Enhancement Solution to Improve Remediation of Soil Contaminated with Lead by Electrical Field

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ABSTRACT

A laboratory investigation of six different tests were conducted on silty clay soil spiked with lead in concentrations of 1500 mg/kg. A constant DC voltage gradient of 1 V/cm was applied for all these tests with duration of 7 days remediation process for each test. Different purging solutions and addition configurations, i.e. injection wells, were investigated experimentally to enhance the removal of lead from Iraqi soil during electro-kinetic remediation process. The experimental results showed that the overall removal efficiency of lead for tests conducted with distilled water, 0.1 M acetic acid, 0.2 M EDTA and 1 M ammonium citrate as the purging solutions were equal to 18 %, 37 %, 42 %, and 29 %, respectively. However, introducing the injection wells as another enhancement technique into the tests used the same purging solutions mentioned above which have vital role in increasing the removal efficiency up to 59 %.

Key words: lead, Electro-Kinetic, Purging solutions, injection wells, enhancement.

محاليل التحسين لمعالجة التربة الملوثة بالرصاص بواسطة المجال الكهربائي

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الخلاصة

تم أجراء ستة تجارب مختبرية مختلفة على تربة طينية غرينية ملوثة بالرصاص بتركيز (1500ملغ/كغم). في كل التجارب التي اجريت في هذه الدراسة تم تسليط تيار كهربائي مستمر بين الاقطاب و بفولتية (1 فولط/ سم) خلال سبعة ايام متتالية . أجريت دراسة مختبرية لإنواع مختلفة من محاليل الإزالة متضمنة أسلوب أضافه أبار حقن لتحسين ازالة الرصاص من الترب العراقية خلال المعالجة بالطريقة الكهروحركية. أظهرت النتائج ان كفاءة أزالة الرصاص عند استخدام الماء المقطر، 1مولاري من حامض الخليك، 0.2 مولاري من EDTA، 1مولاري سترات الامونيوم هي 18 %, 37 %, 42 %, 29 % على التوالي . أن أستخدام تقنية أبار الحقن كتقنية محسنة لنفس محاليل الأزالة المذكورة انفًا تعتبر طريقة مبتكرة اخرى وذلك لأهميتها الفعالة في زياده كفاءة المعالجة لتصل الى (59 %).

الكلمات الرئيسية: الرصاص, الطريقة الكهروحركية، محاليل الازالة، ، أبار الحقن، تحسين.

INTRODUCTION

Soil contamination is placing human health at a great risk. It is becoming a key environmental issue, due to its importance in ecosystems, the influence it has on the quality of groundwater, plants and food. Some of the most common and most damaging types of soil contaminants are heavy metals, **Saleem et al., 2011**. Unlike organic contaminants that can be eliminated or reduced by microbial activity and chemical oxidation techniques, heavy metals cannot be degraded. Soil is a biochemically and geochemically complex material and is highly heterogeneous in composition and therefore it retains the spilled heavy metals much longer than air and water, **Kamari, 2011**.

In recent years, there has been considerable interest in the application of new and innovative ways for removal of pollutants from soil and groundwater, but most methods have high cost, and they are unsuitable in low permeability soils. Electro-kinetic is a relatively new way to remove environmental pollution from these soils. It is using intensity direct current (DC) or a low electric potential difference to an array of electrodes placed in the soil for removing organic, inorganic and heavy metal particles from low permeable soils, mud, sludge, slurries, sediments and groundwater by electric potential, **Acar et al., 1995; Hosseini et al., 2011; Mosavat et al., 2012**. Electro-kinetics is defined as the physicochemical transport of charge, action of charged particles, and effects of applied electric potentials on formation and fluid transport in porous media. Essentially, electro-kinetics involves the inserting of electrodes into the region nearby the contaminated site. Thereafter, a low potential gradient can be supplied between the positively charged anode electrode and the negatively charged cathode electrode. Accordingly, positive charged ions are moved to the negatively charged electrode and negative ions attracted to the positively charged electrode. Also, it has been experimentally proven that non-ionic species are also transported along with the electro-osmosis induced water flow and migrates mainly from anode towards cathode. The quantity and direction of pollutant migration is influenced by the soil structure and type, pollutant concentration, the mobility of metal ions and the conductivity of the purging solution, **Reddy et al., 2002; Ahmed, 2004**.

The migration of charged species through the soil involves three complex mechanisms which are electro-osmosis, electrophoresis and electro-migration. In the other words, the formation of electric diffuse double layer at the charged surface of clay particles is responsible for electro-Kientic phenomena, namely electrophoresis, electro-migration and electro-osmosis, **Mosavat et al., 2012**. These processes force the aqueous phase and ions to desorb from the sediment surface and migrate through the electric field either towards the anode or the cathode, depending on the speciation. Electromigration is the movement of ions and ionic complexes in a soil solution due to an applied electric field. The ions move towards the electrode of opposite charge: anions towards the anode and cations towards the cathode. Electro-osmosis is the movement of water in a porous media in an applied electric field. Soil particles are negatively charged, which creates a diffuse double layer of water and dissolved cations around the soil particles. When an electric field is applied, the cations will migrate in the direction of the cathode along with the water molecules. The final phenomenon affecting electro-kientic remediation is electrophoresis. Electrophoresis is the transport of particles in an applied electric field and includes all charged particles (e.g. colloids, clay particles, organic particles), **Niroumand et al., 2012**.

In addition, electrolysis reactions occur at the electrodes during the electro-Kinetic processes. These reactions (Eqs. 1 and 2) dominate the chemistry at the boundaries as well as the soil chemistry in the electro-kinetic remediation. The electrolysis reactions generate hydrogen ions at the anode and hydroxide ions at the cathode. These ions migrate into soil via electromigration and this result in changing the chemistry of soil. Since the hydrogen ions possess greater ionic mobility and the electroosmotic flow is towards the cathod, by the end of the electro-kinetic remediation processes, almost entire soil mass is subjected to acid conditions while the small fractions of soil mass near the cathode remain under alkaline conditions, **Asavadorndeja et al., 2005**.

At the anode: $2H_2O - 4e^- \rightarrow O_2\,(g) + 4H^+$ (1)

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

This situation has important consequences that may affect the electro-kinetic remediation process. In unenhanced electro-kinetic remediation, the increasing of the soil pH near the cathode electrode may cause a negative complexation of metal ions within the zone of pH jump, where they can precipitate as insoluble compounds. The formation of low conductivity zone, where metals are precipitated, can be avoided by using different acidic purging solutions to depolarize the cathode. This process is called as enhanced electro-kinetic remediation, **Ferrarese, 2008**.

The aim of the present study was to conduct laboratory investigation in order to study the ability and efficacy of applying the enhancement solutions such as acidic solution (acetic acid) and chelating agents (ethylene diamine tetraacetic acid and ammonium citrate) in improving the removal efficiency of lead from contaminated soil with a novel injection well proposed here for removing lead from low permeable Iraqi contaminated soil under the effect of electric field.

2. MATERIALS AND METHODS

2.1 Materials

Naturally Iraqi soil was used as a porous medium in the experiments conducted in the present study. The physicochemical properties of used soil are explained in **Table 1**. To prepare a soil sample with lead concentration equal to 1500 mg/kg and initial moisture content equal to 50% by weight , 2.397 g of $Pb(NO_3)_2$ was dissolved in 500 mL of distilled water and 1Kg of dry soil was then artificially contaminated by solution. The contaminated soil was left for 24 h before it was packed into the reactor cell to attain equilibrium.

2.2 Electro-Kinetic Test Setup

Fig.1 shows the electro-kinetic test setup used in the present study. The schematic diagram of this setup consists of an electro-kinetic cell (10 cm D × 5 cm W × 30 cm L), including two electrode compartments, a power supply, and a multi-meter as illustrated in the **Fig. 2**. The actual length of the soil specimen in this cell equal to 20 cm. Top side of the reactor was opened to the atmosphere to allow the escape of the gases produced during the electrolysis process. Each electrode compartment consists of a valve (to control the flow of purging solution into the cell), a slotted graphite electrode, and a filter paper. Perforated plastic plates were used to separate the various sections within the cell and filter paper was used to hinder the soil sample in the cell from going to the electrode compartments. Two cylindrical graphite electrodes that are chemically inert to electrolysis reactions were used both at the anode and the cathode. Inert electrodes prevent introduction of additional chemical species that might be complicated the electrochemistry during processing. Their uses are necessary specifically at the anode, since the oxidation reaction has a highly corrosive effect on the electrode (**Acar** and **Alshawabkeh, 1996**). The diameter and length of the electrodes were 2.5 and 10 cm. Two perforated polyethylene cylinders (outer diameter was 2.5 cm, inner diameter was 2 cm and 20 holes of 0.2 cm) were vertically implanted in the soil sample to the bottom of the cell, at two locations, to enhance the propagation of the acidic front. This is a novel technique to determine the efficacy of using injection wells in actual soil remediation of polluted sites. A DC power source was used to apply a constant voltage to the electrodes, and a multi-meter was used to monitor the voltage and measure the current flow through the soil sample during the test.

2.3 Testing Procedure

The soil samples were artificially contaminated with lead in all electro-kinetic tests. The contaminated soil was placed in the electro-kinetic cell in layers and compacted uniformly using wooden rod. The exact weight of the soil used in the cell was determined and the soil was equilibrated for 24 hrs. Filter papers were inserted at the ends of the soil sample. Two perforated polyethylene cylinders were vertically implanted in the soil sample to the bottom of the cell, at two locations, to enhance the propagation of the acidic front. The electrode compartments were filled with a purging solution (PS) to the same level and maintained as such to prevent a hydraulic gradient from forming along the specimen. The electro-kinetic cell was then connected to the power supply and a potential gradient of 1 V/cm was applied to the soil sample. The electric current across the soil sample as well as the water flow, pH and electrical conductivity in both the anode and cathode were measured at different time periods throughout the duration of the experiment. The test was terminated when the current stabilization or no significant change in PS flow was observed.

At the end of each test, aqueous solutions from the anode and cathode compartment were collected. Then, the soil specimen was sectioned into five parts and each part was weighed and subsequently preserved in a glass container. From each soil section, 10 grams of treated soil was added into glass vial containing 30 mL of distilled water. The mixture was stirred thoroughly for several minutes and the solids were then allowed to settle for 1 hour. The pH of the soil samples as well as aqueous solutions from the electrode compartments were measured, **Hansen et al., 2007**. Description of different tests conducted in the present study is given in **Table 2**.

2.4 Chemical Analysis

Contaminant in different soil sections were extracted by performing acid digestion in accordance with the same procedure adopted by **Haswell (1991**). Total concentration of lead was determined using this extraction procedure. In this procedure, the soil samples were crushed and approximately 1 g of a representative sample from each section was weighed accurately in a beaker (capacity of 250 mL) and then mixed with 15 mL of concentrated hydrochloric acid (HCl) and 5 mL of concentrated nitric acid (HNO_3). The mixture was then heated in the heating sandy bath until the brown evaporation was disappeared and the sample arrived to dry state, this step takes about (45-60) minutes. Then the beaker was left for (5-10) min in the lab temperature and 5 mL of concentrated (HCl) was added. The beaker was heated again in the sandy bath, thereafter the beaker was cooled and 5 mL of concentrated HCL and 50 mL of heated distilled water were added to wash the sides of beaker from remains dissolved sample. Heating the mixture to the boiling points for (2-3) min was required. The sample was filtered on the paper No. 42, and then keeps it in volumetric flask capacity of 100 mL. Then washing the precipitation with distilled water and addition of the previous washed water to filtration and complete the size to 100 mL. Finally, the metal concentration was measured by Atomic absorption spectrophotometer (AAS).

Precautions were taken in order to ensure the accuracy of the test results. These precautions included: (1) new electrodes and filter papers were used for each experiment; (2) the electro-kinetic cell and compartments were soaked in a dilute acid solution for 24 h and then rinsed first with tap water and finally with distilled water to avoid cross contamination between the experiments; and (3) checking the atomic absorption calibration after testing every five samples.

3. RESULTS AND DISCUSSION

3.1 Experiment of Unenhanced Condition

Electro-kinetic remediation experiment to remove lead from silty clay soil by using distilled water as purging solution are conducted. Clean soil in these experiment was spiked with 1500 mg/kg of contaminant and potential gradient of 1 V/cm was applied EK-1 was conducted under unenhanced condition.

The main physicochemical conditions of the soil that control the migration and sorption of contaminants are pH and electrical conductivity. Consequently, during each experiment, the following parameters were measured: pH and electrical conductivity at the anode and cathode compartments, electric current and electro-osmotic flow. At the end of electro-kinetic treatment, another set of measurements were taken and included: soil pH and residual concentration of the contaminant in the soil. The direct indication of overall remediation was expressed by the changes in the concentration of the pollutant; and profile of the current, as well as the effluent flow, conductivity of fluid was used as indirect indicators of remediation efficiency.

Fig. 3 shows the current and current density variations for the experiment (EK-1) that was performed under unenhanced conditions, i.e., using distilled water in both the anode and cathode compartments. It is clear that the current increased from an initial value of 34 mA to peak values of 60 mA in approximately 12 and 24 h. The current then decreased to a low value and stabilized at approximately 16 mA. The maximum current densities for this experiment was1.52 mA/cm^2. The current density values stabilized at 0.4 mA/cm^2 toward the end of the testing.

Fig. 4 shows the electro-osmotic flow and electro-osmotic velocity as function of processing time for the experiment. The electro-osmotic flow was increased with the time and maximum values of 50 mL was obtained in 48 h and 18 h of testing. These values were remained constant until the end of mentioned tests. The electro-osmotic velocity increased to a high value of 3.7×10^{-5} cm/s in the first 3 h, and then it started decreasing. Average electro-osmotic velocities of 1.17×10^{-5} cm/s was observed during these experiment. The velocity values are consistent with the range of values reported in the literature, **Reddy,** and **Chinthamreddy**, **2003**. Based on these low electro-osmotic flow and flow velocity measurements, it appears that electro-osmotic mechanism had a less role in the migration of heavy metals, and electro-migration was probably the more dominant contaminant transport mechanism.

The pH of anolyte decreased from an initial value of 6.8 and stabilized of approximately 2 because of the formation of H^+ ions (**Fig. 5**). Whereas, the same figure shows that the pH of cathode compartments for these test increased from 6.8 and stabilized at approximately 12.5 due to the formation of OH^- ions.

Total Pb(II) concentrations in each section of the treated soil for EK-1 was determined and plotted at **Fig. 6**. These sections are corresponding to distance 0.1, 0.3, 0.5, 0.7 and 0.9 of the total length (L) of the treated soil from the anode side. The initial concentration of each contaminant throughout the soil was 1500 mg/kg. Final concentration of Pb after 7 days was lower and varied from 1100-1250 mg/kg near the anode to 1300-1600 mg/kg near the cathode. The concentration profile in **Fig. 6** indicates removal of lead from the soil system in this test as all of them are below the initial concentration. Increased contaminant concentration was observed near the cathode. The pH distribution is also shown to further explore the observed heavy metal distribution. The pH of the soil was reduced throughout two-thirds of the soil beginning at the anode, while the pH of the soil increased in the vicinity of the cathode. The pH changes that were observed are fairly consistent with other reported electro-kinetic studies. Due to the smaller ionic radius, the mobility of an H^+ ion is approximately twice the mobility of an OH^- ion, and some researchers showed that this is the reason why H^+ ions migrate farther into the soil as compared to OH^+ ions, **Acar** and **Alshawabkeh, 1993**. The reaction kinetics and the type and concentration of the ions at the graphite electrodes may also affect the generation rate and migration of the H^+ and OH^- ions, and the effects of the electro-kinetic transport processes, electro-migration and electro-osmosis, should also be considered. The observed migration of Pb was consistent with the changes in the soil pH.

Fig. 6 shows that the lead successfully migrated toward the cathode and, consequently, larger amount of contaminant was found in the soil near the cathode. However, the lead removal efficiency into the cathode compartment was low (18 %), and this low removal may have been due to the precipitation of lead that occurred within the soil in the high pH regions near the cathode .

3.2 Experiment of Acetic Acid Enhancement

As explained in the **Sec.3.1**, when distilled water is used as the purging solution, the removal lead is severely affected by the precipitation of these metal in the soil near the cathode region. This precipitation can be attributed to development of high pH conditions which result from the water electrolysis at the cathode compartment. To overcome on this fixation mechanism, acetic acid with concentration of 1 M was used as purging solution in the cathode compartment. Acetic acid is able to produce H^+ ions that can decrease the pH of the solution and dissolve metal precipitates. The concentration of acetic acid has been determined in order to maintain a low pH (~ 2.5-3) at the cathode compartment, **Ugaz et al., 1994**.

Fig. 7 and **Fig. 8** showed the current and electro-osmotic flow through the soil specimen for the acetic acid enhancement experiment, respectively. This experiment was conducted for a total 168 h. The current increased to high value of 89 mA in 96 h, and then decreased to a low value of 75 mA at the end of the test. It is clear that the current density was less than (4 mA/cm^2) throughout the entire experiment duration. At such low current densities, the heating effects produced by the electric current do not need to be considered, **Reed et al., 1995**. It is clear from the **Fig .8** that the flow volume toward the cathode increased to about 125 mL in 132 h , and then approximately stabilized on these values. The electro-osmotic flow velocity increased rapidly to a value of 7.04×10^{-5} cm/s during the first 3 h, and then it decreased as a function of the time until to reach the value of 8.27×10^{-6} cm/s after 168 h. The average electro-osmotic velocity observed over the entire experiment duration was calculated to be 2.44×10^{-5} cm/ and these values are greater than that values for (EK-1).

Fig. 9 illustrate the lead distributions along with pH values after the electro-kinetic treatment. The pH profile shows that, although the pH in the cathode compartment is maintained at approximately 3, the pH in the soil near the cathode reached a value of almost 8. These pH values indicate that the cathode reaction may not have been completely depolarized during the experiment. The lead distribution profile is shown in **Fig. 9** and this profile clearly demonstrates the migration of contaminant toward the cathode. **Table 3** shows that the using acetic acid in the cathode was beneficial and the introduction of acetic acid allowed significantly higher removal and migration of lead toward the cathode in comparison with unenhanced condition when distilled water was the purging solution.

3.3 Experiments of Ethylene Diamine Tetraacetic Acid Enhancement

Fig. 10 and **Fig. 11** shows the current, current density, electro-osmotic flow volume, and electro-osmotic velocity variations for the 0.2 M EDTA enhancement test in the silty clay soil, respectively. The current increased to peak values of 190 for EK-3 with the first 84 h, then decreased to values of 135 mA in 132 h, while the current density was not exceeding 5mA/cm^2. The electro-osmotic flow occurred toward the cathode from the beginning of the experiment, and the accumulative electro-osmotic flow volumes were about 203 mL at the termination of EK-3 test. The electro-osmotic flow velocity increased rapidly to a value of 5.56×10^{-5} cm/s during the first 3 h, and then it decreased as a function of the time until to reach the value of 1.34×10^{-5} cm/s after 168 h. The average electro-osmotic velocity observed over the entire experiment duration was calculated to be 1.74×10^{-5} cm/s (for EK-3) and these values are greater than that values of (EK-1).

Fig. 12 shows the contaminant profile and the pH profile throughout the soil specimen after electro-kinetic testing. The pH for test EK-3 was about 2 in the anode compartment and below 10 along the entire soil specimen. According to this figure, the migration of Pb occurred toward the anode which is opposite to the migration direction observed in unenhanced test **(Fig. 6)**. This contaminant migrated from the soil sections near the cathode and accumulated in the soil sections near the anode. The removal efficiencies of (Pb) is 42%.

3.4 Experiment of Ammonium Citrate Enhancement

Ammonium citrate (1 M) with pH adjusted to (9-10) in the cathode compartment was tested as enhancement solution for soil contaminated with initial concentration of lead equal to 1500 mg/kg**. Fig. 13** shows the residual concentration profiles for this contaminant and pH profiles at the end of experiments EK-4. It is seen that the concentration of lead is decreased and the removal (29%) and no accumulation within the soil was observed. **Fig. 13**. showed that lead was removed from the soil as anions,. In other words, lead was transported towards both electrodes during the experiments because the complexes with ammonia and with the citric part were formed. These results are consistent with findings of, **Ottosen et al,. 2005**.

3.5 Experiment of Injection Wells Enhancement

As explained in previous sections, the electro-kinetic tests performed using 1 M acetic acid or 0.2 M EDTA or 1 M ammonium citrate as purging solutions in the cathode significantly affected the transport of lead through the soil in comparison with unenhanced experiments. Based on the results of these experiments, it can be concluded that the effective removal of lead may not be possible with only a single enhancement; rather, this removal may require an additional process which is represented by adding an injection wells proposed in the present study. **Fig. 14** and **Fig. 15** show current and electroosmotic flow volume variations with time for EK-5 and EK-6, respectively. In EK-5, , initially, the current was high (68 mA), and subsequently increased, which may be owing to the injection of ions of the PS (acetic acid) during the test. In contrast, the current reached a high value within the range 12-18 h after the EK-6 test begun, then it decreased, and finally the current stabilized at the end of tests. The cumulative effluent collected at the end of the experiments EK-5 and EK-6 ranged from 245 to 330 mL. The reason behind this great difference (i.e. collected effluent from these experiments is 10 times greater than of corresponding value collected from unenhanced condition) because the electro-osmotic flow is directly proportional to current and dissolved contaminants present in the pore fluid. Replenishing of the soil-solution system with PS by using injection well will decrease the pH values through the soil. The low pH may cause the increasing of solubility of metal species and/or salts which resulted in a high ionic concentration, an increase of the electrical current and, consequently, an increase of the electro-osmotic flow volume.

The electrical conductivity (EC) values for EK-5, EK-6, tests (**Fig. 16**) are increased with the time in anode and cathode compartments. The high EC values are reflected higher ionic concentration in the anode and cathode electrode solutions.

The lead concentration for these experiments in each section of the treated soil was determined and plotted, as shown in **Fig.17** and **Fig.18** The concentration profiles presented in these figures indicated that the removal of lead from the soil system in all these experiments was below the initial concentration profile and that increased contaminant concentrations were observed near the cathode. Also, these figures show the pH variations along the treated soil for the same tests. The changes in the pH profiles along the soil had a great influence on contaminant migration. Injection wells were proved a good methode in the enhancement propagation of the acidic front towards the cathode and, consequently, this will decrease the soil pH as shown in the comparison between the tests EK-5 & EK-6 with EK-1. It can be clearly seen from these figures that the acidic front extended along the most length of the soil specimen for tests with injection well enhancement. This will increase the removal of lead from the soil specimen due to decreasing the buffering capacity and, consequently, decreases the amount of calcite and carbonate in the soil specimen. This will be the basis for formation and development of acidic front phenomena. Therefore, a relatively high removal of lead can be achieved.

3.6 Contaminant Removal Efficiency and Electro-osmotic Permeability

The removal efficiencies were calculated based on the residual contaminant masses in the soil for all tests mentioned above. The lead removal efficiencies from the soil were 18% in EK-1(unenhanced test), 37% in EK-2, 42% in EK-3, 29% in EK-4, 59% in EK-5, and 37.5% in EK-6. The test results showed that the contaminant removal for silty clay soil was the highest when 1M acetic acid was used as the purging solution with introducing two injection wells along the soil bed as in the EK-5 test. The higher flow in this soil was probably responsible for removing more contaminant when the 1 M acetic acid purging solution was employed.

As expected, the direction of electro-osmotic flow was from the anode to the cathode for all tests. It is clear from **Fig. 14** and **Fig. 15** that the injection wells play a potential role in the increasing the collected cumulative effluents and these value continued until the end of these tests in comparison with other tests where injection wells are not used.

The flow rates, given by the slopes of the curves, were approximately ranged from 0.146 to 1.964 mL/h for all tests. The higher flow rate can be related to the zeta potential of the soil particles. The electro-osmotic flow rate, Q_e (mL/h) for a cylindrical soil core of length L and cross-section area of A under a potential difference of V (V) can be described by (**Vane and Zang, 1997; Kim et al., 2002**):

$$Q_e = \frac{\zeta \varepsilon q}{4\mu}\frac{V}{L}A \tag{3}$$

where ζ, μ, ε, and q are the zeta potential, viscosity of the fluid, permittivity of the fluid, and empirical constant related to the soil physical properties, respectively. Apparently, the electro-osmotic flow rate is directly proportional to the applied electrical potential gradient, zeta potential, and cross-section area of the soil core. This means that the zeta potential value in tests with injection wells is greater than those other tests. However, Eq.3 can be rewritten in the form similar to the Darcy's law (**Weng and Huang, 2004**):

$$Q_e = k_e i_e A \tag{4}$$

where k_e and i_e are defined as the electro-osmotic permeability and the potential gradient, respectively. With a potential gradient of 1 V/cm and cross-section area of soil specimen is 25 cm^2, the average k_e values according to Eq.4 were ranged from 1.62×10^{-6} to 2.183×10^{-5} cm^2/V 4.4. The magnitude of k_e is related to the resistance buildup during electro-kinetic treatment. As described previously, a higher current indicated that a rather low resistance occurred in the electro-kinetic system and, as such, it resulted in a higher k_e value. These obtained k_e values are in good agreement with the literature (**Weng et al., 2001**).

Overall, this study demonstrates that the enhancement by using injection wells can be effective for the removal of contaminant from the soil adopted in the present study.

4. CONCLUSIONS

The main conclusions that can be drawn from the experimental work of this research are as follows:

1) The electro-kinetic removal of lead from silty clay soil using distilled water as the purging solution was very low. The removal of lead based on residual soil concentrations was 18 %. The low removal was attributed to Pb(II) adsorption/precipitation in the cathode region due to high soil pH.

2) The removal efficiency of lead increased to become 37 % when 1 M acetic acid was used as the purging solution in the cathode compartment. The use of acetic acid with maintaining the pH at approximately 3 in the cathode compartment significantly affects the migration of contaminant adopted in the present study because it is able to produce H^+ ions that can decrease the pH of the solution and dissolve metal precipitates. Consequently, the electro-osmotic cumulative volume and coefficient of electro-osmotic permeability were increased in comparison with unenhanced tests.

3) The lead removal was the highest using the 0.2 M EDTA purging solution in the cathode. In this case, 42 % of lead was removed into the anode compartment. The migration of Pb occurred toward the anode which is opposite to the migration direction observed in unenhanced test. Also, the migration of lead is opposite to the electro-osmotic flow direction and this certifies that the electro-migration was the predominant mechanism in this situation.

4) In comparison with EDTA, when 1 M ammonium citrate with pH adjusted to (9-10) in the cathode compartment was used as the purging solution, the residual concentrations of Pb was less than their initial values in all sections of the soil and the achieved removal efficiencies were 29 %. This certifies that lead was removed from the soil as anions.

5) The results proved that the injection wells approach proposed in the present study for enhanced electro-kinetic remediation technology can be effective for the removal of lead from the silty clay soil with removal efficiencies ranged from 37 to 59 %. Drastically changes were recognized in the electro-osmotic cumulative volume and coefficient of electro-osmotic permeability in comparison with unenhanced test. These changes may be probably responsible for removing more contaminant due to decreasing the buffering capacity and, consequently, decreases the amount of calcite and carbonate in the soil specimen.

6) The results proved that the presence of salts in silty clay soil (25.8 % as $CaCO_3$) causes noticeable increase in the buffering capacity of soil. This increase may be the basis for a delay in the formation and development of acid front phenomena. Therefore, for this reason a relatively low removal of contaminant (≤ 59%) in this soil occurred.

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NOMENCLATURE

A = the total cross-sectional area normal to the flow direction, m^2.
i_e = potential gradient, V/m.
Ke = electro-osmotic permeability coefficient, $m^2\ V^{-1}\ s^{-1}$.
q = empirical constant related to the soil physical properties.
Q_e = electro-osmotic flow rate, ml/hr.
ε = permittivity, F m^{-1}.
μ = viscosity of the fluid, N. S. m^{-2}.
ζ = zeta potential, V.

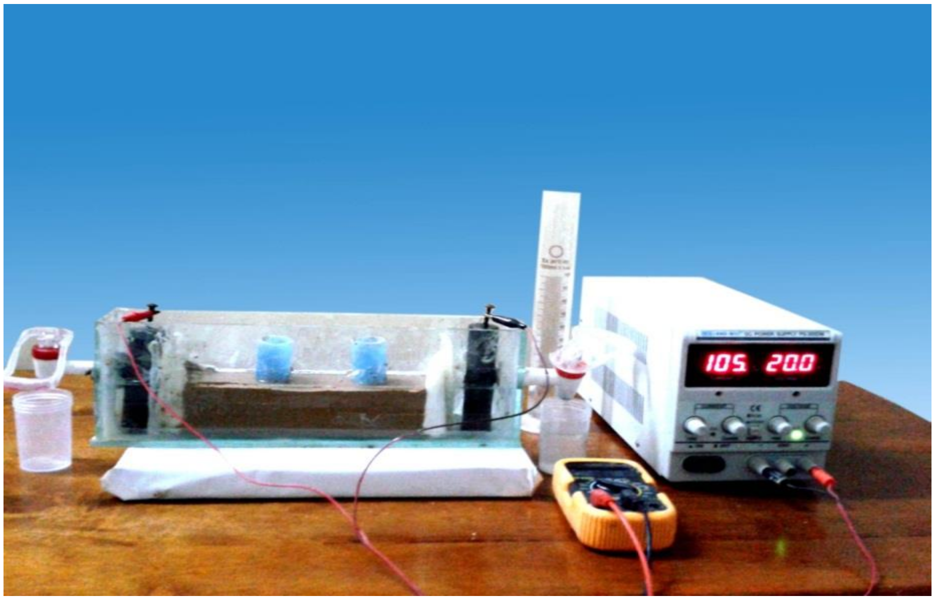

Figure 1. Experimental set-up of electro-kinetic cell used in the present study.

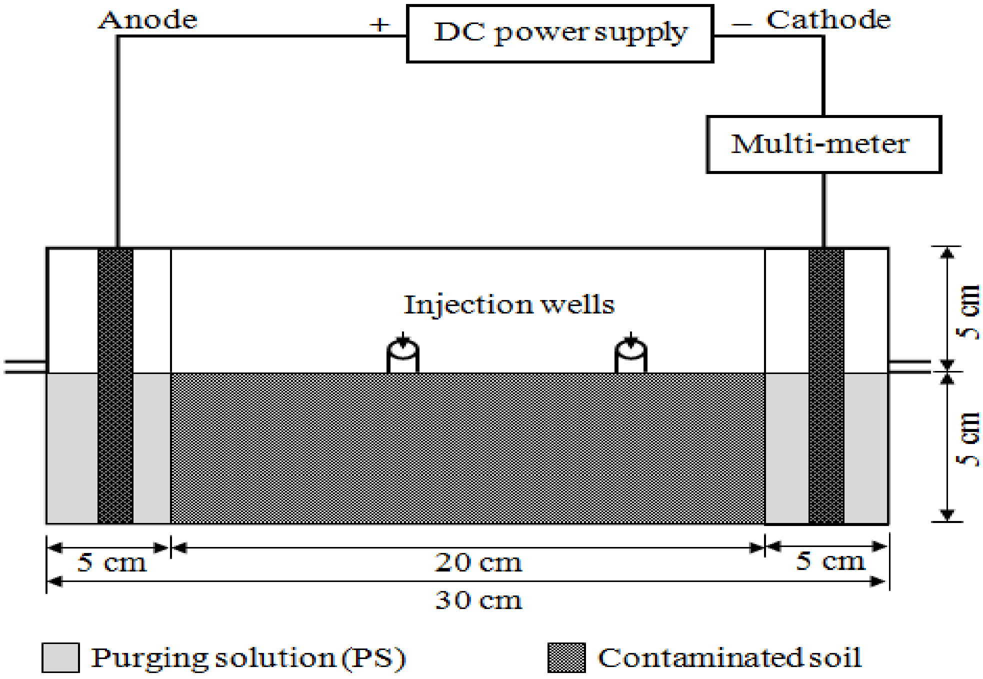

Figure 2. Schematic representation of electro-kinetic cell.

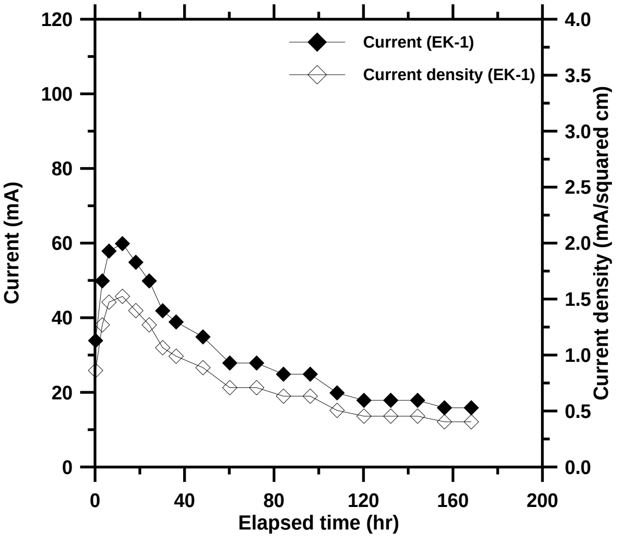

Figure 3. Current and current density as function of time for experiment of unenhanced conditions .

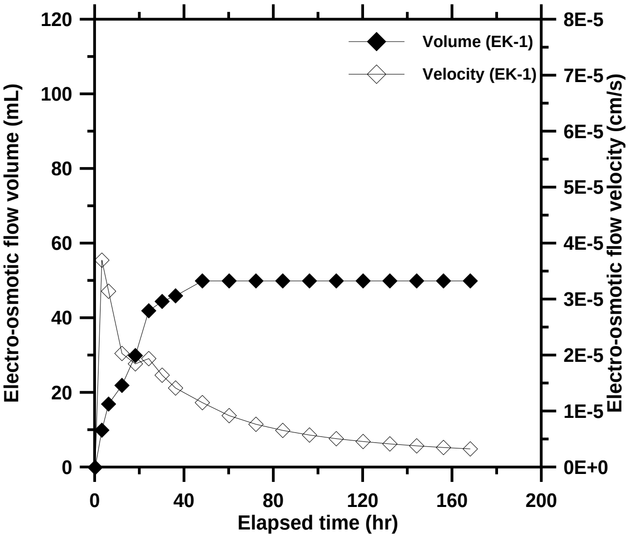

Figure 4. Electo-osmotic flow volume and velocity as function of time for experiment of unhanced conditions.

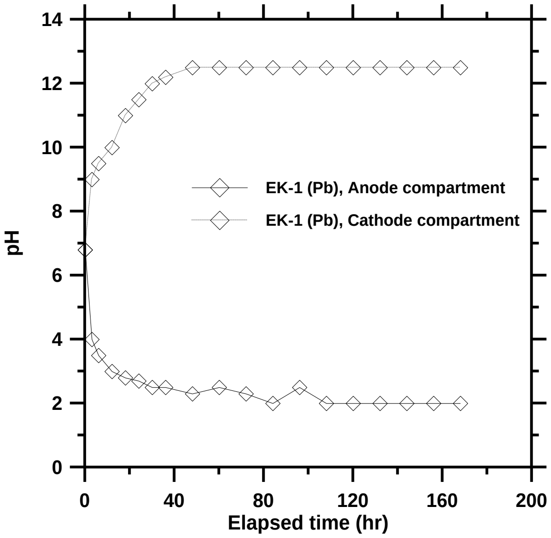

Figure 5. pH variation in the anode and cathode compartments versus time.

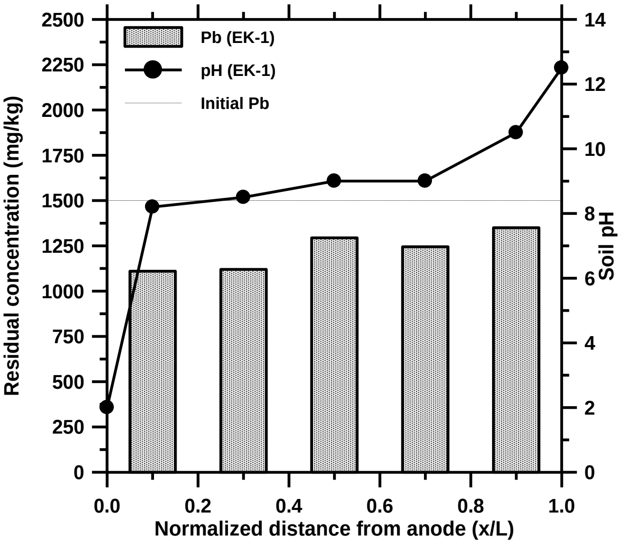

Figure 6. Lead distribution in soil after electro-kinetic treatment: unenhanced condition.

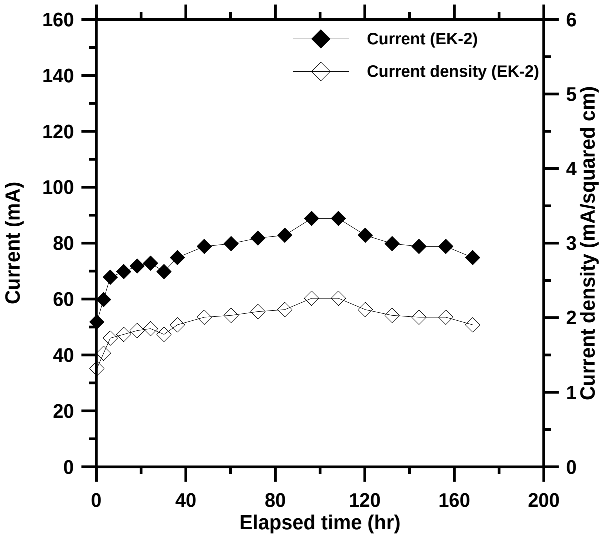

Figure 7. Current and current density variation:Aceticacidenhancement.

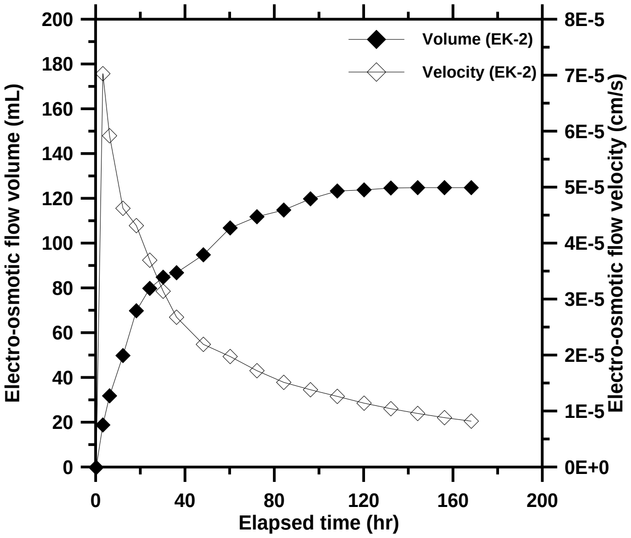

Figure 8. Electro- osmotic flow volume and velocity variations: Acetic acid acid enhancement.

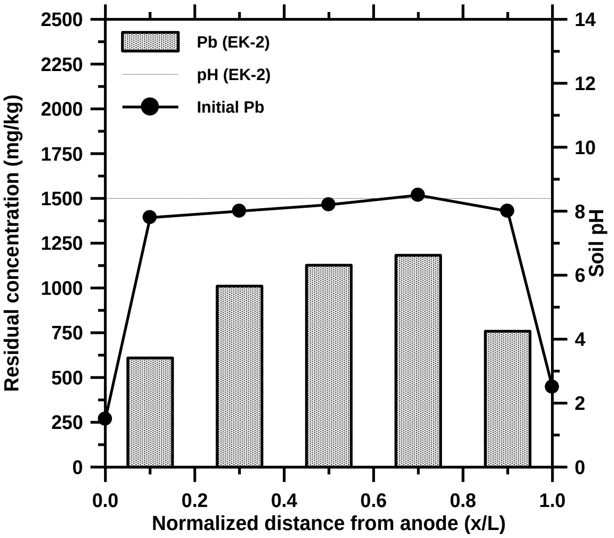

Figure 9. Lead distribution in soil after electro-kinetic treatment: . Acetic acid enhancement

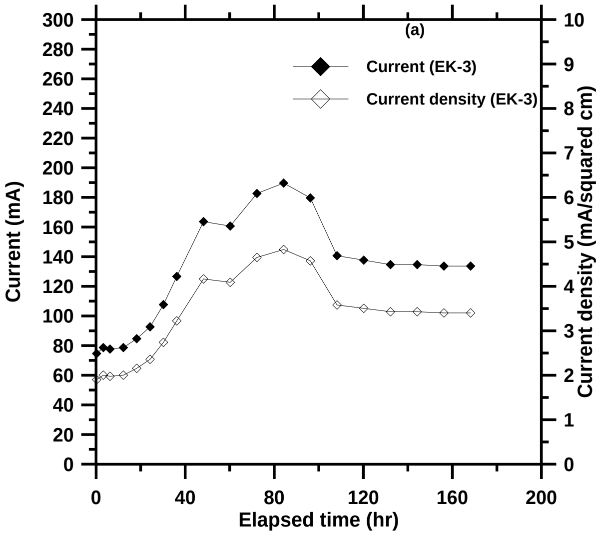

Figure 10. Current variations: EDTA enhancement.

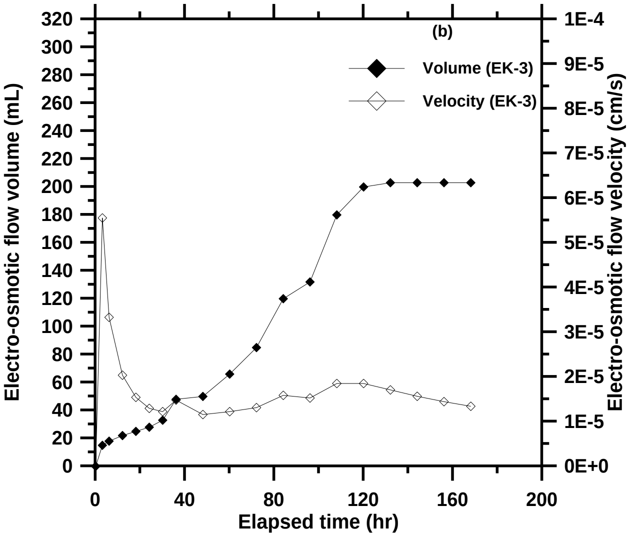

Figure 11. Electro-osmotic flow variations: EDTA enhancement.

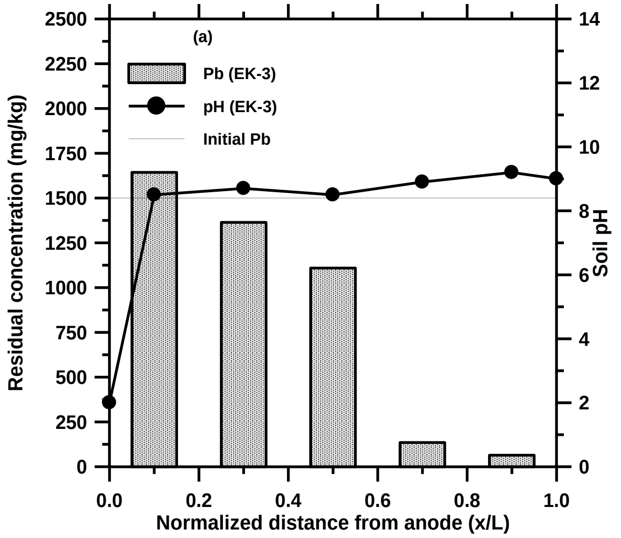

Figure 12. Lead distribution in soil after electro-kinetic treatment: EDTA enhancement.

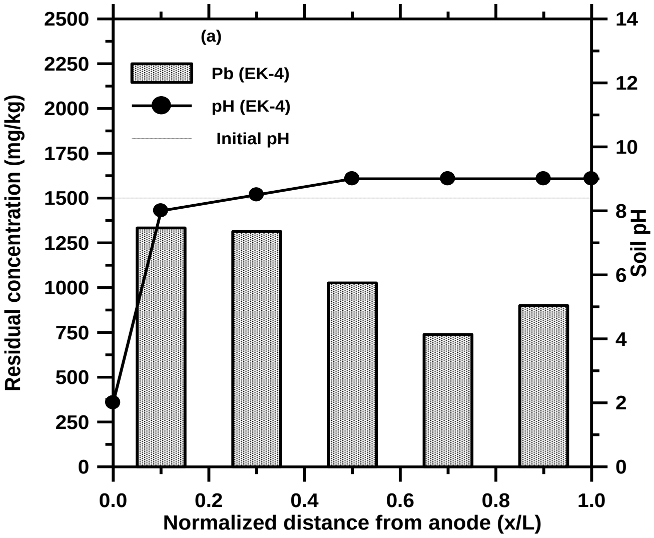

Figure 13. Lead distribution in soil after electro-kinetic treatment: Ammonium citrate enhancement.

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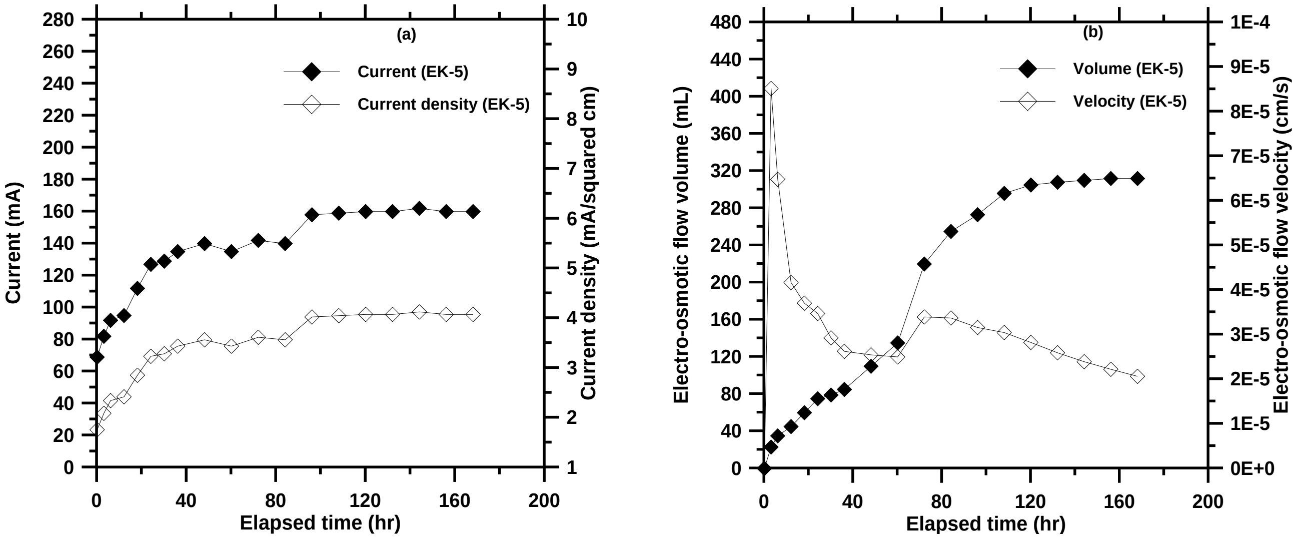

Figure 14. Current and electro-osmotic flow variations: Acetic acid and injection wells enhancement.

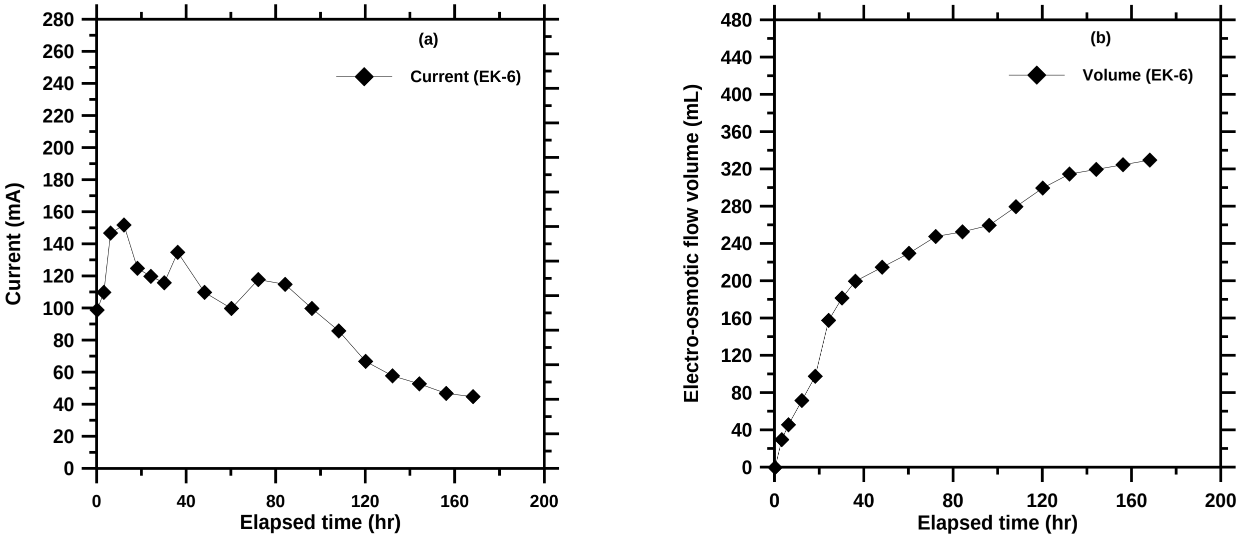

Figure 15. Current and electro-osmotic flow variations: Ammonium citrate and injection wells enhancement.

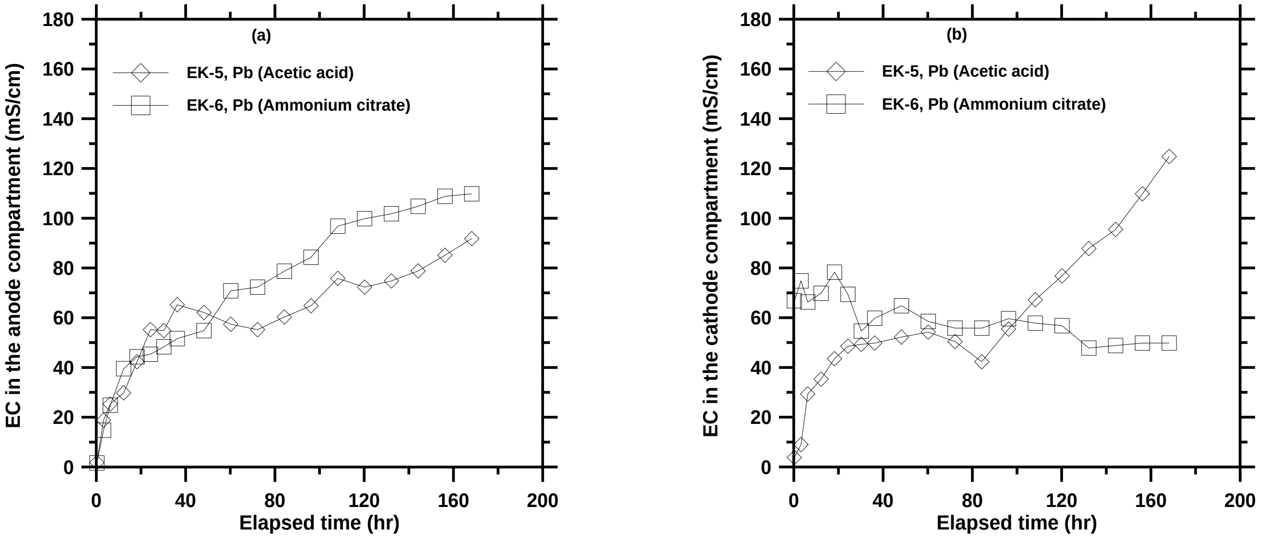

Figure 16. EC variation in the anode and cathode compartments versus the time.

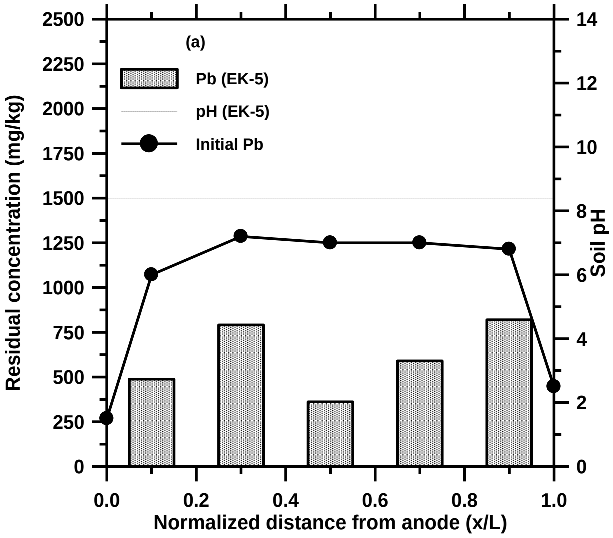

Figure 17. Lead distribution in soil after electro-kinetic treatment:Acetic acid and injection wells enhancement.

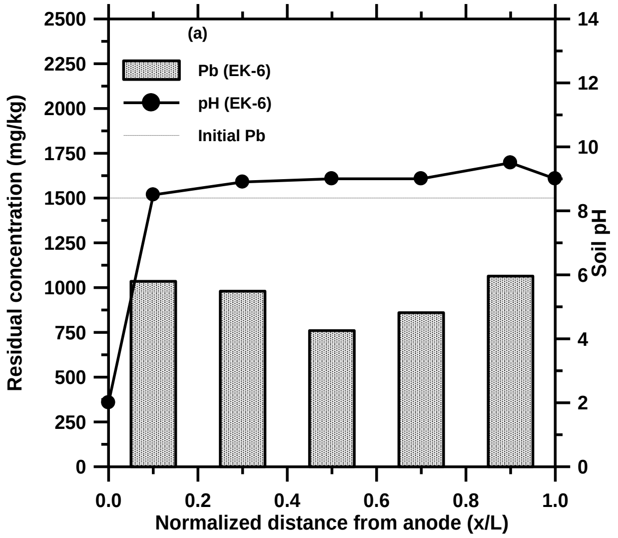

Figure 18. Lead distribution in soil after electro-kinetic treatment: Ammonium citrate and injection wells enhancement.

Table 1. Composition and properties of the soil.

Property	Value
Particle size distribution (ASTM D 422) Sand (%) Silt (%) + Clay (%)	 2 49 + 49
Atterberg limits (ASTM D 2487) Liquid limit (%) Plastic limit (%) Plasticity index (%)	 26 17 9
Cation exchange capacity (meq/100g)	21.4
pH	8.5
Organic content (ASTM D 2974)	0.28
Electrical conductivity EC (µS/cm)	4500
Porosity (n)	0.49
$CaCO_3$ (%)	25.8
Soil classification	Silty clay

Table .2 Details of electro-kinetic remediation experiments.

Experiment designation	**Conc. (mg/kg)**	**Time (days)**	**PS (pH)**		**No. of Wells**
			Anode	**Cathode**	
EK-1	1500	**7**	DW	DW	-
EK-2	1500	**7**	DW	1M AA (~3)	-
EK-3	1500	**7**	DW	0.2M EDTA	-
EK-4	1500	**7**	DW	1M AC (~9)	-
EK-5	1500	**7**	DW	1M AA (~3)	2
EK-6	1500	**7**	DW	1M AC (~9)	2

Table 3. Removal efficiency (R) of lead from different sections along electro-kinetic cell.

Section	1	2	3	4	5
R (%) with AA	59	33	25	21	49
R (%) with DW	26	25	14	17	10