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Removal of zinc, lead and nickel from contaminated soil by electro-kinetic technology under the influence of washing and buoyance forces with different purging solutions

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Abstract: The effects of the washing process, purging solution, and buoyance force (inclined topography action) on the effectivity of the electro-kinetic method used to remediate of a silty clay loam and natural soils contaminated with Zn, Pb, and/or Ni were investigated by applying 12 different experiments. The results revealed that the washing process and buoyance force can cause a small increase in the Zn removal efficiency (≤ 31%) when compared with non-washing approach using distilled water purging solution. Using 0.1 M of EDTA solution for the soil contaminated with listed metals in combination with washing can lead to significant increase in the removal efficiencies with percentages not greater than 58.4, 60.68 or 42.8%, respectively. In the presence of EDTA, however, the majority of metals passed through the soil media to the anode area. In contrast, these metals are accumulated near the cathodic region in the presence of distilled water. The results demonstrated that the buoyance force (resulted from inclination angle of 30^o) with EDTA had adverse influence on the metal profile along the treated soil. Finally, the results certified that EDTA in electro-kinetic process coupled with soil washing is a new hybrid technique which achieved Pb removal efficiency from natural soil reached to 58% by improving the solubilization and transport of metal ions.

Keywords: Electro-kinetic; Electro-osmosis; Electro-migration; EDTA; Washing process

1. Introduction

The existence of contaminated sites is quite common and their cleanup represents a paramount issue. This issue has been exacerbated by a variety of industrial and agrochemical processes like the presence of minerals from mining activities, petroleum spills from leaking tanks, and usage of chemicals for agricultural facilities [1,2]. As a consequence, many treatment technologies being applied in the treatment of contaminated sites including the bioremediation regime, thermal desorption, flushing and soil vapor extraction. Environmental Protection Agency (EPA) reported the ineffectiveness of various remediation methods used at a number of contaminated sites. The following difficulties were cited as reasons for poor performance: (1) it is difficult to treat clayey soils due to their complexity (contain mixture of minerals and organic substances) with low hydraulic conductivity; (2) the heterogeneous of the subsurface can cause obvious failure for several applied techniques (for example; presence of clay lenses within the sand aquifer); (3) the treatment of organic pollutants like polycyclic aromatic hydrocarbons and polychlorinated biphenyls, and

(4) sites polluted by mixture of heavy metals with organic compounds and/or radionuclides [3].

It is necessary to establish cost-effective techniques that address the aforementioned issues. One of these innovations, in-situ electro-kinetic remediation, has a lot of promise. The electro-kinetic remediation for soil is a new approach that has attracted scientists' attention due to many promising results of laboratory experiments and pilot-scale studies. A low-level DC electric field must apply along the porous bed where electro-osmosis, electrophoresis, electro-migration, and diffusion represent the key processes for removing of pollutants from the soil. For the cleanup of contaminated soils, this technique has proved to be a viable alternative to conventional methods [3–5].

Several studies have shown that electro-kinetic remediation can remove heavy metals from low permeability soils using horizontal DC [6–11]. The experimental investigation on the cleaning characteristics of Cd, Cu, Pb, As, and Zn; the direction of electro-osmotic flow; the profile of soil pH; and the behaviour of citric acid as purging agent were presented [7]. The application of ammonium citrate as a desorption solution for Cu, Zn, and Pb during electro-dialytic treatment was investigated. The results showed that this enhancement approach was successful in mobilizing these contaminants. However, the authors pointed out that ammonium citrate concentration and pH must be optimized [8]. Contaminant’s polarity, soil’s type, and the treatment’s period have significant influence on the flow of electro-osmotic as well as extent and direction of contaminant with its removal efficiency [9]. The carbonate or calcite effect on the removal of contaminant was investigated. Findings revealed that the soil has a high ability to retain of contaminant when carbonate forms appreciable proportion in its composition [10]. Different types of soil, enhancement solutions, and voltage gradients were investigated [12–19].

The ability of an activated carbon barrier to prevent reverse electroosmotic flow, which has a negative impact on Cu removal and migration path, was investigated using an electro-kinetic remediation technique in combination with an activated carbon barrier. Also, numerical modeling was developed to understand the mechanics of migration during the electro-kinetic soil remediation [20]. When there is an electric field, acid-injection well as novel technique was used to improve copper remediation from three different forms of soils in Iraq. For silty loam, sandy loam, and sandy soils, overall efficiencies of 34, 58, and 85 percent, respectively, were achieved [21]. Different flushing solutions and additions configurations were tested to remove of lead from Iraqi soil using electro-kinetic method. The efficiencies of lead removal for the experiments performed with distilled water, 1 M ammonium citrate, 0.2 M EDTA, and 0.1 M acetic acid was equivalent to 18, 29, 42, and 37 percent, respectively. According to the results of the tests, adding injection wells as a further optimization technique to the previous experiments improved removal efficacy by 59 percent [22]. Organic acids were used as facilitating agents in the electro-kinetic remediation of a heavy metal-polluted agricultural soil [23].

A project for “Strengthening environmental governance in Iraq through environmental assessment and capacity building” was granted by United Nations Environment Programme (UNEP) in July 2004. The required fund for this project was supplied by Japan government. The project was aimed to evaluate the contaminated sites in Iraq, in partnership with Environment Ministry of Iraq. The outputs of this project [24] proved that there are many sites in Iraq contaminated with zinc, lead, and nickel ions due to either fire, looting, conflict or poor operating practices. The maximum concentrations of these metals have been reached to 5072, 33860, and 605 mg/kg, respectively; so, the remediation of such sites with suitable technique may represent a strong justification for present work. Hence, this research is aimed to find out the efficacy of electro-kinetic system for decontamination of zinc, lead, and/or nickel from simulated and naturally polluted soil under the influence of enhancement conditions such as washing, purging, and buoyancy control.

2. Electro-kinetic Phenomena

At the turn of the nineteenth century, direct current on a clay water mixture was applied by Reuss and electro-kinetic effect recognized. Helmholtz and Smoluchowski, on the other hand, were the first to suggest a theory involving a fluid's electro-osmotic velocity and the zeta potential during an imposed electric gradient [25]. The use of two electrodes in electro-kinetic remediation is a relatively simple method. These are positioned inside the polluted soil volume and an electrical field is generated by passing a direct electric current (DC) between them. Accordingly, one electrode becomes the anode, while the other becomes the cathode, and a complete creation of transport mechanisms occurs in the "treating region" that divides these two electrodes. Contaminants concentration and mobility, the type of soil and composition, and hydraulic conductivity of soil are main parameters that specify the quantity of moved contaminants and their direction. Water electrolysis is the most common reaction that can occur at electrodes as follows [25,26]:

Anodic reaction:

$$2H_2O - 4e^- \rightarrow O_2(g) + 4H^+ \qquad (1)$$

Cathodic reaction:

$$4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^- \qquad (2)$$

During the H^+ ions propagate towards the cathode and the movement of OH^- ions in the direction of the anode, the gases of hydrogen and oxygen at these electrodes respectively can be emitted to the atmosphere. Based on the propagation of OH^- and H^+ ions across the soil, remarkable changes in the values of pH can be observed. The acidic front is always appeared near the anode region while the basicity front is formed in the cathodic side. The mechanisms of precipitation and dissolution, adsorption and desorption, as well as oxidation and reduction, would be affected by pH changes. The lower soil pH near the anode allows cationic (positively charged) metals to desorb and solubilize, increasing their electro-migration to the direction to cathode. Although the presence of higher pH close to the cathode allows chemicals to precipitate and/or adsorb, electro-migration and reduction at the cathode are hampered [27].

3. Experimental Methodology

3.1 Soil sample preparation and contamination

Soil samples were collected, cleaned and sorted based on the distribution of particle size. Table 1 presents the specifications of these soil samples which classified as “silty clay loam”. The samples were synthetically contaminated with zinc, lead and/or nickel using solutions of $Zn(NO_3)_2.6H_2O$, $Pb(NO_3)_2.6H_2O$ and/or $Ni(NO_3)_2.6H_2O$ (manufactured by Scharlau Company/European union) to obtain an average concentration of 1000, 500 and/or 250 mg/kg; respectively, with an initial moisture content of 40%. The $Zn(NO_3)_2.\ 6H_2O$ has a molecular weight of 297.51 g/mole and atomic weight of zinc ions is 65.39 g/mole. To prepare a soil sample comprising 1000 mg/kg of zinc and water content (ω) of 40% by weight, 5.6855 g of $Zn(NO_3)_2.\ 6H_2O$ dissolved in 500 mL of distilled water (DW) where 400 mL must be mixed with 1 kg of dry soil. Molecular weights of $Pb(NO_3)_2$. $6H_2O$ and $Ni(NO_3)_2$. $6H_2O$ are equal to 331.21 and 291 g/mole respectively. These weights are very important to calculate the required mass of these compounds to prepare the artificial contaminated soil.

In addition, one sample of natural soil contaminated with lead was taken from department of receiving and pumping of Tetraethyl Lead (TEL) in Al-Doura Refinery Plant to find the ability of electro-kinetic technique in elimination of real contamination. This refinery operated since 1933 and is located at the southern region of Baghdad city, Iraq on the right bank of Tigris river in the direction of flow. According to the study conducted in July 2004 mentioned previously, there was 130 tons TEL liquid stored at Khan Dhari site in the 340 kg containers. As a result of military activities, post-conflict damage and looting, these chemicals are spilled directly to the soil [24].

3.2 Purging solution

To test the effectiveness of an electro-kinetic remediation procedure (without the use of an enhancement solution), purified water was used to extract zinc from a soil sample. In certain cases, the use of enhancement agents to solubilize the contaminant in high-buffering-capacity soils is needed for cost-effective implementation. The purging solution in this analysis was a complexing agent called ethylene diamine tetraacetic acid (EDTA). EDTA is a powerful chelating agent that readily available, environmentally friendly, and has no effect on soils. It's a great solubilizer for a variety of metals, including lead, zinc, and nickel. This agent has four acetate groups and two nitrogen atoms to create of coordinate bonds, and each EDTA ion could bind to a metal ion in six various locations [28]. It's worth noting that EDTA has been used in terms of medicine to aid in the removal of lead from the human body, as well as a cleanable ingredient for floor polishes containing zinc binders [29]. The previous study [30] signified that the 0.1 M EDTA was more effective than 0.01 or 0.05 M in the elimination of metal ions from polluted soil; so, this value had been adopted in the present work.

3.3 Setup of the electro-kinetic test

Fig. 1(a) depicts a conceptual diagram of the electro-kinetic device installed in this research, which was modified from that proposed by [28]. An electro-kinetic cell, two electrode reservoirs, two electrode compartments, a power supply, and a multi-meter comprised the device (Fig. 1(a & b)). The introduced change is that this setup can now be angled up to 30 degrees from horizontal. The inside diameter of the Plexiglass electro-kinetic cell (Fig. 1(c)) was 6 cm, and the overall length was 20 cm. A valve to regulate the flow into the cell, a porous stone and a graphite electrode were all included in each electrode compartment. Tygon tubing was used to connect the electrode reservoirs to the electrode compartment, which were constructed of 4 cm inner diameter Plexiglas tubes. Each electrode compartment was supplied with thin tube named “gas vent’ to escape of produced by the electrolysis of water. The reservoirs were attached to the other ends of the gas vents to collect any removed water. During the test, a constant voltage was applied to the electrodes using a power source (type PS-305DM), and the values of current and voltage have been measured along the soil sample by multi-meter.

3.4 Experimental design

To accomplish the objectives of this study, a three series of tests (series-1, series-2 and series-3) as illustrated in Table 2 were performed using a strict methodology. The series-1 was included the EK-1 and EK-2 tests. While the tests from EK-3 to EK-11 were grouped in the series-2. The series-3 was included one test designated as EK-12 to deal with natural contaminated soil. The overall aims of these tests were to investigate:

1) Response of contaminated sites to the use of the different purging solutions specifically distilled water and EDTA.

2) Competitive response between zinc, lead and nickel metals for removal by EDTA.

3) Study the effects of using washing and buoyance forces (i.e. reactor inclination) as enhancement methods on the contaminant distribution along the soil column in comparison with horizontal non-washing one.

Distilled water (EC=22 µS/cm, pH=6.8) was utilized in the compartments of cathode and anode for EK-1 which represents a baseline experiment. Under the same operational conditions of EK-1, EK-2 was conducted under the effect of inclination angle of electro-kinetic cell to investigate the influence of buoyance force increase on the remedial efficiency.

The conducted experiments address one of the major defects of traditional electro-kinetics; namely, the precipitation of metal hydroxides in a region extending from the pH front (or junction) to the cathode. This precipitation results in a sharp decrease in the process's efficiency. Such a problem is especially acute when the contaminated soil is basic (pH>>7) with a considerable buffering capacity as is the case in this work. Series-2 was carried out to avoid this precipitation and to improve remedial performance thus reducing treatment time. DW for EK-3 and 0.1 M EDTA for EK-4 to EK-11 were used to wash the soil in the presence of an electrical field, buffering the produced hydroxide ions and achieving a low pH. The EDTA in anode side was applied to improve the reactivity of H^+ with metal ions by boosting their dissemination in the soil bed. The purging solution, the number and concentration of applied metal ions, and the inclination angle of the reactor setup are all altered in the series-2 experiments. The series-1, -2, and -3 experiments show how pH front propagation, metal concentrations, electrical conductivity, electro-osmotic flow and electrical current values change over through experimental test.

3.5 Procedure of testing

The electro-kinetic cell was filled with layers of synthetically prepared contaminated soil sample that were compacted randomly with a wooden rod. Soil weight in the cell were measured, beside, it has been equilibrated for 24 hours. The electro-kinetic cell was then bound to the electrode compartments. Filter papers must be situated between the soil, porous stone and electrode for each electrode compartment. Tygon tubing can be utilize to connect the anode and cathode reservoirs with the electrode compartments. The purging solution was then incorporated to the reservoirs, which was either purified water or 0.1 M EDTA (PS). In the electro-kinetic tests of series-1, the elevation of PS in each compartment was maintained constant to prohibit the creation of a hydraulic gradient; however, the hydraulic gradient was formed in tests of series-2 and 3 to achieve the necessary washing process. The cell of electro-kinetic was connected to a supply of electricity, and the soil specimen was exposed to a steady gradient of voltage 1 V/cm. The electrical charge through the soil specimen and the flow of water have monitored at various time intervals during the experiment. The stabilization of current or effluent flow of water means the test of electro-kinetic can be stopped; so, the electrode assemblies and reservoirs are disconnected and the soil can remove from the setup. This soil was divided into 5 sections, each of which was weighed and stored. Approximately 10 g was taken from each soil segment and blended with 25 mL deionized water. Solids must leave for 1 h to settle after being thoroughly shaken by hand for several minutes. The pH and electrical conductivity for soil and water samples collected from the compartments of electrode were all tested [31]. Acid digestion was applied to extract of zinc, lead, and nickel from various soil sections, following protocol of [32]. An atomic absorption spectrophotometer (AAS) was utilized to calculate metal concentrations (novAA300, Germany). New filter papers and electrodes were applied for each test to prevent the possible contamination, as well as the cell and chambers were immersed in a dilute acid solution for 24 h before being washed with tap water then filtered water.

4. Results and discussion

4.1 Experiments without soil washing (series-1)

Fig. 2(a) illustrates the profile of electric current throughout the EK-1 and EK-2 tests. The current initially was quite high in the range from 35 to 38 mA which decreased beyond 20 hrs and finally stabilized at 10 mA. In comparison with EK-1, the buoyancy force in EK-2 is caused a significant decrease in the current value due to wash out dissolved species present in the solution and this has positive effect on the performance of the system. Also, water was flowed from anode to cathode reservoirs because of negative value of zeta potential. Fig. 2(b) illustrates the accumulative volumes of effluent versus time and remarkable difference in the values of collected effluents from EK-1 and EK-2 can be recognized. It is obvious that the buoyancy force can enhance the electro-osmotic flow and collected effluent reached to 100 mL after 40 h; however, the flow rate for horizontal position (EK-1) was stabilized at 60 mL 168 h. The zinc can react with hydroxides ions in the cathodic region; so, the resulted metal hydroxides will be deposited in the pores causing the cease of the electro-osmotic flow. Furthermore, calcium precipitation near the same region can also clog the pores, preventing the transportation of further zinc ions [10].

Fig. 2(c) shows the total zinc concentrations in each portion of the remediated soil for EK-1 and EK-2. Sections 1, 2, 3, 4, 5, 6 and 7 correspond to distances of 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1 of the total length (L) from the anode, respectively. Initially, the Zn concentration in the soil was 1000 mg/kg, but after 7 days, the final concentrations were decreased to (500-600) mg/kg near the anode and (669-780) mg/kg near the cathode. The higher concentrations of Zn near the cathode in comparison with concentrations near anode may result from high electric conductivity of the soil near to cathode. It is evidence that the buoyance forces have clear effect on the migration of zinc when the position of reactor setup at 30^0 (EK-2).

The pH changes versus normalized distance along the treated soil for the tests under consideration are shown in Fig. 2(c). The soil pH appears to have decreased to 2.5-8 near the anode for (2/3) of the specimen, but increased to 10.5-13 near the cathode zone. The production of H^+ ions at the anode compartment was the main cause of low pH at the anode zone, while the production of OH^- at the cathode zone would increase the pH of the soil. Electro-migration, diffusion, and advection transport H and OH ions in opposite directions across the specimen. Because of the opposing electro-osmotic flow and the fact that H^+ has 1.76 times the ionic mobility of OH^-, the propagation of the basic front is slower than the acidic front [33]. Water is formed where the acid and base fronts intersect, resulting in a sharp change in pH that affects metal ion solubility and adsorption on soil particles. The pH of the soil has a major effect on Zn migration, according to tests. The Zn concentration dropped at the anode due to the decrease of pH. The high pH meant that some OH ions had made their way into the soil, potentially interfering with zinc ion mobility. However, the increased buoyance forces will enhance the propagation of H^+ front toward the cathode region due to the increase of electro-osmotic flow; consequently, this can decrease of pH and increase the remediation efficacy. Measurements proved that the electrical conductivities have varied from 1100 to 3100 µS/cm at the anode side while they value in the range from 600 to1100 µS/cm at the cathode. Higher soil conductivity near anode compared to cathode means there is relatively higher desorption of ionic species such as zinc at the anode zone.

Finally, the Zn removal efficiency from the soil was 24% in the EK-1, and 29.8% in the EK-2. These efficiencies were determined from the residual metal quantities in the soil. The maximum reduction during the period of remediation was achieved in EK-2 and this can result from the increase of the buoyancy forces (inclination angle), which cause relatively increasing in the electro-osmotic flow and, consequently, relatively increasing in the removal efficiency. The reason for inclination was to use the effect of buoyancy forces along with the flow of electro-osmotic to enhance the hydrodynamic flow, which on the other hand can flush out metals from the reactor. The theoretical analysis conducted previously [34] signified that an inclined position of the electro-kinetic cell may considerable affect flow regimes at the capillary level. Also, it is clear that the Zn concentrations were distributed uniformly along the soil sample in EK-2 and accumulated towards the cathode side.

4.2 Experiments with soil washing (series-2)

One of the most important problems in the EK technique is the evolution of high pH in the cathode region which creates precipitation hindered the remediation process. Lowering the pH of the cathode region can be a good choice for enhancing the mobilization and accessibility of heavy metals to electro-kinetic transport. Therefore, soil washing under specific hydraulic gradient in EK process will wash out OH^- ions that are generated continuously in the cathode region during electro-kinetic process. The EK-3 was applied to identify the effect of washing process on the performance of present technique in comparison with EK-1. The tests from EK-4 to EK-8 have been implemented to specify the effects of chelating agent (EDTA) as enhancement chemical in the improvement of the zinc, lead and/or nickel removal from soli sample. The last three tests (EK-9, EK-10 and EK-11) within series-2 were applied under the influence of the buoyancy forces to enhance the electro-osmotic flow which in turn could wash out the metal ions.

4.2.1 Effect of washing process

Current values for EK-1 and EK-3 tests with two different hydraulic velocities (zero and 3.24×10^{-4} cm/hour), respectively are illustrated in Fig. 3(a). These values in EK-3 during the remediation process were less than the corresponding values in EK-1. This may result from washing process which can be responsible of decreasing Zn ions in the treated soil as illustrated in Fig. 3(b). The overall removal efficiencies were 24 and 31% for these tests respectively; however, this increase in velocity can be the cause for this increase in efficiency due to enhance the electro-osmotic and electro-migration. This figure plots the pH variation in these tests where the pH levels have approximately similar values except the pH of EK-1 is recognized with higher value (≈12.9) near the cathode. Electrolysis, which produced OH^- and H^+ ions, is thought to be the cause of the pH difference at the boundaries.

4.2.2 Effect of EDTA in the single, binary, and tertiary contaminated system

After electro-kinetic inspection, the profiles of Zn, Pb, and Ni ions with pH variance in the soil specimen are shown in Fig. 4(a, b, & c). This graph shows that the pH values for EK-4, EK-5, and EK-6 were all lower than 10 in the soil specimen. The migration of an acidic front along the soil bed may result from combined effect of electrolysis reaction, electro-migration and electro-osmotic movement [28]. According to this diagram, Zn, Pb, and Ni migrated toward the anode, which is the opposite of the migration path shown in EK-3 (Fig. 3(b)). The majority of these pollutants moved from the soil near the cathode to the soil near the anode, where they accumulated. The remediation efficiencies for Zn, Pb, and Ni are respectively 58.4%, 60.68%, and 42.8 percent. Furthermore, in the parts near the cathode, lead concentrations were lower than zinc or nickel concentrations, indicating that either zinc or nickel adsorption to the soil was higher, or EDTA tends to form a complex with lead from a thermodynamic standpoint [28] .

An additional test (EK-9) was applied to determine the influence of buoyance forces on residual Zn concentration and soil pH in comparison with test (EK-4). Total zinc concentrations and pH along the soil bed for these tests were signified in Fig. 4(d). The two tests had the same conditions (initial Zn concentration of 1000 mg/kg, purging solution of 0.1 M EDTA and processing time of 4 days) but the difference in the inclination angle. This figure certifies that the increase of buoyance force will have adverse role on the metal distribution along the treated soil. Indeed, the increase of inclination angle will enhance the electro-osmotic and hydraulic flow from the anode toward the cathode. In contrast, the contaminant transport with aid of EDTA was from cathode toward the anode. This means that there are two opposite mechanisms governed the Zn profile along the treated soil. This reason explains the difference of Zn distribution pattern between EK-9 and EK-4. So, the removal efficiencies of EK-4 and EK-9 are 58.40 and 18.68% respectively. Also, the soil pH of EK-9 was less than that of EK-4 because the increasing of the electro-osmotic flow will wash out the OH^- ions generated in cathodic region. Consequently, the acidic front will be controlled on the soil pH behavior along the treated soil.

Fig. 5 plots the variation of Zn and Pb ions with pH profile along the soil specimens at the end of EK-7 and EK-10 tests. For EK-7, residual zinc concentration (Fig. 5(a)) in soil column decreased near the anode and cathode to form a value of 38% of its initial concentration and accumulated at the middle of this column. When both lead and zinc are present, EDTA thermodynamically tends to form complexes with lead; as a result, when EDTA reaches the soil, it forms complexes with lead first. The lead has then moved deeper into the soil toward the anode (Fig. 5(b)), and the new EDTA molecules that have entered the soil will then complex with zinc. As a result, EDTA-Zn complexation may not be important early on, and Zn may migrate toward the cathode as the Zn cation. EDTA-Zn complexes will form later near the cathode and they will migrate toward the anode. Such inconsistencies in zinc directions at the beginning and later stages may result in Zn accumulation in the center of the soil specimen [28]. The same figure plots the effect of buoyance force on the simultaneous migration of Zn and Pb ions in EK-10. However, the increasing of inclination angle for reactor setup will have adverse role on the migration of Zn ions (Fig. 5(a)) and this due to the presence of two opposite mechanisms governed the Zn profile along the treated soil. First mechanism is the enhanced electro-osmotic flow toward the cathode while the second one represents the metal transport with aid of EDTA toward the anode. In spite of this effect is obvious for removal of Zn but it can’t be recognized for Pb removal. This may be due to the fact that EDTA prefers to constitute complexes with lead when both lead and zinc are present together as explained previously. Finally, the removal efficiencies of Zn and Pb ions from soil sample with the aid of EDTA for horizontal reactor (EK-7) were equal to 60 and 55% while these values become 28 and 54% for inclined position (EK-10).

In Fig. 6, the concentrations of Zn, Pb, and Ni in electro-kinetically treated soil are plotted against soil sections from the anode for the EK-8 and EK-11 systems. Pb and Ni levels in EK-8 showed a similar pattern and activity along the treated soil. The majority of the Ni migrated from soil sections near the anode and collected in soil sections near the cathode in EK-11. There was no Ni migration into the cathode reservoir, in reality. When Zn, Pb, and Ni are present, EDTA tends to form complexes with Ni thermodynamically. As a result, when EDTA was introduced to the soil, it formed complexes with Ni. The new molecules of EDTA entering the soil will then complex with lead and zinc after Ni has migrated deeper into the soil toward the anode in EK-11. As a result, Pb and Zn, which exist as cations, will migrate toward the cathode during the early stages. This reason in combination with the effect of buoyance force may explain the low concentrations of Zn and Pb as well as high concentrations of Ni in EK-11 compared to EK-8 system; however, the mentioned cause may be responsible of low Ni concentrations in EK-8 in comparison with EK-11. Table 3 shows the removal efficiencies of Zn, Pb and Ni for EK-8 and EK-11 systems. It can be observed that the maximum removal efficiencies were achieved when the system was purged with EDTA enhancement solution for horizontal reactor.

4.3 Experiments with natural contaminated soil (series-3)

In the series-3 for EK-12, an electro-kinetic remediation technique was used on a natural soil specimen contaminated with lead. The initial Pb concentration measured was 300 mg/kg, with 0.1 M EDTA-PS and the reactor set up horizontally. At the end of the EK test, Fig. 7 indicates the distribution of Pb ions and the pH profile along the soil bed. The pH of the EK-12 test was fairly consistent in the treated soil, hovering about 8.5. Furthermore, Pb migrated toward the anode, with the majority of metal ions migrating from the soil section near the cathode and accumulating near the anode. Furthermore, in all parts of the treated soil, lead concentrations were less than 58 percent of their initial value, resulting in a removal efficiency of 57.56 percent.

5. Conclusions

The washing process with hydraulic gradient of 3.24×10^{-4} cm/h and buoyance force play significant role in the removal of OH^- ions generated continuously in the cathode region during operation of electro-kinetic cell. This can enable the acidic front spread faster, increase electro-osmotic flow and improve the decontamination of metal ions from soil. In spite that the maximum increase in the removal efficiency of Zn from soil due to washing and buoyance force using distilled water as purging solution was not exceeding 6%, most metal ions have been accumulated near the cathode region. Results certified that the washing of soil bed with 0.1 M EDTA can cause remarkable increments in the removal efficiencies of Zn, Pb, and/ or Ni with percentages reached to 58.4, 60.68 or 42.8%, respectively and this associate with significant decrease in pH values to be less than 10. Measurements signified that the most of these metals migrated throughout the soil towards the anode area in the presence of EDTA. Also, present findings demonstrated that the buoyance force with existence of washing by EDTA have adverse effect on the distribution of Zn, Pb, and/

or Ni along the treated soil and, consequently, a significant reduction in removal efficiency can be reordered. So, the soil washing with EDTA in horizontal EK reactor under electric current represents the best hybrid technique for treating of contaminated soil and this configuration was able to remove 58% of 300 mg Pb in 1 kg of natural soil.

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Conflict of interests

The authors declare no conflict of interest.

References

[1] Faisal, A.A.H.; Kassim, W.M.S.; Hussein, T.K. Influence of clay lens on migration of light nonaqueous phase liquid in unsaturated zone. *J. Environ. Eng.* 2011, 137(1), 9–14.

[2] Faisal, A.A.H.; Ibreesam, M.M.; Al-Ansari, N.; Naji, L.A.; Naushad, M.; Ahamad, T. COMSOL multiphysics 3.5a package for simulating the cadmium transport in the sand bed-bentonite low permeable barrier. *J. King Saud Univ. - Sci.* 2020, 32(3), 1944–1952.

[3] Reddy, K.R. Technical challenges to in-situ remediation of polluted sites.

Geotech. Geol. Eng. 2010, 28(3), 211–221.

[4] Virkutyte, J.; Sillanpää, M.; Latostenmaa, P. Electrokinetic soil remediation — critical overview. *Sci. Total Environ.* 2002, 289(1–3), 97–121.

[5] Sumbarda-Ramos, E.G.; Guerrero-Gutierrez, O.X.; Murillo-Rivera, B.; González, I.; Oropeza-Guzman, M.T. Electrokinetic treatment for clayed and sandy soils. *J. Appl. Electrochem.* 2010, 40(6), 1255–1261.

[6] Reddy, K.R.; Saichek, R.E. Effect of soil type on electrokinetic removal of phenanthrene using surfactants and cosolvents. *J. Environ. Eng.* 2003, 129(4), 336–346.

[7] Lee, H.S.; Lee, K.; Kim, S.S.; Ko, S.H. Effects of buffering capacity and citric acid in electrolyte on electro-kinetic remediation of mine tailing soils. *J. Ind. Eng. Chem.* 2003, 9, 360–365.

[8] Ottosen, L.M.; Pedersen, A.J.; Ribeiro, A.B.; Hansen, H.K. Case study on the strategy and application of enhancement solutions to improve remediation of soils contaminated with Cu, Pb and Zn by means of electrodialysis. *Eng. Geol.* 2005, 77(3–4), 317–329.

[9] Al-Hamdan, A.Z.; Reddy, K.R. Transient behavior of heavy metals in soils during electrokinetic remediation. *Chemosphere* 2008, 71(5), 860–871.

[10] Ouhadi, V.R.; Yong, R.N.; Shariatmadari, N.; Saeidijam, S.; Goodarzi, A.R.; Safari-Zanjani, M. Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method. *J. Hazard. Mater.* 2010, 173(1–3), 87–94.

[11] Castellote, M.; Botija, S.; Andrade, C. Assessment of electrophoresis and electroosmosis in construction materials: effect of enhancing electrolytes and heavy metals contamination. *J. Appl. Electrochem.* 2010, 40(6), 1195–1208.

[12] Chen, J.-L.; Yang, S.-F.; Wu, C.-C.; Ton, S. Effect of ammonia as a complexing agent on electrokinetic remediation of copper-contaminated soil. *Sep. Purif. Technol.* 2011, 79(2), 157–163.

[13] Lee, K.-Y.; Kim, H.-A.; Lee, W.-C.; Kim, S.-O.; Lee, J.-U.; Kwon, Y.-H.; Kim, K.-W. Ex-situ field application of electrokinetics for remediation of shooting-range soil. *Environ. Geochem. Health* 2012, 34(S1), 151–159.

[14] Cameselle, C.; Pena, A. Enhanced electromigration and electro-osmosis for the remediation of an agricultural soil contaminated with multiple heavy metals. *Process Saf. Environ. Prot.* 2016, 104, 209–217.

[15] Zhang, Y.; Huang, T.; Huang, X.; Faheem, M.; Yu, L.; Jiao, B.; Yin, G.; Shiau, Y.; Li, D. Study on electro-kinetic remediation of heavy metals in municipal solid waste incineration fly ash with a three-dimensional electrode. *RSC Adv.* 2017, 7(45), 27846–27852.

[16] López Vizcaíno, R.; Yustres, A.; Asensio, L.; Saez, C.; Cañizares, P.; Rodrigo, M.A.; Navarro, V. Enhanced electrokinetic remediation of polluted soils by anolyte pH conditioning. *Chemosphere* 2018, 199, 477–485.

[17] Zhang, Y.; Chu, G.; Dong, P.; Xiao, J.; Meng, Q.; Baumgartel, M.; Xu, B.; Hao, T. Enhanced electrokinetic remediation of lead- and cadmium-contaminated paddy soil by composite electrolyte of sodium chloride and citric acid. *J. Soils Sediments* 2018, 18(5), 1915–1924.

[18] Ji, H.; Huang, W.; Xing, Z.; Zuo, J.; Wang, Z.; Yang, K. Experimental study on removing heavy metals from the municipal solid waste incineration fly ash with the modified electrokinetic remediation device. *Sci. Rep.* 2019, 9(1), 8271.

[19] Cameselle, C.; Gouveia, S. Removal of multiple metallic species from sludge by electromigration. *J. Hazardous, Toxic, Radioact. Waste* 2020, 24(1), 04019030.

[20] Faisal, A.A.H.; Hussein, A.A. Modeling and simulation of copper removal from the contaminated soil by a combination of adsorption and electro-kinetic remediation. *J. Eng.* 2013, 19(6), 695–716.

[21] Faisal, A.A.H.; Hussein, A.A. An acidic injection well technique for enhancement of the removal of copper from contaminated soil by electrokinetic remediation process. *Sep. Sci. Technol.* 2015, 50(16), 2578–2586.

[22] Faisal, A.A.H.; Rashid, I.T. Enhancement solution to improve remediation of soil contaminated with lead by electrical field. *J. Eng.* 2015, 21(11), 111–129.

[23] Cameselle, C.; Gouveia, S.; Cabo, A. Enhanced electrokinetic remediation for the removal of heavy metals from contaminated soils. *Appl. Sci.* 2021, 11(4), 1799.

[24] MoEn, M. of the E. Assessment of environmental (Hot Spots) in Iraq. UNEP: Switzerland, 2005; 166 pp.

[25] Acar, Y.B.; Alshawabkeh, A.N. Principles of electrokinetic remediation. *Environ. Sci. Technol.* 1993, 27(13), 2638–2647.

[26] Wang, Y.; Li, A.; Cui, C. Remediation of heavy metal-contaminated soils by electrokinetic technology: Mechanisms and applicability. *Chemosphere* 2021, 265, 129071.

[27] Acar, Y.B.; Gale, R.J.; Alshawabkeh, A.N.; Marks, R.E.; Puppala, S.; Bricka, M.; Parker, R. Electrokinetic remediation: Basics and technology status. *J. Hazard. Mater.* 1995, 40(2), 117–137.

[28] Reddy, K.R.; Chinthamreddy, S. Sequentially enhanced electrokinetic remediation of heavy metals in low buffering clayey soils. *J. Geotech. Geoenvironmental Eng.* 2003, 129(3), 263–277.

[29] Wong, J.S.H.; Hicks, R.E.; Probstein, R.F. EDTA-enhanced electroremediation of metal-contaminated soils. *J. Hazard. Mater.* 1997, 55(1–3), 61–79.

[30] Lo, I.M.C.; Yang, X.Y. EDTA extraction of heavy metals from different soil fractions and synthetic soils. *Water Air Soil Pollut.* 1999, 109, 219–236.

[31] Hansen, H.K.; Rojo, A.; Ottosen, L.M. Electrokinetic remediation of copper mine tailings. Electrochim. *Acta* 2007, 52(10), 3355–3359.

[32] Haswell, S.J. Atomic absorption spectrometer; theory, design and applications. Elsevier: Amsterdam, 1991; 529 pp.

[33] Saeedi, M.; Jamshidi, A.; Shariatmadri, N.; Falamaki, A. An investigation on the efficiency of electro-kinetic coupled with carbon active barrier to remediate nickel contaminated clay. *Int. J. Environ. Res.* 2009, 3(4), 629–636.

[34] Oyanader, M.A.; Arce, P.; Dzurik, A. Avoiding pitfalls in electrokinetic remediation: Robust design and operation criteria based on first principles for maximizing performance in a rectangular geometry. *Electrophoresis* 2003, 24(1920), 3457–3466.