar, and their mixture, as an adsorbent (Ghobadi et al., 2020, 2021) to improve the efficiency of the EK system and facilitate its applicability for the removal of heavy metals. This combined remediation has been successful in single heavy metal (Cu) spiked model soil such as kaolin (Ghobadi et al., 2020; 2021) with the removal efficiency of approximately 26% by EK-biochar and the highest efficiency of 84.1% by EK-compost. Thus, the feasibility studies and optimization of the design and operation of the EK-RFM technique require the development of techniques for predicting the performance of full-scale EK (Villen-Guzman et al., 2015). On the other hand, most of the anthropogenic activities caused serious contamination in soil with not just one single heavy metal, but often with multiple heavy metals such as Pb, Zn, Cu and Cd, which are frequently found as complex mixtures (Yuan et al., 2016b; Nguyen et al., 2019). As many heavy metals co-exist in soil, they can compete with each other for desorption. Therefore, it is essential to consider the simultaneous removal of co-existing heavy metals from the real soils.

The objectives of this chapter were to investigate the simultaneous removal efficiency of multiple heavy metals by EK-RFM remediation from natural soil under different operating conditions and the distribution of heavy metals in soil sections during EK treatment. Compost was chosen as an RFM to enhance the EK remediation in the multi-heavy metals contaminated real soil. The performance of compost RFM was studied in the EK-RFM system in **Chapter 5** for heavy metal removal and demonstrated a successful cost-effective heavy metal extraction efficiency. However, the application was limited to only a single heavy metal (i.e., copper) extraction from spiked kaolinite soil, and its performance for other heavy metals in the real soil has not been evaluated yet. The results reported in this study will be valuable in optimizing the design of the EK-RFM system and extending its application to field-scale systems.

6.2. Methodology

Detailed descriptions about the materials, natural soil preparation, EK apparatus, and analysis are found in **Chapter 3**. The characteristics of collected natural soil before preparation were provided in **Chapter 3** (**Table 3.2**). A total of 1400 g of contaminated soil was mixed with a measured amount of deionized water to get the target water content (34%) and then placed in the experiment apparatus using a tamper (Ma et al., 2010; Yuan et al., 2017). The measured amount of compost (90g–120g) was filled into the RFM section. The compost RFM properties in this study were recorded in our previous work (Ghobadi et al., 2021). Both anolyte and catholyte solutions were provided using deionized water. The experimental apparatus was shown in **Chapter 3** (**Figure. 3.1**). In each remediation test, 1400 g of contaminated soil was put into the EK reactor.

To quantitatively assess the heavy metals remediation performance of the EK-RFM in the contaminated natural soil, a series of experiments were conducted. Exp1 and Exp5 were run as conventional EK tests without any RFM, and to compare their performance under different voltage, current, and operation time. To further enhance the heavy metals removal efficiencies for the natural soil and attain the optimum performance, four operating factors, including the electric current, voltage gradient, amount of RFM, and the operating time were considered in the design of the enhanced EK-RFM process (Exp2, Exp3, Exp4, Exp6, Exp7). The details of the different EK experiments are displayed in **Table 6.1**. All the analysis was performed in triplicate, and the result was calculated as the average (Ma et al., 2010). The functional groups of the soil were detected using an FTIR spectrometer before and after the EK-RFM application. EDS-SEM was taken for detecting the soil and RFM elemental composition with an acceleration voltage of 15 kV for EDS collection. The removal efficiency and the specific energy consumption for heavy metals were calculated according to Eqs. (3.1) and (3.3), respectively (Y. Liu et al., 2016).

Table 6.1. Summary of EK experimental conditions for heavy metal removal in soil.

Test	Experiment type	Amount of RFM (g)	Applied voltage (V)	Applied current (mA)	Operation time (d)
Exp1	EK only	N/A	10.00		7
Exp2	EK-RFM	90	10.00		7
Exp3	EK- RFM	90		20.00	7
Exp4	EK- RFM	120		20.00	7
Exp5	EK only	N/A		20.00	14
Exp6	EK- RFM	90		20.00	14
Exp7	EK- RFM	90		30.00	14

6.3. Results and discussion

6.3.1. Electric current and voltage

Figure 6.1 illustrates the electric current and potential variations in the soil during different EK experiments. The electric current is considered as a prominent factor influencing the extraction efficiency for heavy metals. In general, the intensity of the electric current in the specimen was positively correlated with the level of the electric charge passing through the pore solution of soil within unit time, with the inverse direction of the movement of the electrons (Ji et al., 2019).

As shown in **Figure 6.1a**, Exp1 and Exp2 showed the same trend of electric current reduction while the voltage gradient maintained constant at 10.00 V. The similar change pattern was also reported in the EK remediation of heavy metals in contaminated natural soil (Fu et al., 2017; Reddy and Ala, 2005; Sun et al., 2019; Yuan and Chiang, 2007). The level of electric current was higher in Exp2, which can be explained by the presence of RFM in the EK process, which deterred the advancement of the alkaline front and promoted the transportation of heavy metal ions in the soil. The electric current for Exp3 and Exp4 was kept stable at 20.00 mA. As observed in **Figure 6.1b**, it seemed that the impact of RFM amount would be insignificant on the EK-RFM processes since variations of voltage for both experiments were relatively similar. Exp5-Exp7 demonstrated the effect of processing time and electric current value, respectively, on the efficiency of the EK process. According to **Figure 6.1**, the electric current in Exp6 was stable and maintained at approximately 20.00 mA after eleven days; however, the current had undergone a sharp decrease from day 2 before it restabilized on day 4. During that time, the voltage gradient has reached a maximum of 35.21 V, which was the limited voltage range for the power supply. The sharp drop in the electric current is probably due to increasing resistance of the natural soil under the applied electrical field caused by premature precipitation of metal ions in the soil. After day eleven, the electric current descended and reached 12.01 mA at the end of the operation (Exp6). This descending trend would be attributed to the decreasing mobility of the heavy metal ions during the final stage of the EK-RFM process, caused by the precipitation of metal ions. The average electric current used in Exp6 was 18.22 mA, and the voltage was 10.67 V at the beginning of Exp6, then increased to the highest value of 35.21 V from days two to four. Afterwards, the voltage fluctuated between 28.89 V and 35.21 V until day seven and remained at 35.21 V until day fourteen. The average electric current in Exp5, performed as a control experiment without any RFM, was slightly less than that in Exp6. In Exp7, the electric current was fixed at 30.00 mA, but it sharply decreased after day one when the voltage gradient reached the highest value of 35.21 V. The sharp drop in the electric current could be attributed to the premature precipitation of heavy metal ions, reducing the concentrations of soluble metal ions in the pore solution. The electric current showed a fluctuating trend ranging from 16.98 mA to 23.71 mA by the end of the Exp7, and the average values of the electric current and voltage were 21.73 mA and 34.39 V, respectively.

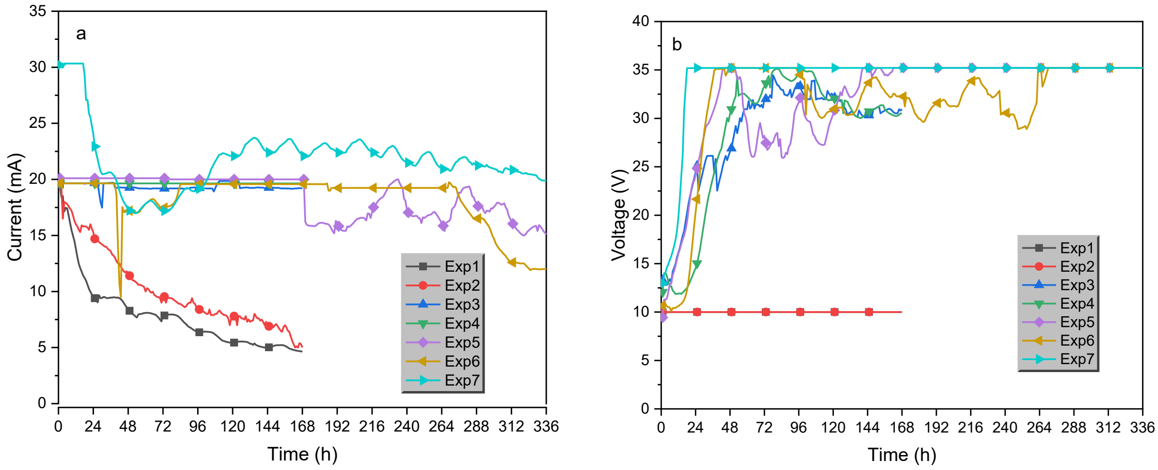


Figure 6.1. Changes of (a) electric current, and (b) electric potential during different EK operations.

6.3.2. Soil pH

Figure 6.2 illustrates the EK-RFM experimental results of the pH profile. The existence of a pH gradient from low pH at the anode to high pH at the cathode was due to electrolysis during the EK process (Gidudu and Chirwa, 2020). At the anode, the dissociation of water because of oxidation reactions generated H^+ ions, which decreased the pH of the anolyte. Simultaneously, the catholyte was broken down into OH^- ions through reduction reactions, resulting in a pH increase (Ghobadi et al., 2021; Gidudu and Chirwa, 2020; Wang et al., 2019). These reactions lead to forming the acid front at the anode and an alkaline front at the cathode (Gidudu and Chirwa, 2020; Wang et al., 2019). Hence, during the EK process, the pH dynamically changed across the system as the hydrogen ions moved towards the cathode and caused the heavy metal ions to start migration in the soil. Therefore, the adsorption/desorption of heavy metal ions on the soil surfaces can be assessed corresponding to the soil pH (Fu et al., 2017; Ortiz-soto et al., 2019). Heavy metals solubilization was accomplished at low pH values, which promoted their movement under the effect of a continuous electric field (Fu et al., 2017; Ortiz-soto et al., 2019).

According to **Figure 6.2**, the initial soil pH was approximately 4.3, and gradually reduced because of the advancement of the acid front from the anode end. In effect, all experiments demonstrated an ascending pattern of the soil pH from the anode to the cathode (S1-S5). In Exp7, the lowest soil pH was in soil sections S1 to S3 due to the high intensity of the applied current. In general, the decrease in the soil pH was in the following order: Exp1 > Exp2 > Exp3 ≈ Exp4 > Exp5 > Exp6 > Exp7. The electric potential in Exp 1 and Exp 2 was 10 volts, but soil pH was lower in Exp2 than in Exp1, particularly in S2, as the alkaline front movement was suppressed by the RFM near the cathode in Exp2 (Ghobadi et al., 2021). Exp3 and Exp4 showed an approximately similar soil pH and it was lower than in Exp1 and Exp2, due to maintaining the electric current at a higher level. The results also revealed that increasing the amount and thickness of compost RFM from 90 g in Exp3 to 120 g in Exp4 had no further effect on the pH of the soil. In contrast, in the case of Exp6, the soil pH significantly decreased in S2-S4 by increasing the treatment time, which generates H^+ ions at the anode, which are responsible for lowering the soil pH. However, the pH of S5 was higher for Exp6 due to the advance of the alkaline front from the cathode electrode. Compared to Exp5 (without RFM), soil pH was observed to be significantly lower in S3- S4 for Exp6 because of the integration of RFM in the EK process. It relied on RFM in the EK process for the mobilization of metal ions by lowering soil pH. An increase of the electric current from 20 to 30 mA in Exp7 led to a highly acidic condition in the soil specimen, especially in S1-S4, which promotes more heavy metal ions desorption and movement. The pH profile was stable at pH 2.5 in S1-S4 and increased to the initial soil pH at 4.3 in S5, reducing heavy metal cations removal and resulting in precipitation in section S5.

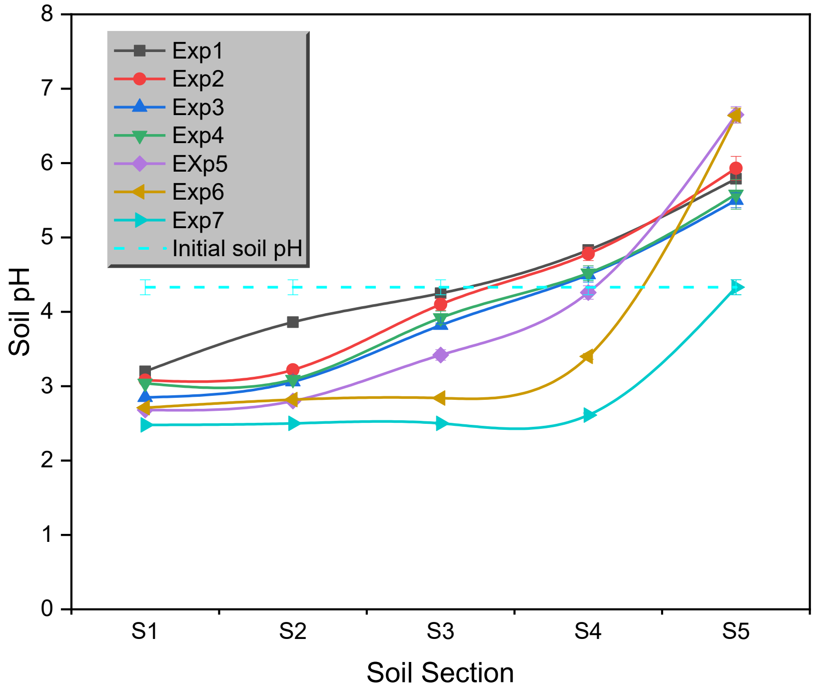


Figure 6.2. Soil pH profile after different EK treatment.

6.3.3. Removal of heavy metals from soil

The experimental results of heavy metal contents after EK-RFM experiments were reported in **Figure 6.3** as the C/C_0 ratio across the specimens, where C and C_o represent the final and initial heavy metal concentrations in each soil column, respectively. The heavy metals movement matches fairly well with the soil pH profile in all cases (**Figure 6.2**). It can be explained by the low soil pH from the anode region and resulting in the desorption of the heavy metal ions from the porous solid surface (Rezaee et al., 2019).

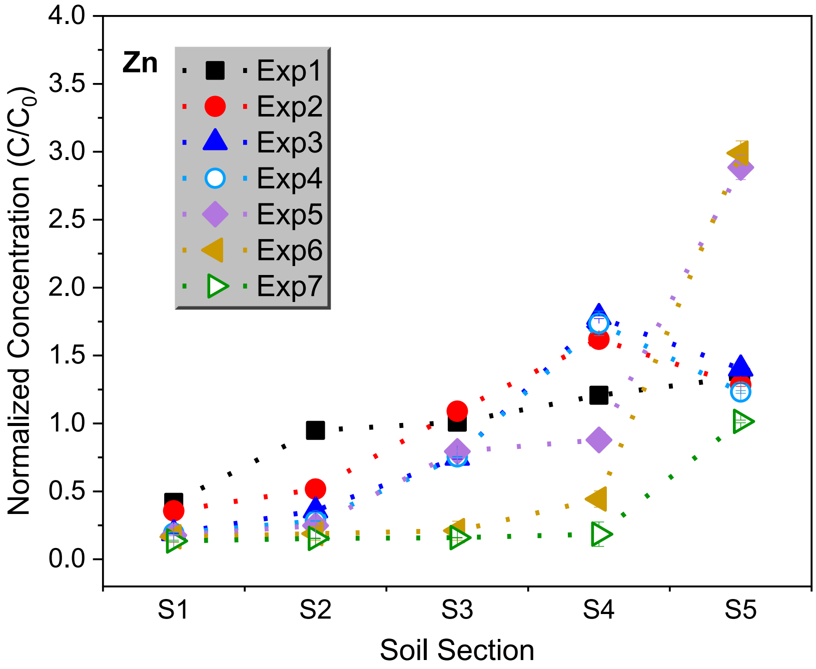
According to **Figure 6.3**, heavy metal migration (e.g., Zn, Cd, Mn, Cu, and Pb) typically occurred towards the cathode compartment because of their positive charge, as previously reported in the literature studies (Iannelli et al., 2015; Xu et al., 2019; Zhu et al., 2015). The results of Exp1 (EK without RFM) evidenced a slight mobilization of Zn, Cd, and Mn from the soil section close to the anode (S1) and precipitation in the final soil section near the cathode (S5). The observed behavior could be described by the fact that the pH across the middle soil sections (ranged from 3.9-4.8) practically remained unchanged in regard to the initial soil (pH 4.3), because of the high buffering capacity of the soil.

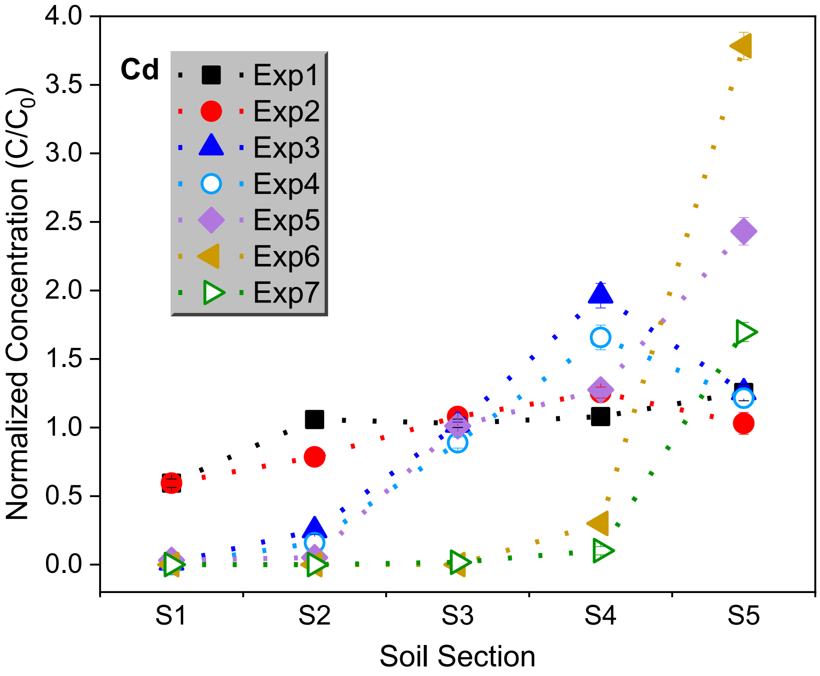
The concentration profiles of Cd and Zn across the soil columns present moderately sharp concentration gradients from anode to cathode for all tests, except Exp1 (EK without RFM). In the case of Mn, the increasing trend was observed relatively steady, particularly for Exp2 to Exp7. In the case of Cu and Pb, the final concentrations were nearly equal to the initial ones in Exp1; however, the metal distribution profiles were slightly changed, with a minor mobilization close to the anode end in the enhanced EK tests (Exp2 to Exp7). Overall, there was no appreciable improvement in both Cu and Pb removals when enhancing the EK-RFM system. The results confirm that the advancement of the acid front was not effective in the extraction of Cu and Pb. From the literature, it was found that the mobility of Cd and Zn in the soil could increase under low pH condition, while Cu and Pb remained insoluble due to the formation of highly stable metal-organic complexes (Giannis et al., 2009; McLean and Bledsoe, 1992; Yang et al., 2014).

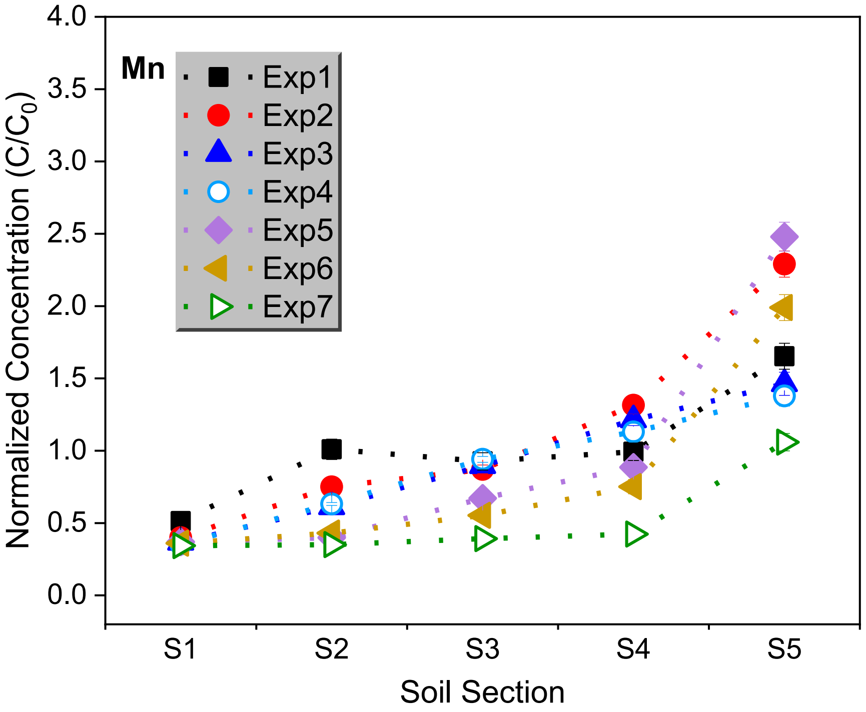
Compared to Exp1, Exp2 had a lower content of Cd, Zn and Mn in S2 when applying RFM in the EK process and resulted in a decrease in the soil pH. It was also observed that experiments Exp3 and Exp4, which configured under a constant current of 20.00 mA represented a lower level of those metals than that in the experiment operated at a fixed voltage of 10.00 V (Exp1 & Exp2) because of the lower soil pH caused by faster advancement of the acid from towards the cathode. Exp3 and Exp4 were found to be relatively similar in the heavy metal distribution profiles, although the amount of RFM was varied, indicating that increasing the amount of RFM has an insignificant impact on the process performance.

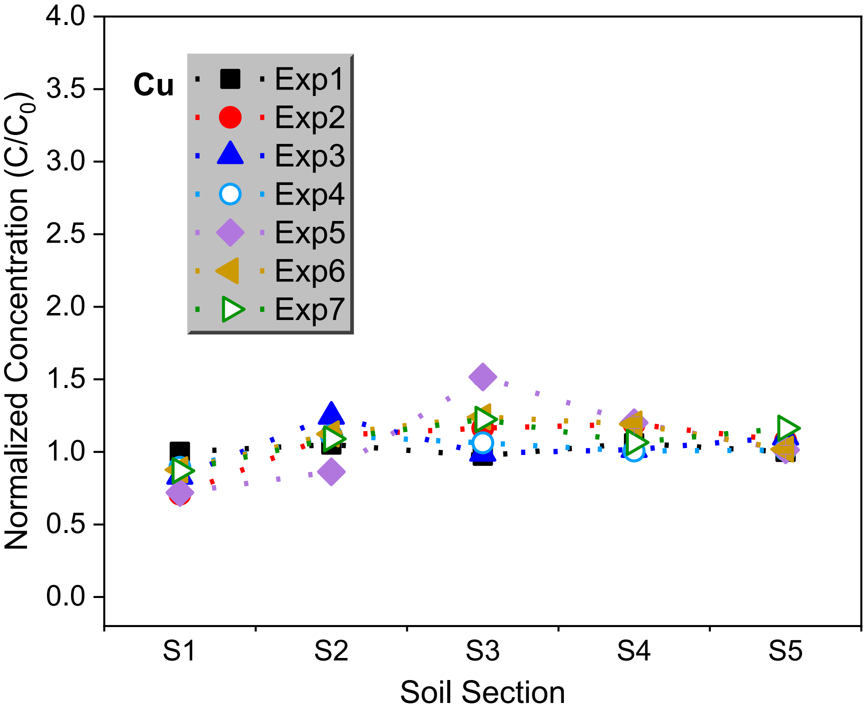
The experimental results of Exp6 noticeably demonstrated that processing time is a key parameter that specifies the extent of pH decrease (**Figure 6.2**) and heavy metals mobilization (**Figure 6.3**) under the electric field. Again, at short operation durations (Exp2-Exp4), soil pH was not found to be considerably affected, and slight metal transportation towards the cathode was achieved. These behaviors were clearly found different in Exp6, as the final concentrations of heavy metals such as Zn, Cd and Mn have drastically decreased in sections S1-S4. The normalized concentration of Cd and Zn were found approximately zero in the majority of soil specimens S1-S3 in Exp6. Compared to Exp5, Exp6 demonstrated the positive impact of RFM in the performance of the EK process for a longer processing time, especially for the transportation of metal ions in S3 and S4.

Exp7 also contributed to the different behavior of the system in terms of both pH and metal mobilization in the soil near the cathode (S5) compared to Exp6 for the case of Cd, Zn, and Mn. The higher current in Exp7 provided a low pH condition of the system which was highly effective for the mobilization of heavy metals (i.e., Cd, Zn, and Mn) that were retained in the soil because of adsorption/ion exchange interactions. As observed in **Figure 6.3**, both Exp6 and Exp7 had nearly similar behavior from S1 to S4 for the case of Zn, Cd and Mn; however, this behavior was entirely different in S5. It would be concluded that a higher rate of current would affect the electromigration and mobilization of metal ions in experiments Exp6 and Exp7 due to the advancement of the acid front, but also more effective for Exp7 in heavy metals reduction from S5 by increasing RFM adsorption capacity.


Zn
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Normalized Concentration (C/C_0)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
S1
S2
S3
S4
S5
Soil Section


Cd
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Normalized Concentration (C/C_0)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
S1
S2
S3
S4
S5
Soil Section


Mn
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Normalized Concentration (C/C_0)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
S1
S2
S3
S4
S5
Soil Section


Cu
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Normalized Concentration (C/C_0)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
S1
S2
S3
S4
S5
Soil Section

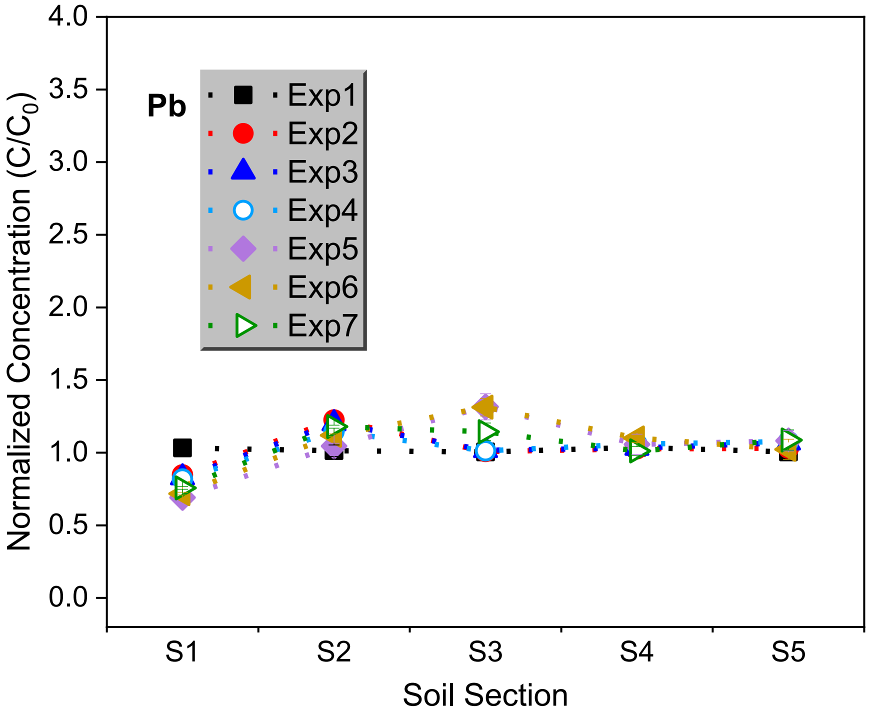


Figure 6.3. Residual heavy metals across the soil from anode to cathode after EK operations.

Heavy metals removal efficiencies along the specimen from anode to cathode after the EK treatments is shown in **Figure 6.4**. In the enhanced EK-RFM, the remediation efficiencies varied with the operating conditions. Indeed, for the EK-RFM experiments Exp2-Exp4 and Exp6-Exp7, the profiles of heavy metals distribution across the soil were found to be more influenced by the electric current level and the treatment duration (**Figure 6.3**).

Compared to other EK-RFM tests, Exp7 had the highest removal efficiency for Zn, Cd and Mn across the soil, due to higher electric current and longer operation duration, leading to a faster migration of ions by highly soil acidification. Consequently, more heavy metal ions migrated in soil towards the cathode, that were adsorbed and reduced by the RFM. For Zn, it ranges between 81.5%-86.6% from S4 to S1 and small precipitation (-19.4%) in S5 close to the cathode. All Cd were successfully removed through S1-S3, and the removal efficiencies were 89.8% in S4 and -69.6% in S5. Mn removal efficiency was observed between 57.6%-65.6% from S4 to S1 with slight precipitation (-5.9%) in S5. The high remediation efficiency obtained in Exp7 confirms the abovementioned results, pointing out the increasing demand for appropriate operating conditions such as an increase in the current gradient/processing time to improve heavy metal transport.

In general, Pb and Cu were difficult to solubilize in the enhanced EK-RFM processes and only small extractions of 28.2% and 29.1%, respectively, were found in the specimen near the anode. It may be associated with the strong binding of these metals to the insoluble soil organic matter which increased their retention in soil (Elbana et al., 2018; McLean and Bledsoe, 1992). In contrast, enhancing the EK-RFM process represents an interesting effect in the extraction of Cd, Zn and Mn.

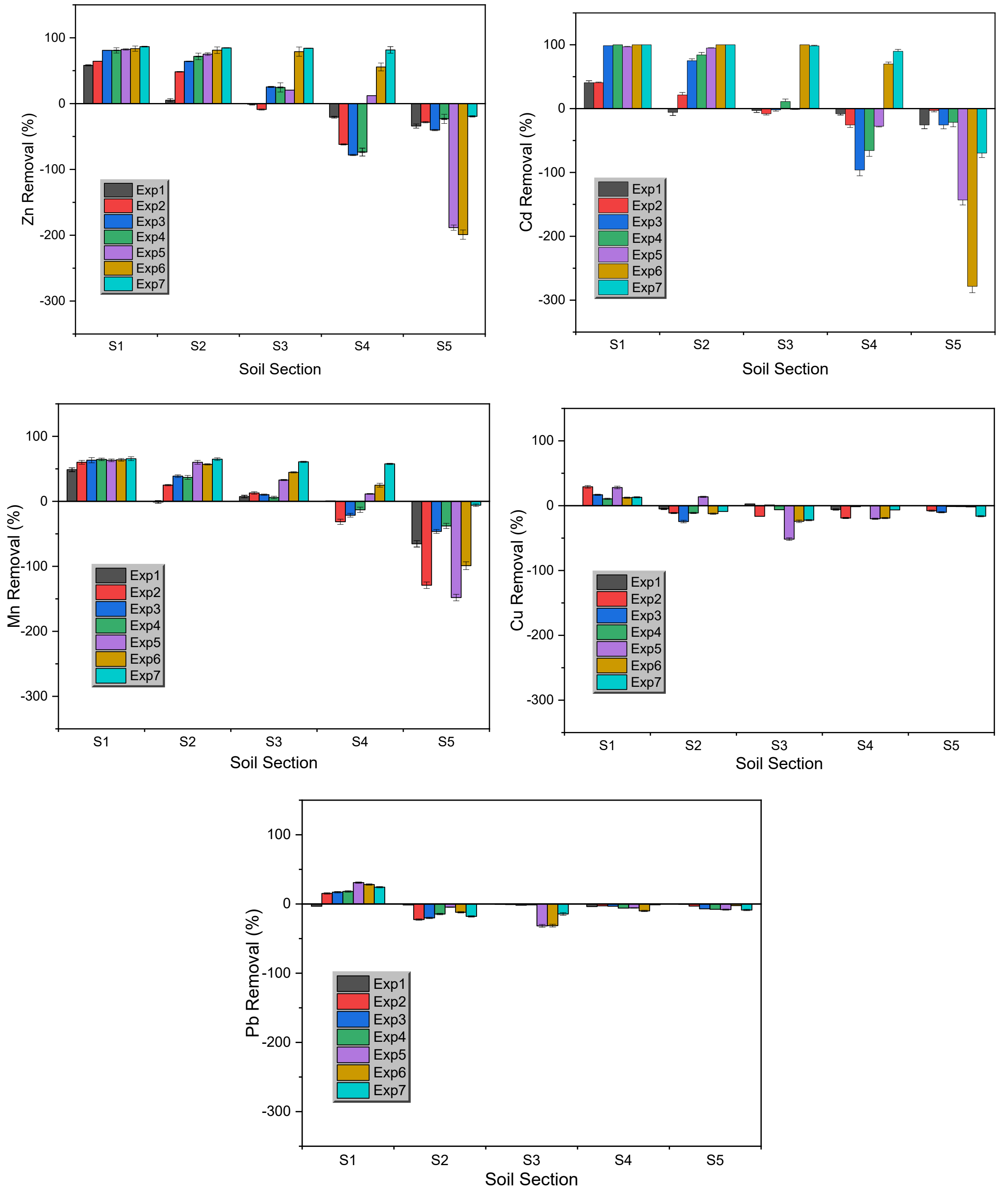


Figure 6.4. Heavy metals removal efficiency across the soil after EK treatments.

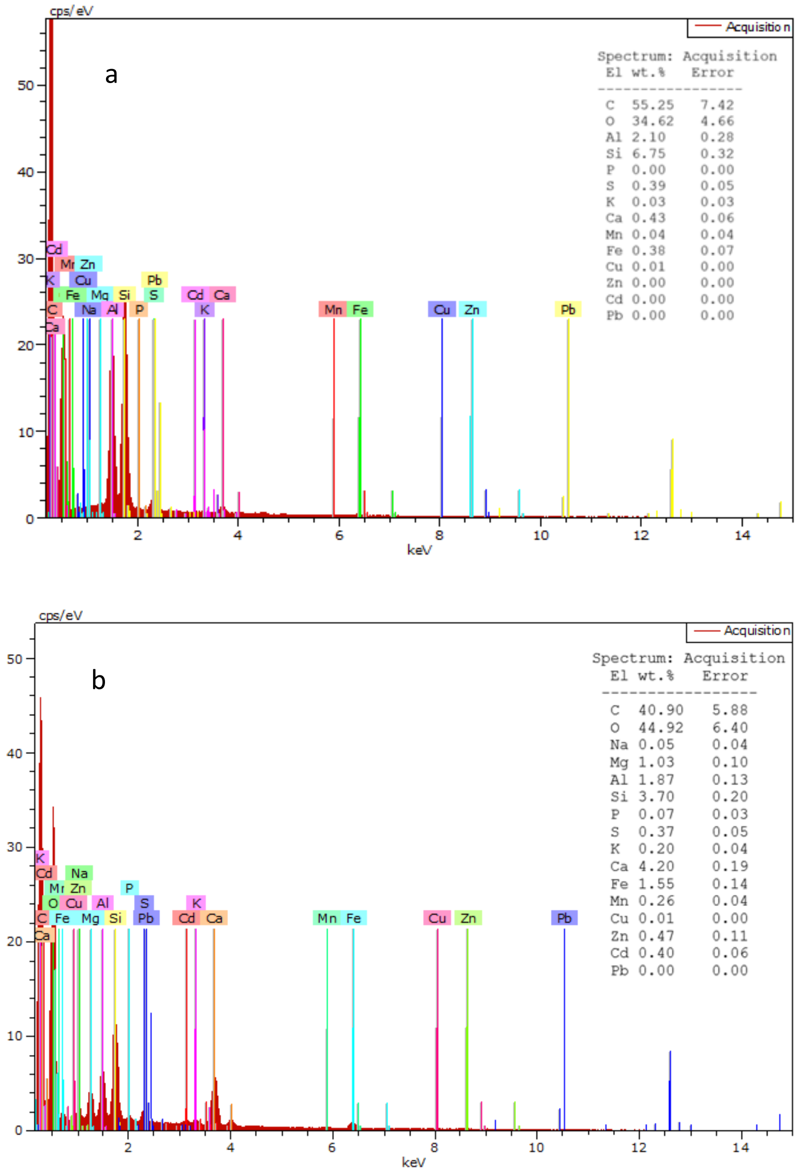
6.3.4. Remediation mechanism for heavy metals

Generally, in the EK process for heavy metals removal, ionic migration is the main transport mechanism under the effect of an electrical field, rather than diffusional or electroosmotic flow (Wang et al., 2021). The ionic migration is associated with the total charge transferred to the reactor from the power supply. Thus, as derived from the experimental results, each heavy metal extraction/mobility yield was consistent with the total charge applied (Ortiz-soto et al., 2019). The likely mechanisms of heavy metals removal in the enhanced EK-RFM system would be derived from the exchange of ions between heavy metals and cations in the RFM, resulting in co-precipitation (Ghobadi et al., 2021); and the electrostatic attraction between metallic cations and negatively charged ions of the compost RFM which can be involved in the adsorption process (Wang et al., 2021).

According to the experimental analysis, soil organic matter could resist the mobilization and migration of heavy metals such as Cu and Pb. In comparison, a previous study (Ghobadi et al., 2021) demonstrated the successful Cu removal in the EK-RFM process for the kaolinite soil containing negligible organic matter. Previous studies revealed that Cu and Pb ions could form strong and stable metal-organic complexes, the stability of which is in the following order Cu > Pb > Zn > Cd (Overcash and Pal, 1979). Copper and lead removal could be due to precipitation as metal hydroxide, complexation with organic ligands, or adsorption (Bahemmat et al., 2016; Giannis et al., 2009; He et al., 2021; Yuan et al., 2017). Metal removal would also be affected by the soil pH (Martínez and Motto, 2000). Metal ion’s solubility in soil depends on the soil components, pH, and soil mineralogy (Martínez and Motto, 2000). Giannis et al. (2009) reported that Pb as a redox-stable divalent cation had a much higher affinity for natural soil surfaces than Cd and Zn. Copper and lead could be retained significantly by natural soil even in conditions of low pH (Elbana et al., 2018; Giannis et al., 2009), which explains the low transport of Pb ad Cu and the removal efficiency. The presence of organic matters in the natural soil also significantly affects the Pb and Cu adsorption capacity of soil components and forms complexes on the surface that are more stable for Cu and Pb than for Zn and Cd (Echeverria et al., 1998; Fontes et al., 2000; Saminathan et al., 2010). Moreover, Cu and Pb can be stabilised on the soil surface via hydrolysis reactions, producing non-exchangeable forms (Echeverria et al., 1998; Sipos et al., 2005). Therefore, strongly sorbed heavy metals ions such as Pb and Cu are not easily affected by leaching with less potential mobility in the soil profile (Elbana et al., 2018). Electronegativity is also an important factor that can determine the ability of metals to chemisorb and form strong covalent bonding in the soil (Gomes et al., 2001). Üçer et al. (2006) and Gomes et al. (2001) reported that the order of the electronegativities for the metal ions was Cu(1.9) > Pb(1.8) > Cd(1.7) > Zn(1.6). The larger metal electronegativity would lead to the easier dissociation of the hydrogen from the functional groups of the soil mineral and organic particles, which forms covalent bonding and strong complexes (Gomes et al., 2001). Overall, enhanced electromigration incorporated with adsorption/reduction is the main removal mechanism for Zn, Cd and Mn during the EK-RFM operation.

EDS-SEM was used to confirm the RFM's capacity for the adsorption of heavy metals from the contaminated soil during EK-RFM treatment. **Figure 6.5** indicated that the RFM was capable of capturing Zn, Cd, and Mn rather than Cu and Pb. FTIR spectra analysis was used to further analyze and understand the mechanisms of heavy metals removal according to their structure, composition, and structural changes upon electrochemical reactions. Since Exp7 had the highest performance of metal removal, FTIR spectra of the initial soil sample and the soil columns collected at the end of Exp7 were determined and presented in **Figure 6.6**. In the FTIR spectra of all soil samples, whether before or after treatment, the vibration peaks were exhibited at wavenumbers of 3700-3600 cm^{-1}, 1630 cm^{-1} and 1030 cm^{-1}, which could be attributed to the oxygen groups such as -OH, -C=O and -C-O, respectively (Maneechakr and Mongkollertlop, 2020). Two vibration peaks were also observed at approximately 779 cm^{-1} and 679 cm^{-1}, usually ascribed to C-O-C bending (Liu et al., 2016).

As shown in **Figure 6.6**, the intensity of the absorption band at 1030 cm^{-1} was significantly changed after the EK-RFM treatment, especially in S1 and S5, which were the closest to the anode and cathode zones. It would be indicated in the high reduction/precipitation of heavy metals for those soil columns during the EK-RFM process.



```
Spectrum: Acquisition
 El wt.%    Error
-----------------
 C  55.25    7.42
 O  34.62    4.66
 Al 2.10     0.28
 Si 6.75     0.32
 P  0.00     0.00
 S  0.39     0.05
 K  0.03     0.03
 Ca 0.43     0.06
 Mn 0.04     0.04
 Fe 0.38     0.07
 Cu 0.01     0.00
 Zn 0.00     0.00
 Cd 0.00     0.00
 Pb 0.00     0.00
```

```
Spectrum: Acquisition
  El wt.%    Error
-----------------
  C  40.90    5.88
  O  44.92    6.40
  Na 0.05     0.04
  Mg 1.03     0.10
  Al 1.87     0.13
  Si 3.70     0.20
  P  0.07     0.03
  S  0.37     0.05
  K  0.20     0.04
  Ca 4.20     0.19
  Fe 1.55     0.14
  Mn 0.26     0.04
  Cu 0.01     0.00
  Zn 0.47     0.11
  Cd 0.40     0.06
  Pb 0.00     0.00
```

Figure 6.5. EDS analysis of RFM (a) before and (b) after EK treatment, showing the detection of different heavy metals.

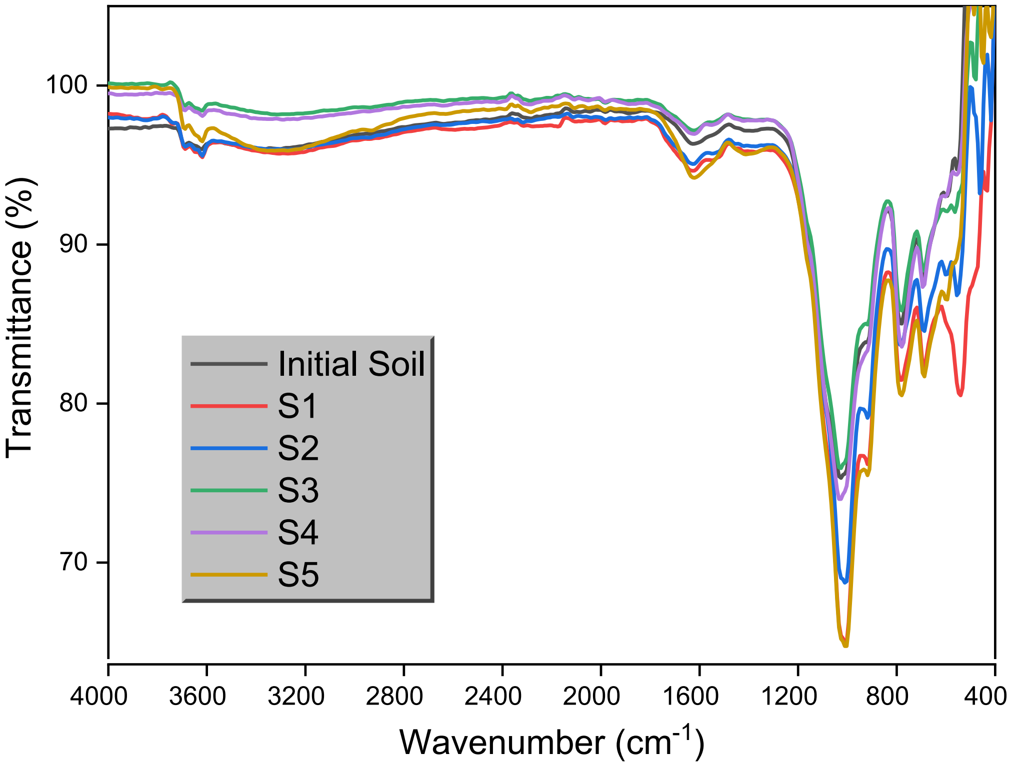


Figure 6.6. FTIR spectra of the soil before and after EK operations.

6.3.5. Electricity consumption analysis

The operating current is a dominant factor in the EK process, and it has a significant impact on the reaction kinetics and power consumption (Streche et al., 2018). **Figure 6.7** shows the changes in the total heavy metals removal rate, referred to the mass of dry soil, and the specific energy consumption of the EK-RFM process for different experimental and enhancement conditions. The effects of current and processing time were investigated in the EK-RFM system, and the total removal rate and energy consumption have been affected by varying both parameters (as observed in **Figure 6.7**). The total removal rates of Cu and Pb were insignificant for all tests. Power consumption calculations illustrated that the SEC increased from 0.01 kWh kg^{-1} to 0.17 kWh kg^{-1} treated soil when changing both the electric current level and the treatment duration in the EK-RFM system. The results in **Figure 6.7** indicate that more heavy metals would be extracted at a higher electric current, but the power consumption of the remediation process will also increase.

The comparison between Exp3 and Exp4 showed that the total removal rate of Zn and Mn slightly increased by changing the amount of RFM from 90 g to 120 g, but the energy consumption remained the same (0.06 kWh kg^{-1}). Under the same current (20.00 mA), additional energy consumption was dramatically increased to 0.14 kWh kg^{-1} in the EK remediation after increasing the processing time in Exp5 and Exp6. However, the total removal rate (18.3%-20%) was significantly higher for Cd, Zn, and Mn in Exp6 (with RFM) than that (0%-3%) in Exp5 (without RFM). Compared to other EK-RFM experiments (Exp2-Exp4), the total heavy metal removal rates in Exp6 were slightly affected by changing the treatment duration under the same electric gradient due to substantial metal precipitation in S5 near the cathode region. In contrast, the impact of electric current in the EK-RFM was promising with the highest removal of Zn, Cd and Mn (51.6%–72.1%) in Exp7, while SEC was marginally increased from 0.14 kWh kg^{-1} in Exp6 to 0.17 kWh kg^{-1} in Exp7. Overall, the total removal rate was found to decrease in the order of Exp7 (14 d, 30 mA) > Exp6 (14 d, 20 mA) > Exp4 and Exp3 (7 d, 20 mA) > Exp2 (7 d, 10 V) > Exp5 (14 d, 20 mA) > Exp1 (7 d, 10 V) as shown in **Figure 6.7**.

The mass balance and RFM adsorption efficiency of heavy metals in all tests are shown in **Table 6.2**. All treatments presented a mass balance of 95.49%–108.42%. **Table 6.2** indicates that RFM adsorption efficiency has also significantly been affected by the changing current rate. RFM adsorption efficiency was the greatest in Exp7, ranging from 50.5% to 73% for Zn, Cd and Mn. These values were between 16.6%–24.7% for Exp6. RFM adsorption efficiency was relatively negligible for the case of Cu and Pb for all experiments. The results showed that high removal efficiency of metal ions occurred in the EK-RFM processes performed at higher electric current and longer processing time, which however increased the specific power consumption of the remediation process. However, the application of renewable energy, such as solar power, would reduce the energy demand of the EK process.

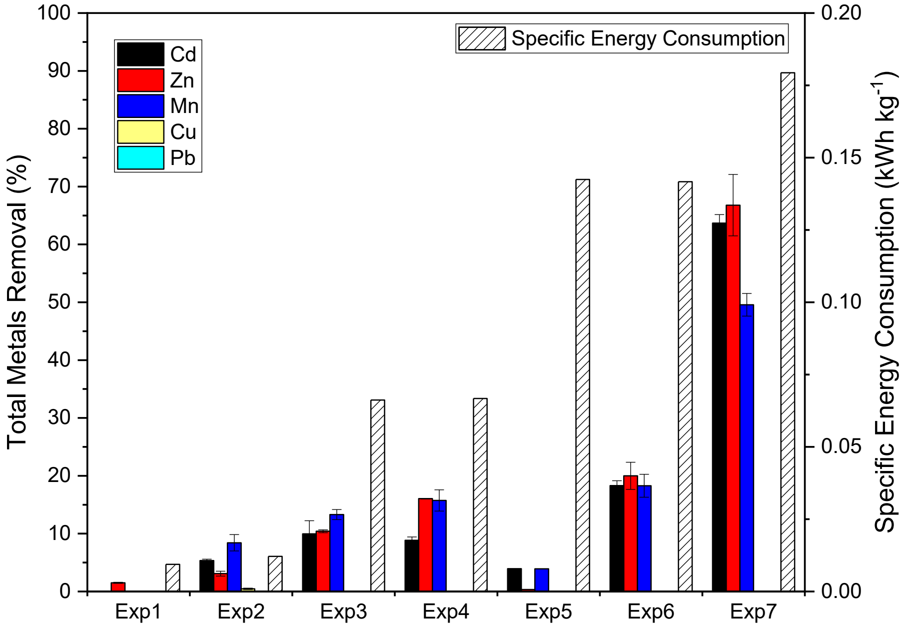


Figure 6.7. Total heavy metals removal and specific energy consumption during EK-RFM treatment of soil.

Table 6.2. Mass balance (%) and RFM adsorption efficiency (%) of heavy metals during different EK-RFM tests.

Metal	Exp1	Exp2		Exp3		Exp4		Exp5	Exp6		Exp7	
	Mass balance	Mass balance	RFM adsorp.	Mass balance	RFM adsorp.	Mass balance	RFM adsorp.	Mass balance	Mass balance	RFM adsorp.	Mass balance	RFM adsorp.
Zn	98.5	100.8	3.5	100.5	10.9	99.9	16	99.6	104.7	24.7	106.6	73
Cd	100.4	100.5	5.6	95.5	5.5	98.8	7.7	96	98.3	16.6	97	60.7
Mn	101.9	102.8	9.8	98.3	12.4	103.7	19.4	96.1	104	22.3	101.9	50.5
Cu	101.6	99.7	0.2	101.1	-0.6	101.4	-0.3	106.3	108.4	-0.6	107.7	-0.6
Pb	101.8	102.8	0	103	0	102.3	0.1	103.7	105.5	0	103.8	0.2

6.4. Conclusions

This work confirms that the applicability of RFM, such as compost with excellent adsorption capacity in the EK process for simultaneous heavy metals removal from natural soil. RFM acting as an adsorbent could significantly capture and reduce heavy metals in the soil. The results showed that elevated electric current and processing time considerably decreased soil pH and simultaneously enhanced the removal efficiencies, especially for Zn, Cd and Mn. Hence, electromigration was enhanced by increasing the applied current from 20.00 mA to 30.00 mA, which improved the total heavy metals removal to 51.6%–72.1% for Zn, Cd and Mn due to the advancement of the acid front across the soil, although with the additional specific energy consumption of 0.17 kWh kg^{-1}. In comparison, Pb and Cu were more difficult to solubilize during the enhanced EK-RFM treatments, with smaller extractions of 28.2% and 29.1%, respectively, near the anode. Lead and copper have a strong affinity for organic ligands, resulting in the formation of insoluble complexes in the soil. In general, enhanced electromigration coupled with RFM adsorption is the crucial mechanism of heavy metals extraction in the EK-RFM system. EK incorporating compost RFM is promising for its potential applications to in situ remediations of heavy metals contaminated sites.

Faculty of Engineering and Information Technology

CHAPTER SEVEN:

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

CHAPTER SEVEN: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1. Conclusions

This study focused on improving the EK process for capturing heavy metals in the soil matrix using different reactive filter media (RFM). The lab-scale experiments have resulted that the EK remediation as a single technique was not capable of decontaminating the kaolinite clay soil (as a surrogate soil) from copper due to the high pH distribution and copper precipitation in the soil near the cathode zone; however, copper was successfully removed close to the anode only. Therefore, the EK technique was integrated with RFM placed in the soil cell near the cathode region, which could trap contaminants transported through the soil toward the cathode. Initially, biochar and activated carbon have been used in the EK process to enhance contaminant removal. Biochar, compared to activated carbon, could offer a better contaminant removal. More negative charges available in biochar than activated carbon could offer a better copper removal from contaminated kaolinite soil in the EK-BC test. Biochar could be easily recovered by acid leaching after EK treatment; however, it has lower permeability than activated carbon. The application of fixed electric current could not significantly enhance the average removal rate of copper in EK-BC; however, it could remarkably increase the copper removal in a large amount of the soil (except section 5) up to 88% near the anode compartment by lowering the soil pH. Compost as an RFM enhanced copper removal up to 45.65% under a constant voltage (10 V). Application of fixed electrical current in the EK-compost would increase the removal efficiency by approximately 84.09%. Moreover, compost could be easily recycled by acid leaching due to its high permeability. Compared to compost itself, the mixture of biochar and compost (BC+C) would not offer a significant removal. However, adding the compost percentage in the mixture would be observed an increasing trend in the copper removal. Overall, the removal efficiency of the EK-RFM experiments was in the following order: EK-Compost > EK-(10%Biochar+90%Compost) > EK-Biochar > EK-Activated carbon > EK. The efficiency of compost in copper removal in the EK system over other RFMs was due to its high buffering and adsorption capacities, which allowed the acid front to sweep across the soil specimen resulting in the removal of copper ions. Also, compost contains a high concentration of organic matters, which behaves as a complexing ligand to increase the adsorption capacity of copper. It seems that humic acid in the compost would reduce the copper precipitation by lowering the soil pH near the cathode region during the EK process and consequently enhancing the copper removal. The advantages of compost are its low cost, environmentally friendly, and would easily gain public acceptance.

The applicability of compost RFM with excellent adsorption capacity was also confirmed in the EK process for simultaneously multi-heavy metals (i.e., Zn, Cd, Cu, Pb, and Mn) removal from natural soil. Compost RFM acting as an adsorbent could significantly capture and reduce heavy metals in real soil. An increase in the amount of compost RFM had no significant effect on the heavy metal removal rate. However, the elevated electric current and processing time considerably decreased soil pH and simultaneously enhanced the total removal efficiencies to 51.56–72.09% with the additional specific energy consumption of 0.17 kWh kg^{-1}, especially for Zn, Cd, and Mn, due to the advancement of the acid front across the soil. Only slightly better results for Pb and no significant change for Cu were observed. Pb and Cu were difficult to solubilize during the enhanced EK treatments (EK-RFM), and only small extractions were found in the soil specimen near the anode. The natural soil was anticipated to be highly resistant to the mobilization and transport of Cu and Pb due to a very low hydraulic permeability and containing organic matter. The experimental results showed that the removal efficiency of the EK-RFM process from the natural soil was lower than from the kaolinite soil.

This was due to the interaction of heavy metals with organic and inorganic matters in the soil and the reaction of the acid front with organic matters in soil, slowing its advancement in soil.

In general, enhanced electromigration coupled with RFM adsorption is crucial for heavy metals extraction in the EK-RFM system. Compost RFM is of importance for potential practical application to in-situ remediations of heavy metal contaminated sites.

7.2. Research Significance and Contributions to the Field

The main significance of this research was to develop an RFM of high adsorption capacity and hydraulic permeability for EK treatment of heavy metals contaminated soil. The developed RFM was suitable for reuse by changing the pH of the leaching solution to reduce soil treatment costs. The study provided useful knowledge of the performance of the reactive filter media in the EK system while comparing them in terms of removal efficiency and the ability of regeneration. The advantages of integrating RFMs with EK include no need to recycle the electrolyte (no contamination in electrolyte solution); no long treatment; easy to install; better removal efficiency, and no chemical adding. Besides, some RFMs could provide long-term services, as there was the feasibility of their regeneration by acid leaching.

To the best of my knowledge, RFMs such as compost and its mixture with biochar have never been applied in the EK system, and only their individual applications have been investigated in soil and water remediation. Among different RFM studied in this work, compost is the best sorbent for removing heavy metals from contaminated soil. The experimental results of the study indicate that most soil samples were generally below the guideline values (**Table 7.1** and **Figure 6.3**) for the target heavy metals (e.g., zinc) after the EK-RFM treatment, proving the feasibility of the technique for the field application. Therefore, this study facilitates the effective applications of these enhancement techniques in the field of EK remediation of contaminated soil and will be useful in optimizing the design of the EK-RFM system, which can then be extended to field-scale. EK-RFM remediation, as an in-situ technique, does not require the excavation of contaminated soil, reducing the human risk associated with soil excavation, minimum site disruption, low energy, and can be combined with solar energy.

Table 7.1. Soil quality guidelines for Zn from different countries (NEPC, 2011)

Zinc limit	Numerical value of the limit (mg/kg)
Dutch intervention level 1	720 (added Zn)
Dutch maximum permissible addition 1	20 (added Zn)
Canadian SQG (residential) 2	200 (total Zn)
Eco-SSL plants 3	160 (total Zn)
Eco-SSL soil invertebrates 3	120 (total Zn)
Eco-SSL avian 3	46 (total Zn)
Eco-SSL mammalian 3	79 (total Zn)
EU soil guidelines using negligible risk 4	67-150 (total Zn)

1 = VROM, 2000
2 = CCME, 1999a and 2006 and http://www.ccme.ca/publications/list_publications.html#link2
3 = http://www.epa.gov/ecotox/ecossl/
4 = Carlon, 2007

7.3. Recommendations for Further Research

Based on the experimental results of this research, the following recommendations are proposed for future study:

- Since heavy metal contaminants such as Cu and Pb are common in the soil, and their extraction could not be enhanced by the EK-RFM treatment, further research should be conducted to improve the mobilization of Cu and Pb during the EK-RFM operation. The application of environmentally friendly complexing agents may increase the mobility of heavy metals such as Cu and Pb during the EK-RFM process, resulting in further removal efficiency. Integrating humic acids or fulvic acids (without potential toxicity) with the EK-RFM can be investigated to enhance heavy metal extraction.

- Considering the occurrence of biological processes in the EK-RFM, more studies need to be conducted for RFMs in order to demonstrate the impact of biological reactions on the heavy metals' adsorption by RFMs during the EK process.

- EK technology is an effective soil remediation technique that can remove inorganic contaminants in either charged species, i.e., anions and cations from the soil. However, in this research, removing cationic heavy metals was only investigated in the EK-RFM process from the contaminated soil. Mobilization and distribution of different heavy metals with negative charges such as As and Cr can be studied in the EK-RFM process.

- Most of the anthropogenic activities caused severe contamination in the soil with heavy metals and organic species. Therefore, the performance of RFM can be investigated in combination with the EK process for the simultaneous removal of mixed inorganic and organic contaminants.

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