Electro-Kinetic Removal (EKR) of Heavy Metals from Contaminated Soil using Palm Fibers and Organic Material

S Ajjam and M Karbool

College of Engineering, University of Babylon, Babylon, Iraq
E-mail: maryam.s@uokerbala.edu.iq

Abstract. The heavy metals that are contaminating the soil considered a global problem and especially in Iraq. One of the latest techniques is EKR that can hand a senior promise to clean the contaminated soil with heavy metals. Iraq is the top country in terms of the number of palm trees and the dates that are produced each year, which eliminates thousands of tons of waste are eliminated. This study involves, firstly, mediating an EKR off-site pilot study of impact assessment of the organic material in the soil at a pH of 3. Regent HNO₃ and diluted NaOH were chosen to set the samples of distilled water, reaching the desired pH value. Secondly, test the capacity of date palm fibers (DPF) as a low cost, obtainable, and eco-friendly invert osmosis blocker. In this pH 3, organic removal of copper is more active than without the organic material of the same pH; 50%, 47%, on the way. However, it was concluded that in Iraq, the utilization of organic materials and fibers of the palm are available at low cost, and materials of eco-friendly have succeeded to improve the removal of copper method in the EKR Reactor; via raising the efficiency of copper (%R) removal to be around 50%.

Keywords. Electro-kinetic, Copper removal, Soil remediation, Palm fibers, Organic material.

1. Introduction
Heavy metals lead to polluting the surface of the earth, and this is truly widespread. To clean up these polluted sites and to accelerate this process, high efforts were made with the observance of the physicochemical and biological sides of the type of pollution [1]. Even though they are successful and ecological kindly soil remediation technologies, nevertheless, they have not been fully calculated and performed. Numerous mechanisms have fascinated the attention of scientists and manufacturing administers. These are biotreatment, extraction of the vapor of soil, thermal desorption, and washing and flushing of soil [2]. EKR for soil is a modern technology that has attracted considerable attention in the past decade as it aims to remove soil pollutants with permeable permeability of heavy metals under the influence of direct current.

The advantages of the electro-kinetic treatment, as compared with the conventional treatment methods, are (1) easy, (2) safe to avoid workers and people from contaminants, (3) a large area of polluting media which used for soils, mud, sediments, and groundwater that proper for low permeability and non-homogeneous soil deposits within the fades area where traditional remedial ways have certain unsuccessful or costs, (4) an extensive domain of pollution, applied for metals, radionuclides, or groups of...
these pollutants, (5) resilience, applied as an on-site or off-site management way and can be easily inserted with other treatment techniques like as biological treatment [3]. In this work, an exhaustive work by utilizing an EK study on an industrial copper polluted soil (600 ppm of Cu) has been conducted. A clay soil sample was taken from an agricultural area in the Al-Mahawil district north of Babylon province. The Cu removal was 50% by using organic material, and 47% without using organic material (at pH 3). The aims of this study are: (1) applying and testing the use of an ex-situ EKR to take away copper from synthetically Cu-polluted soil, (2) the fibers of palm are used as a bio sorbent to avoid the reverse osmosis method in the treatment reactor, (3) using organic material as an enhancing conditioner and select the best circumstances for higher effectiveness of copper elimination.

2. Experimental work

2.1. The sample of soil
The soil was taken from a depth ranging from 30 to 50 cm below the ground surface from an agricultural area, as mentioned previously. It was cleaned by removing the stones and plant roots in it, and then it is further desiccated and sift subsequent with a sieve of 2mm to get satisfying uniformity. Table 1 shows the soil composition and properties that are considered in this work. The soil has 13% sand, 21% CaCO₃, 24% clay, and pH 7.7. The soil hence can be classified as a clay soil.

| Property                          | Value     |
|----------------------------------|-----------|
| Particle size distribution(ASTM D 422) |           |
| Sand (%)                         | 13        |
| Silt (%)                         | 61        |
| Clay (%)                         | 24        |
| Carvel (%)                       | 0         |
| Atterberg limit (ASTM D 2487)    |           |
| Liquid limit (%)                 | 42.10     |
| Plastic limit (%)                | 28.48     |
| Plasticity index (%)             | 14.60     |
| Compaction text                  |           |
| Max dry density (gm/cm³)         | 1.74      |
| pH                               | 7.7       |
| CaCO₃ (%)                        | 21        |

2.2. Copper pollutant
The pollution of the soil is simulated using copper; a Cu(NO₃)₂.3H₂O solution was added to the specimen to get an envoy concentration. As a calculation sample for producing (600 mg/kg) copper to the weight of soil and primary humidity satisfied equivalent to 30%, a quantity of 2.26g of Cu(NO₃)₂.3H₂O molecular weight of 241.g/mol was dissolved in 500 ml of distilled water. Then 1 kg of dry soil is added to 400 ml.

2.3. Purging solutions
To examine the effectiveness of the EKR procedure (not including improvement solution), the pH of the distilled water is restricted to be 3.
2.4. Date palm fibers (DPF)
DPF was composed of the trunks and cut into little pieces and then washed using distilled water to eliminate grimes and dehydrated at 80°C to remove the humidity. It was argumint and sifter to different particle sizes by vibratory sieve after the drying process. By the SEM testing, the good bio sorbent DPF showed that they contain many physical and chemical properties [4].

2.5. Organic materials
The bio-organic used a natural product containing one or more of the unknown micro-organic microorganisms that did not contain any adverse or pesticides, safe for health, and cheap. It is also appropriate and effective for more than chemical fertilizers, and this helps in reducing the values of pH in the soil [5]. The amount of 5% of the organic substance is added to the soil in the experiment.

2.6. Reactor setup
The treatment of EK includes applying the low-level D.C. current or low voltage slope traverse electrodes that are at polluted soil. Nearly every significant electron move reactions that happen at the electrodes through the way are the water electrolysis [6], and the EK trial system that utilized at work was shown in Figure (1). The setup contains a cell of electro-kinetic, two electrode sections, a multi-meter, and a power supply. The inter dimensions of the glass cell of electro-kinetic equal to (40 cm * 8 cm * 10 cm high) but the real length of the soil specimen equal to 20 cm. The electro-kinetic cell barrier is a DPF that is between the cathode section and the soil that is having a 4 cm thickness. The valve of each electrode is to control the cell flow. Perforated Plastic Plates were utilized to divide the DPF blockade as of one end soil and to the other end cathode electrode. The plates dimensions are 8 cm x 12 cm, and they contain holes of 6 mm diameter, the space between the center of two holes is 1 cm.

![Figure1. Schematic diagram of the Electro-Kinetic Cell, (1) glass basin, (2&3) graphite electrodes, (4) soil, (5) DPF, (6) perforated plastic plates, (7) filter paper, (8) purging solution, (9) multi-meter, (10) DC, (11) electrical wires, (12) valve.](image)

2.7. Experimental methods
The polluted soil layers were put in the sheer glass motor cell, and, after that, homogeneous compression using a manual compressor is done and then left for one day to stabilize and reach the equilibrium state. The compartments are filled at the cell ends with a cleansing solution subsequent to the soil putting into the cell. To avoid the heat generation, the two tests were prepared below a steady voltage grade, which is 30 V. Different trials were done to study the effect of employing organic matter in the soil, and the
experiments form summary is shown in Table 2. In the preliminary testing (EX-1), distilled water of 3pH has been utilized together with the anode and cathode partitions at a voltage equal to 30, soil with 600 mg/kg copper concentration, and without organic matter. In the second experiment (EX-2), organic matter and other situations are conserved as in (EX-1). To maintain the pH in distilled water at 3 in the two experiments, HNO₃ was added to the section of the cathode, in the anode chamber, NaOH is added. The DPF and the soil part are extracted from the cell at the end of each experiment, where the soil part is separated into five sections and then weighted and stored in a glass container. Dry soil is mixed and then mixed with distilled water by 5 g and 12.5 ml, respectively. The combination is then shaken by hand for a bit long time, and the solids left to settle for an hour, and the pH and soil EC are measured.

Table 2. Experiment conditions and purposes.

| Exp. NO. | Duration (Process) (days) | Initial Copper Conc. (mg/kg) | pH of Purging Solution | Type of Purging Solution | Experiment purpose |
|----------|---------------------------|-----------------------------|------------------------|--------------------------|-------------------|
| EX-1     | 4                         | 600                         | 3                      | Distilled Water          | Baseline Exp.     |
| EX-2     | 4                         | 600                         | 3                      | Distilled Water          | Effect of organic material |

2.8. Chemical analysis
The total copper content in different soil sections was removed by acid digestion [7]. The oven-dried samples were ground into fine particles by a soil grinder mill. Then, 1 g of the specimen was scaled and set in a 50 ml Teflon tube, and 15 ml of HNO₃ and 5 ml of HCl with concentration of 69.9% were added to the sample. The mixture was heated for about (45-60) minutes, in the erinaceous bath awaiting the brown steams vanished, and the specimen reaches the dry case. Then, the beaker was left for (5-10) min in the lab temperature; after that, a 5 ml of HCl centered is added, and the mixture is heated for a second time in a sandy bath. It is then cooled, and 5 ml of HCl centered is added, and 50 ml of heated distilled water to clean the beaker from residue dissolved specimen. The mixture was heated to the boiling points for (2-3) min. The specimen was filtered using paper filter paper No. 42, and then it is saved in a volumetric vial ability of 100 ml. The precipitation is washed with distilled water and before washed water and filtration and full of 100 ml. Lastly, the copper concentration was calculated by atomic absorption spectrophotometer (AAS).

3. Results and discussion
3.1. Organic materials as an enhancing conditioner
Figures (2), (3), (4), (5), and (6) illustrate the variation between the soil with organic matter and the soil without organic matter, which were used as distilled water at pH of 3. These figures show the copper concentration, EC, electro-osmotic flow, current, and pH all along with the soil sample subsequent to the completion of the EKR. As shown in these figures, the organic matter is then primary source of microbiology energy in the soil as well as the source of electrons, and these organisms in the soil are important in the secretion of organic acids, which lead to the reduction of pH in the soil [8][9]. As confirmed, the organic matter has the ability to capture copper by adsorption or composition of complexities such as Cu(OH)₂ and that organic compounds have the ability to remove elements from the soil solution [10]. The best elimination of Cu is in the anodic area, and the copper ions are concentrated in the cathode location. The removal of copper in EX2 was about 50% when the use of dissolved organic material would increase the removal because the organic matter increases the acidity and reduce the pH [11][12]. The removal in EX1 is less than 50%, about 47% appear in Figure (7).
Figure 2. The Cu concentration (mg\kg) versus the distance from the anode (X\L).

Figure 3. The pH of soil versus the distance from the anode (X\L).
Figure 4. The EC of soil (mS/cm) versus the distance from the anode (X:L).

Figure 5. The Volume of electro-osmotic flow (ml) versus the time (hr).
3.2. Palm fiber effect

Based upon this experimental work, DPF has swimmingly vetoed the undo electro-osmotic flux, which negatively affects the path and scale of copper movement through the EK procedure. DPF was efficient in adsorbing copper metal as of the aqueous solution. Because of the high adsorption ability of DPF, little copper ions were adsorbed by the DPF; since the salts ions opposition previously obtainable in the soil specimens as in Table 1 with copper ions [13]. However, the quantity of copper ions adsorbed by DPF was in the range of 43 to 87 mg/kg in experiment-1 and experiment-2, respectively.

Figure 6. The Current (mA) versus the time (hr).

Figure 7. Removal efficiency of copper.
4. Conclusions
The most important conclusion of this study is that the elimination effectiveness of copper raises through organic material in the soil; because the organic materials are doing the acidity of acids that help in reducing the values of pH and therefore increase the efficiency of the removal. As explained in [14] and [15] that the solubility of copper compounds is correlated with pH if this susceptibility decreases by increasing the pH of the soil. The copper elimination effectiveness at pH 3 was great as the utilized organic material for enhancing conditioner is better than pH 3 without organic material (50% and 47%, respectively). DPF was establish to be an efficient ecological bio sorbent matter in avoiding the electro-osmosis method in sandy soils, particularly as the cumulative electro-osmotic effluent developed to be high in such procedure. Though, the EK method by using both of the available date palms proved to be an appropriate solution for treating the heavy metals polluted soils in Iraq.

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