ELIMINATION OF ZINC FROM THE CONTAMINATED SOILS BY ELECTRO-KINETIC REMEDIATION

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Abstract: An electro-kinetic technique was usedin this study for removing of zinc from Iraqi contaminated soil was brought from area close to the Al-Doura refinery plant (silt loam soil). Many experiments were constructed with different electrode purging solutions of tap water at pHof 4.5, 5.5 and 6.5. Chemical anionic surfactant (SDS, sodium dodecyl sulfate) for washing soil and as enhancing conditioner wasalso used.Used tea leaves (UTL) was used as a low cost adsorbent material to prevent reverse osmosis flow, which may affect the removal efficiency.The results showed that the removal efficiency increases with decreasing pH of the purging solution. It was noticed from the first three experiments (using purging solutions with pH of 4.5, 5.5 and 6.5), the best removal efficiency was at pH of 4.5 (64.37%). This because when the pH increases, the tendency for metal ions to become adsorbed onto the soil particles also increases. The removal efficiency was increased when $(10^{-1}M)$ SDS was used as enhancing conditioner (71.87%).The use ofSDS as washing solution has increased both zinc dissolution and desorption from the soil surface and hence the efficiency of electro-kinetic remediation was also increased. This study proved that the (UTL) is a good adsorbent material to prevent the reverse electro-osmotic flow, and hence it could be considered economically and beneficially as a good adsorbent medium.

Keyword: electro-kinetic, zinc, SDS, UTL, soil, efficiency.

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ازالة الزنك من الترب الملوثة بالمعالجة الكهروحركية

الخلاصة: في هذه الدراسة تم استخدام تقنية المعالجة الكهروحركية لازالة الزنك من تربة عراقية ملوثة تم جلبها من منطقة قريبة من مصفى الدورة (تربة مزيجية غرينية). تم اجراء عدد من التجارب باستخدام محاليل ناقلة وكانت المحاليل هي (مياه الحنفية) برقم هيدروجيني (4,5, 5,5 و 6,5). تم استخدام مادة (دوديسيل كبريتات الصوديوم) الانيونية كمادة كيميائية فعاله سطحيا لغسل التربه وكعامل منشط في الازالة.تم استخدام اوراق الشاي المستعمل كمادة مازة قليلة التكلفة لمنع التدفق الاوزموزي العكسي والذي قد يؤثر على كفاءة الازالة. أظهرت النتائج بان كفاءة الازالة تزاد مع تناقص الرقم الهيدروجيني للمحلول الناقل. لوحظ من خلال التجارب الثلاثة الاولى (استعمال المحاليل الناقلة برقم هيدروجيني 4,5, 5,5, و 6,5), إن افضل كفاءة ازالة كانت عند الرقم الهيدروجيني 4,5 (64.37%). هذا لأنه عندما يزداد الرقم الهيدروجيني يزداد ميول المعدن الى الامدصاص على سطح جزيئة التربة. كفاءة الازالة ازدادت عنداستعمال محلول (دوديسيل كبريتات الصوديوم) كعامل منشط بغسل التربة (71,87%). استعمال محلول (دوديسيل كبريتات الصوديوم) كمادة فيغسل التربة, سبب زيادة في كل من عملية انحلال الزنك وامدصاصه من قبل سطح التربة وهذا يؤدي الى زيادة كفاءة المعالجة الكهروحركية. هذه الدراسة أثبتت إن اوراق الشاي المستعمل من المواد المازةالجيدةعند استخدامها كوسط لمنع عملية التدفق الاوزموزي العكسي اثناء عملية المعالجة في المنظومة, وبالتالي فأنها تعتبر مادة اقتصادية ومفيدة عنداستخدامها كوسط في عملية الامتزاز.

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1. Introduction

Several technologies have been developed to remediate contaminated sites, such aschemical treatment, bioremediation, phytoremediation, soil Washing and electro kinetic remediation. These technologies can be grouped as either ex-situ or in-situ technologies.

Electro-kinetic remediation was progressed to overcome the limitations of many in situ remediation methods and also to be applied on fine-grained soil. Electro kinetics is a simple process, two electrodes are located within the soil and a direct electric current is passed between them making one the anode and the other the cathode. This electric current passes into the soil and generates a pathway on which ions can travel[1-3]. There are many advantages of Electro-kinetics: (1) simplicity; minimal equipment requirements, (2) safety; neither personnel nor the public in the nearness are exposed to contaminants, (3) wide range of contaminants; it can be used for metals, organic compounds, radionuclides, or combinations of these contaminants, (4) flexibility; can be used as an in-situ or ex-situ remediation system, (5) cost; effectiveness requires low electrical energy leading to lower overall cost, (6) wide range of contaminated media;it can be used for soils, sludge, sediments, and groundwater.   .

The heavy metals in soil canbe existed as dissoluble compounds such as ions or in commutable shapes. In general, these metals are rendered immobile by incorporating with different soil fractions and compartments like carbonate,organic matters, oxide, hydroxide, and residual materials [4].

Zinc is one of the many mobile heavy metals in groundwater and surface water because it is exist as solvablecomplexes at acidic andbalancedpH values. At greaterpH values, zinc can produce carbonate and hydroxide compounds which control zinc solubility. Zinc easily precipitates under decreasing conditions and in extremelycontaminated systems when it is exist at very high quantities, and may co-precipitate with hydrous oxides of iron or manganese[5].Maximum contaminant level (MCL) of zinc that could be present in Iraqi soils and according to thesoil quality standards instituted by the World Health Organization (WHO) is 300 mg/kg.The soil medium is a main sink for a many of chemicals and heavy metals, which without doubt leads to environmental contamination problems.

The extravagant concentration of metals in soil can also elicit a wide range of visible and physiological syndromes in plants leading to damage in crop productivity. However, heavy metal pollution represents real threat to human health and environment [6].

Theaim of this study is toinvestigate:(1) the ability of using electro-kinetic remediation to remove zinc from Iraqi contaminated soil, (2) the effect of the different pH values of electrode purging solutions (tap water),(3) the influence of using chemical anionic surfactant (SDS, sodium dodecyl sulfate) for washing soil on the electro-kinetic remedial efficiency and (3) the applicability of the used tea leaves, as a material of barrier coupled with electro-kinetic cell, to avoid reverse electro-osmotic flow occurrence during remediation process.

2. Experimental Design

2.1. Materials

2.1.1 Soil Sample

In this study, the soil was used as a porous medium in all experiments.This soil was brought fromarea close to Al-Doura Refinery Plant.Soil analyses were carried out by the State Company of Geological Survey and Mining, Ministry of Industry and Minerals. The composition and properties of the soil are described in Table 1.

Table 1.Composition andproperties of the soil.

Property	Value
Distribution of particle size (ASTM D 422)	
Sand(%)	18
Silt (%)	62
Clay(%)	20
Atterberg limits (ASTM D 2487)	
Liquid limit (%)	28
Plastic limit (%)	21
Plasticity index (%)	7
Organic content (%)	0.21
PrimarypH	7.2
Specific gravity	2.299
Electrical conductivity EC (μS/cm)	2740
Porosity (n)	0.43
Soil classification (USDA)	Silt loam

2.1.2. The Used Tea Leaves (UTL)

The used tea leaves (UTL),used in the electro-kinetic cell to preventreverse electro-osmotic flow occurrence. In this study, a low cost adsorbent(UTL) which is widely available in Iraq,it was obtained freely from thedomesticwastes.(UTL), considered as a natural adsorbent medium. Indeed, the (UTL) have compact structure and homogeneous surface with a developed porosity.In this material, some micro pores are observed and its use can be considered economic, beneficial and eco-friendly.

The used tea leaveswashed with distilled water (to remove any impurities exist on its surface) and dried for 24 hours at 40°C. The (UTL) was sieved to produce a particle size 4mm. Before using, it was enveloped with a perforated 1.5mm plastic package of (4cm by 8cm by 8cm high),then inserted in the reactor.
The (UTL) formula is $(HOCH_2CH_2)_3N$.It contains thousands of chemical compounds break down from complex and from new compounds. Tea compositionsvary greatly with each harvest and change greatly during processing [7].

2.1.3 *SDS (Sodium dodecyl sulfate)*

Sodium dodecyl sulfate is an anionic surfactant. Itis a synthetic organic compound with the formula$CH_3(CH_2)_{11}SO_4Na$.It containson a 12-carbon tail attached to a sulfate group (i.e., it is the sodium salt of dodecyl hydrogen sulfate, the ester of dodecyl alcohol and sulfuric acid).

It is mainly the lauryl; lowersurface tension of aquatic solutions; used as moistening agent, fat emulsifier, pharmaceuticals and toothpastes; detergent in cosmetics,also as research agent in protein biochemistry.

2.2. Reactor Setup

Fig.1 shows the schematic diagram for electro-kinetic cell used in this study. The experimental system in Fig.2consistsof glass rectangular electro-kinetic cell, two electrodes compartments, two roller graphite electrodes (diameter: 5cm, high: 8 cm) placed at the ends of the cell (i.e. in electrodes compartments)which were used as the working electrodes, power supply (LODESTAR LP3005D) and a multi-meter. The glass rectangular electro-kinetic cell has internal dimensions of (40 cm (L) x 8 cm (W) x 10cm (h)). The length of the soil section is 20cm. UTL was used as a barrier in the glass electro-kinetic cell between the soil and the cathode compartmentwith a length of 4 cm. Each electrode compartmenthas a length of 8 cm composed of a graphite electrode, filter paperand valve to control on the flow of liquid out from cell.

Perforated plastic plates were used to separate the used tea leaves barrier from the soil at one end and from the cathode electrode from the other end. The dimensions of plates(8 cm x 10 cm) and have holes 6 mm in diameter at space 1 cm from center of hole to center of another hole. A D.C. power source was used to supply aconstant voltage to the electrodes and a multi-meter was used to monitor the voltage and measure the current flow through the soil section through the experiment.
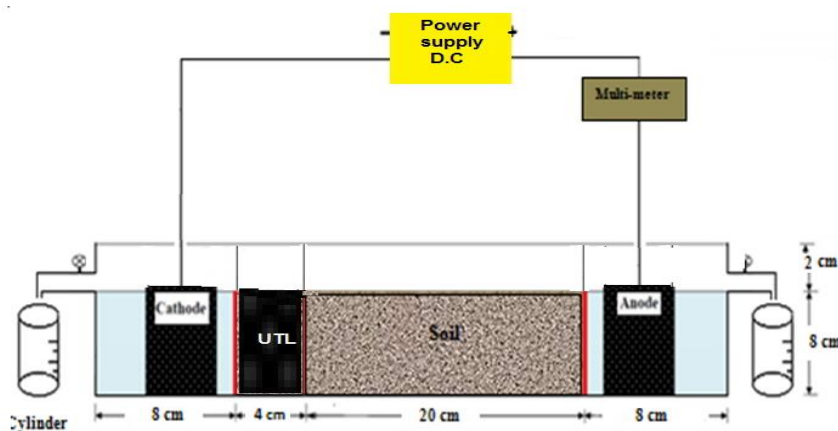

Figure .1 Schematic diagram of electro-kinetic cell.

Figure.2Experimental set-up of electro-kinetic cell.

2.3. Experimental procedure

The contaminated soil was placed in the glass electro kinetic cell in layers and compacted uniformly by a hand compactor. The exact weight of the soil used in the cell was determined and the soil was equilibrated for 24 hrs. The filter papers were inserted at the ends of the soil specimen and the end of the used tea leaves. Thecompartments at the ends of cell were filled with purging solution. The elevation of the purging solutionlevel in the electrode compartments was kept constant to prevent a hydraulic gradient from forming across the specimen. The electro-kinetic cell was connected to the power supply and a constant DC voltage gradient of 1.5 VDC/cm was applied to the soil specimen in all the experiments.

Differentexperiments were performed to investigatethe effect of different pH values ofelectrode purging solutions (tap water) andthe influence ofusing chemical anionic surfactant (SDS, sodium dodecyl sulfate), for washing soil,on the electro-kinetic remedial efficiency. Table 2 shows the summary ofexperiments conditions. At the first experiment(EX-1), tap water withan EC of 1450 µS/cm and pH of 4.5 was used in both the anode and cathode compartments at 30 V and zinc concentration 800 mg/kg and moisture content of 30%. In the second experiment(EX-2), tap water with an EC of 1368 µS/cm and pH of 5.5 was used in both the anode and cathode compartments but other conditions are preserved as (EX-1). The purging solution in the third experiment (EX-3) was tap water atpH of 6.5 used in the electro-kinetic cell but other conditions are kept as (EX-1). The experiments (EX-1, EX-2 and EX-3) were executed to study the effectiveness of increasing pH on the removal efficiency. In (EX-4), 10^{-1}MSDSwas mixed with soil (250 ml for 1000g) in a polyethylene container by hand for several minutes to obtain homogeneity.The other conditions in EX-1 are the same.

To maintainthe pH of purging solution at 4.5, 5.5, and 6.5 in all experiments, nitric acid (HNO_3) was being added to the cathode compartment, while sodium hydroxide (NaOH) was added to the anode compartment.When loss in purging solution is happened, due to evaporation, this loss was compensated by the addition of purging solution into the anode and cathode compartments. At the end of each

experiment, the soil specimen and (UTL) were extrudedfrom the cell. The soil specimen was divided to five parts and each part was weighed and kept in a glass container. From each part of the soil, 5 g of dry soil was taken and mixed with 12.5 ml of distilled water. The mixture was shaken thoroughly by hand for several minutes and the solids were then allowed to settle for 1 hour, pH and EC of the soil were measured [8].

Table2.Conditions of the experiments

EX. NO.	Processing duration (days)	Initial zinc conc. (mg/kg)	Type of purging solution	pH of purging solution	Purpose of Exp.
EX-1	6	800	Tap water	4.5	Baseline Exp.
EX-2	6	800	Tap water	5.5	Effect of pH
EX-3	6	800	Tap water	6.5	Effect of pH
EX-4	6	800	Tap water	4.5	Effect of Enhanced condition (SDS)

2.4. Digestion of the soil sample

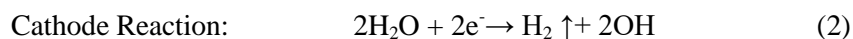One gram of each part of soil was placed in a 250 ml digestion tube and 10ml ofconcentrated nitric acid(HNO_3) was added. The sample was heated in heating sandy bathfor 40 minutes at 95 °C, and thenthe temperature was increased to150 °C, the sample left boiling forat least for a period of 8 hourstill a clear solution was obtained. 5 ml concentrated nitric acid (HNO_3) wasadded to the samplefor at least three timesand digestion completed after the volume was reduced to about 1 ml. The internal walls of the tube were washed with a little distilled water. After cooling, 5 ml of 1% $HNO_3$was added to the sample. The solution was filtered with Whatman No. 42 filter paper. It was then transferred to a 25 ml volumetric flask by adding distilled water [9].

The zinc concentrations in the final solutions were measured by an atomic absorption Spectrophotometer (AAS).

2.5. Reactions in System

The method of electro-kinetic include ofapplyinglow voltage gradient through electrodes or low level D.C. current, which are applied on the contaminated soil. The dominant and most important electron transfer reactions that occur at electrodes during the electro-kinetic processes are the electrolysis of water, equation (1) and (2) show the anode and cathode reactions [1, 10].

$$\text{Anode Reaction:} \qquad 2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \qquad (1)$$

Cathode Reaction: $\qquad 2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH$ $\qquad$ (2)
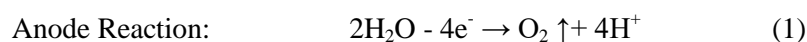
The ion exchange reactions between hydrogen ion and adsorbed metalion onclay particle surface can be illustrated in the following reaction (eq.3):

$$2H^+ + Zn_2 + (clay)^{-2} \rightarrow 2H^+ (clay)^{-2} + Zn^{+2}$$ $\qquad$ (3)
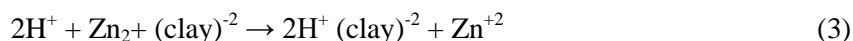
Hydroxide ion formed in the cathode neutralized by hydrogen ion migration, which is produce in the anode. Though, cathode zone shows high pH values due to theoverflow of hydroxide ion that have low mobility, and then precipitation by the reaction with zinc ion.

3. Results and discussion

3.1. *pH of Purging Solution*

Fig.3 showsthe total zinc concentration in eachpart of the treated soil for theexperiments(EX-1, EX-2, and EX-3). The initial concentration of zinc in the soil was 800 mg/kg. Final concentration of zinc was decreased and varied from(285-370) mg/kg near the anode to (365-460) mg/kg nearthe cathode. Increasedzinc concentrations were observed near the cathode, because most of the zinc was desorbed from the soil and mobilizedat pH of 4.5.Hence, thehighest removal efficiency was64.37% at this pH. The Fig.3 indicates that the transport of zinc ions occurredfrom anode to the cathode and the amount of zinc ions transported increased with decrease of pHpurging solution because when pH increased, the tendency for metal ions to become adsorbed onto the soil particles also increases. Fig.4explained the pHvariation along the treated soil for the sameexperiments. The generated hydrogen and hydroxyl ions were transported through the specimensoil in an opposite direction by electro-migration, diffusion and advection.
The advanced of base front is slower than the progress of the acid front because of the confrontation electro-osmotic flow and because the H^+ ions have higher ionic kinetics values than OH^- ions[1].

Fig.5illustrates the EC variation along the treated soil for the same experiments. The EC values were ranged from (3.3 to 4.4)mS/cm near the anode and from(2.3 to 3.2)mS/cm near the cathode. In Fig.6, It could be noticedthat at the beginning of the experiments there is a slight increase in current with time, and the pH of purging solutions also affects the current with changes in the Physiochemical characteristics, like mineral dissolution chemical precipitation/dissolution, etc. When the pHof purging solutionreduced, the current reachesto superior value because of higher solubility of minerals and their migration [11].
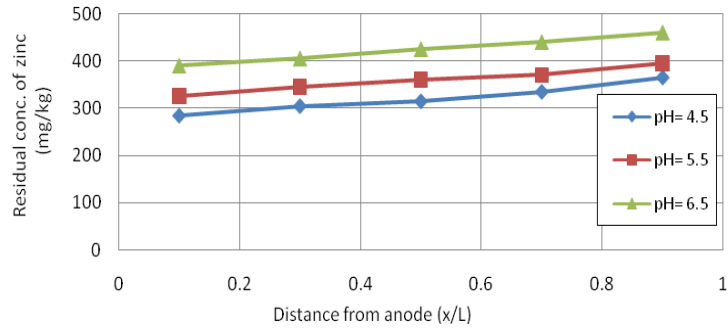
Figure .3 Residual concentrations of zinc (mg/kg) versus the distance from anode at different pH of purging solutions.
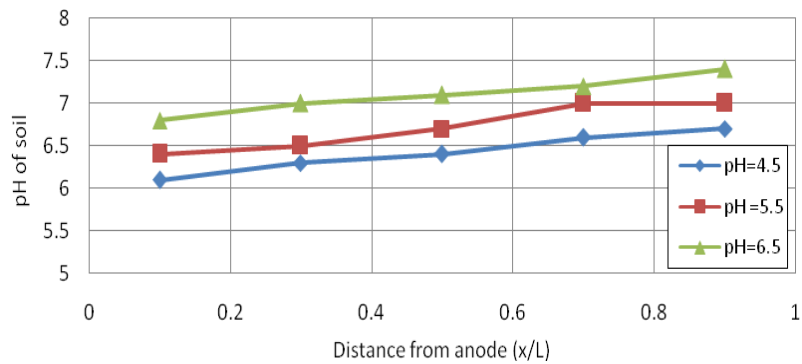

Figure .4 pH of the treated soil versus distance from anode at different pH of purging solutions.
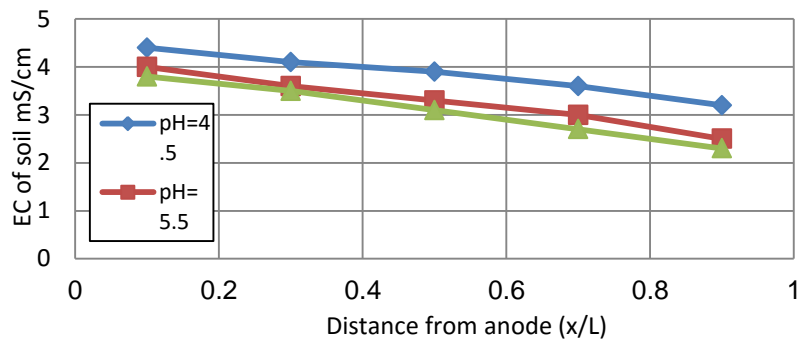

Figure .5 EC of the treated soil versus distance from anode at different pH of purging solutions.
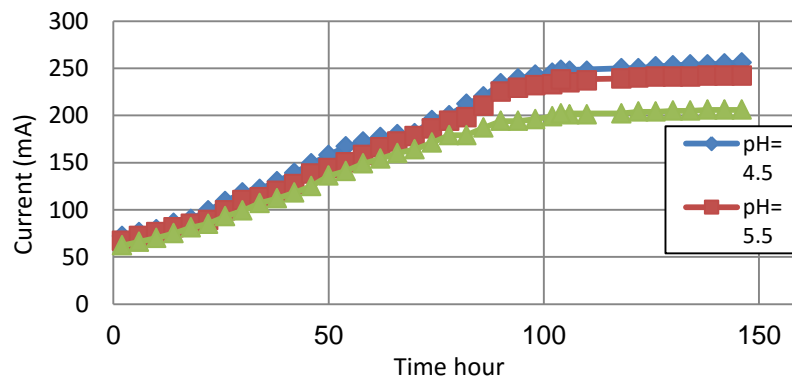

Figure .6 Current (mA) versus time (hour) at different pH of purging solutions.

Fig.7 and Fig.8showed that the pH decreasing in the soil specimen at anode and cathode during the electro-kinetic remediation. The reduction in soil pH indicates that the soil has a certain buffering capacity .

The overall soil pH was lower than 6.5 after the electro-kinetic remediation and during the treatment. H ions can continuously transport into the soils while OH⁻ ions are confined in the cathode compartment.

It is known as that increasing of OH⁻causes the precipitation of metal contaminants, curbing transport of metal contaminants toward cathode electrode. Thus and by lowering pH, more OH⁻would be neutralized, making the reclamation of metallic ions more effective[12].

Because of the high adsorption capacity of (UTL), there are amount of zincions were adsorbed by (UTL) due to the competitiveness of the ions of salts available in the soil samples with zinc ions. The amount of zincions adsorbed by (UTL) was in the range of(38 to 72) mg/kg in EX-1, EX-2 and EX-3, and 80 mg/kg in EX-4.

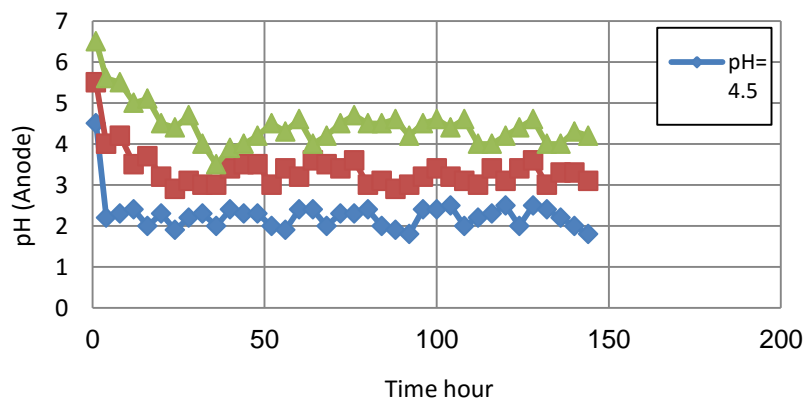Figure .7 pH of purging solutions at anode versus time (hour).
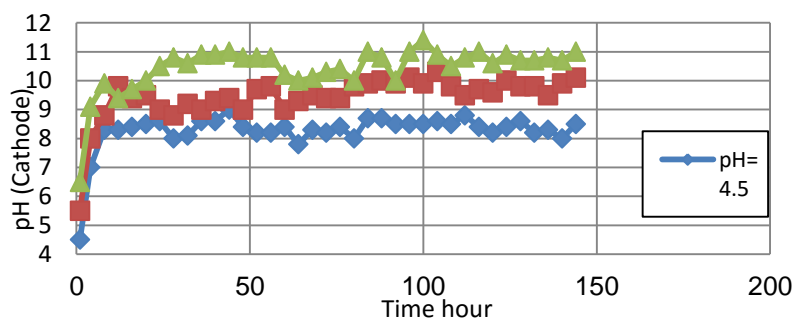

Figure .8 pH of purging solutions at cathode versus time (hour).

3.2. Effect of Using SDS as Enhanced Condition

In Ex-4,soil was washed with $(10^{-1}$ M) SDSand the other conditions are kept as used in EX-1.It appears that the pH along the soilspecimen increased from (4) near the anode to(5.1)near cathode after 6 days of remediation, as shown in Fig. 9. Most of zinc dissolution and desorption from the soil surface occurred after 6 days. Fig.

10 showsa comparison between the residual concentration of zinc along the soilspecimen with and without using SDS as a solution for washing soil after 6 days.
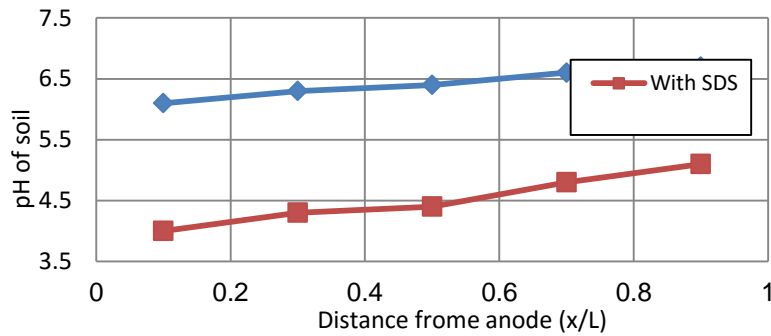

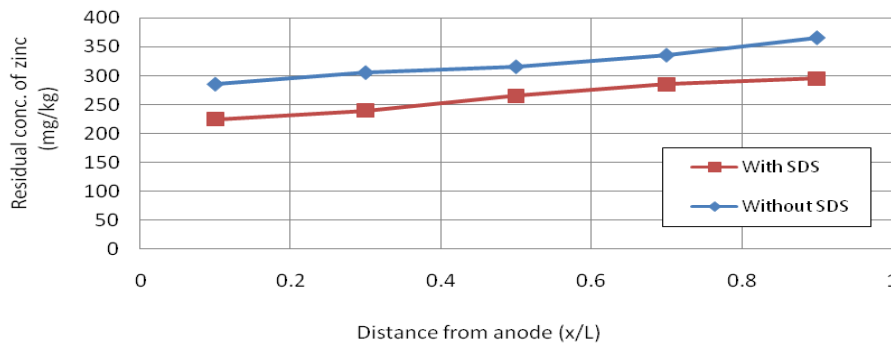Figure .9 pH of the treated soil versus distance from anode under enhanced condition (SDS).

Figure .10 Residual concentrations of zinc (mg/kg) versus the distance from anode under enhanced condition (SDS).

3.3. Removal Efficiency of Zinc

The removal efficiencies of all four experiments were calculated based on the initial and residual zincconcentrations in the soil. The removal efficiency is given by equation (4):

$$R\ \% = \frac{\text{Initial conc.} - \text{Residual conc.}}{\text{Initial conc.}} * 100 \qquad (4)$$

Where:

R %: Removal Efficiency

Fig. 11 showed that the best removal Efficiency of Zinc occurred in EX- 4 (71.87%) when SDS was used as enhanced condition. The other removal efficiencies were (64.37%, 59.4 % and 51.25%) in (EX-1, EX-2 and EX-3), respectively.
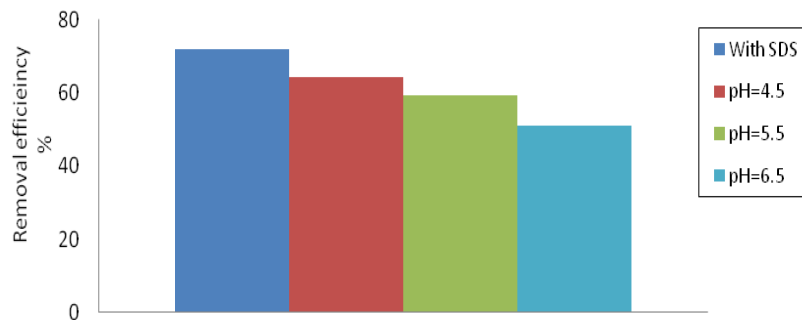
Figure .11 Removal efficiency of zinc (%).

4. Conclusions

The electro kinetic method has shown its success in removingthe zinc from the contaminated soil.

Differentexperiments have been performedwith varying degrees of effectiveness in their results. The results showedthat the removal efficiency of zincincreases with decreasingpHof purging solutions. This because in high pH values, the tendency for metal ions to become adsorbed on the soil particles also increases; where theremoval efficiencies were (64.37%) atpH of 4.5, (59.4 %) at pH of 5.5 and (51.25%) at pH of 6.5.It was also noticedthat the removal efficiency was even higher than 64.37%when SDS was used as washing solution in the soil(71.87%). The used tea leaves (UTL) is a good material to be used as a medium to prevent the occurrence of reverse electro-osmosis flow compared to other commercial adsorbent materials, and the adsorption process by (UTL) can be considered more economic, beneficial and eco-friendly method.

5. References

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