Electro-Kinetic Removal of Heavy Metals from Contaminated Soil Using Palm Date Vinegar and Fibers

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Abstract

Soil pollution by heavy metals is a worldwide problem and in Iraq in particular. Electro-kinetic remediation (EKR) is one of the modern technologies that can give a great promise for the cleaning of heavy metals contaminated soils. Iraq is the first country in palm trees numbers, date production, dates processing and thousands of tons of wastes are disposed each year. This work includes: First, conducting of an ex-situ EKR pilot study to evaluate the effect of different pH-Adjusted tap water. Diluted HNO3 and NaOH reagents were selected to adjust the tap water samples, to reach the required pH values, pH of 4, 6 and 8, and then used as electrode purging solutions to find out the optimum conditions for better lead removal efficiency. Second, studying the use of Iraqi dates vinegar (IDV) as a new, inexpensive, eco-friendly and effective alternative purging solution. Third, testing the ability of date palm fibers (DPV) as a low cost, available and eco-friendly reverse osmosis preventer.
 Among tap water samples, the results showed that tap water of pH 4 has given the highest lead removal efficiency. In this pH (pH 4), Vinegar was more efficient in lead removal than tap water of same pH; 79.5 and 76.0 %, respectively. However, it could be concluded that the use of both dates Vinegar and date palm Fibers, as two available low cost and eco-friendly materials in Iraq, have successfully improved the lead removal process in the Electro-Kinetic Remediation Reactor; by increasing the lead removal efficiency (%R) to about 80%.
Keywords: Electro-Kinetic, Lead Removal, Soil Remediation, Date Vinegar, Palm Fibers.

1. Introduction

The presence of heavy metals contaminated sites on earth surface is quite common and the need for their cleaning is huge and urgent. As a result, many efforts have been made to "clean-up" these contaminated sites considering the most related bio and physicochemical aspects of the contaminant type (Oyanader 2004). Although there are successful and environmentally friendly soil treatment technologies but they have not been completely studied and implemented. There are several techniques which have attracted the interest among scientists and industry officials. These are: bioremediation, thermal desorption, soil vapor extraction, soil washing, and soil flushing (Virkutyte *et al.* 2002). Electro-kinetic soil remediation is an emerging technology that has attracted increased interest in the last decade. This method aims to remove heavy metal contaminants from low permeability contaminated soils under the influence of an applied direct current (Oyanader 2004; Virkutyte *et al.* 2002)**.** Electro-kinetic remediation offers the following advantages as compared to conventional remediation methods: (1) simplicity; minimal equipment requirements, (2) safety; neither personnel nor the public in the vicinity are exposed to contaminants, (3) wide range of contaminated media; it can be used for soils, sludge, sediments, and groundwater (particularly well suited for low-permeability clays and heterogeneous soil deposits within the vadose zone where conventional remedial methods have proven to be ineffective or expensive), (4) wide range of contaminants; it can be used for metals, organic compounds, radionuclides, or combinations of these contaminants, (5) flexibility; it can be used as an in-situ or ex-situ remediation system and is easily integrated with other remediation technologies such as bioremediation (Reddy 2010). Lead is mainly used to produce battery grids, copper alloys and lead alloys – and also semi-finished products - such as pipe, sheet, traps, bend and blocks for ammunition for both military and sports purposes. In addition, lead and its compounds are used in the production of solder, pigments, glass and ceramics, and in lithographic processes. Some fertilizers also have various concentrations of lead. Land application of sewage sludge, animal wastes from animal production, coal residues, municipal refuse incineration, wastewaters, and auto emissions are all anthropogenic sources of lead in soil (Monfared 2011). Most lead that is released to the environment is retained in the soil. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexity with soil organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater (Evanko & Dzombak 1997). In Iraq and because the lead soil contamination, many researches have dealt with this problem. In this aspect and in a similar study, a detailed work by using an electro-kinetic study on a naturally lead contaminated soil (with 1300ppm of Pb), a silty clay loam soil samples brought from the State Battery Manufacturing Company location in east Baghdad, was conducted by the same author (Mutter et. al. 2014). In this study, the Pb removal was 67.6% at pH4 water, 71.45 % with EDTA purging solution, 71.1% when the ZVI powder was used as an enhancing material and Sawdust to prevent the reverse osmosis.

    Vinegar can be produced from various raw materials like fruit juices, distilled alcohol, wine, and any kind of alcoholic solution by several major production techniques such as the Orleans process, generator process and

submerged acidification process (Moraels 2003). Generally, all vinegar products are solutions containing mainly acetic acid (Pinsirodom *et al.* 2010). Vinegar is a liquid consisting of about 5–20% acetic acid (CH_3COOH), water, and other trace chemicals, which may include flavorings. The acetic acid is produced by the fermentation of ethanol by acetic acid bacteria (Nakayama 1959). Iraq is the first country in date palm trees number (about 30 million) and dates production in the world. Therefore, products gained and derived from this tree are very available and thousands of tons of wastes are disposed each year. Date vinegar, as an organic product, does not need sophisticated equipment to be manufactured and can be simply produced even at homes of most Iraqi people and is usually used to prepare homemade pickles. Hence, only 2kg of low cost "Khistawi" dates can yield 5L of 4 % (w/v) acid, which is economically valuable (Matloop & Hamza 2013).

The objectives of this study are: (1) to apply and test the use of an ex-situ (EKR) to remove lead from an artificially Pb-contaminated soil, (2) the use of many tap water solutions of different pH as purging solutions to choose the best conditions for higher lead removal efficiency, (3) the use of both Date Vinegar as a purging solution and Palm Fibers as a bio sorbent to prevent the reverse osmosis process in the Remediation Reactor.

2. Materials and Method

2.1. Soil Sample
The soil, which was brought from a local plant nursery in Baghdad, was artificially contaminated with lead. The composition and properties of soil used in this study are described in the table (1). The soil has 60% sand, 6% $CaCO_3$, 0.51mS/cm EC, 7.7pH and 0.7% organic matter. The soil hence can be classified as a low organic, non-saline, calcareous sandy soil.

2.2. Lead Contaminant
To simulate the soil contamination by lead, a solution of $Pb(NO_3)_2.6H_2O$ (manufactured by the British Drug House, BDH England) were prepared and added to the soil samples to obtain a representative concentration. As a sample of calculation for preparing 1000 mg/kg of Lead to soil weight and initial moisture content equal to 30%, an amount of 15.9g of $Pb(NO_3)_2.6H_2O$ (molecular weight of 331.21g/mole) was dissolved in 1000 ml of distilled water to obtained a 10000 PPM of lead solution. A 30 ml of this solution was taken and completed to 300 ml with distilled water and added to 1 kg of dry soil to reach a 1000mg/kg (ppm) of lead in soil.

2.3. Purging Solutions
To study the performance of electro-kinetic remediation (EKR) process, many tap water samples of different pH values and also Iraqi date vinegar (IDV) were used in this study as a purging solution. Under certain circumstances and in calcareous soils of high buffering capacity (i.e. in the same alkaline soil used in this study , table 1), the use of enhancement agents to increase the contaminants solubility is necessary for cost-effective implementation. In this study, NaOH-pH-Adjusted tap water samples of different pH were used to choose the best pH value for the best lead removal and then compared them with the vinegar of same pH. However, In Iraq most vinegar types in markets are produced from palm date, the most available fruit in Iraq, and Al-Badawi date vinegar was chosen in this study.

2.4. Date palm fibers (DPF)
Date palm fibers (DPF) were collected from the date palm trunks. DPF were cut into small pieces, washed with distilled water to remove dirt and dried at 80°C to remove moisture content. After drying process, DPF were ground and sieved to different particle size using Vibratory Sieve Shaker. However, the scanning electron studies (SEM) show that DPF have many chemical and physical properties that make it as a good bio sorbent (Mohamed & El-Halwany 2013)**.**

2.5. Reactor Setup
The electro-kinetic remediation involves the applying of a low level D.C. current or a low voltage gradient a cross electrodes, which are inserted in the contaminated soil. The dominant and most important electron transfer reactions that occur at the electrodes during the process are the electrolysis of water (Acar & Alshawabkeh 1993). Figure (1) shows the schematic diagram of the electro-kinetic reactor setup used in this study. The system consists of an electro-kinetic cell, two electrode compartments, a power supply and a multi-meter. The glass electro-kinetic cell has an inner dimension of (45 cm x 8 cm x 12 cm). The actual length of the soil specimen of this cell is 20 cm. DPF were used as a barrier in the electro-kinetic cell between the soil and the cathode compartment with a thickness of 5 cm. Each electrode compartment consisted of a valve to control the flow in the cell, a slotted graphite electrode and filter paper. Perforated plastic plates were used to separate the DPF barrier from the soil at one end and from the cathode electrode from the other end. The plates have a dimension of 8 cm x 12 cm having holes of 6 mm in diameter with a space of 1 cm from the hole center to the center of another hole. A D.C. 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.

2.6. Experimental methods

The strata of contaminated soil were placed in the transparent glass electro kinetic cell and then compacted uniformly using a hand compactor. The soil was left for 24 hours in order to settle and reach the equilibrium state. After placing the soil in the cell, the compartments at the ends of cell were filled with purging solution. All tests were done under a constant voltage gradient (of 1.5 VDC/cm) to avoid heat generation. Various tests were carried out to examine both of the effect of using various electrode purging solutions and the effectiveness of using vinegar as a purging solution. Table (2) illustrates a summary of the experiments conditions. In the first experiment (EX-1), tap water at pH of 4 was used in both the anode and cathode compartments at 30 V, soil with lead concentration of 1000 mg/kg and moisture content of 30%. In the second experiment (EX-2), tap water at pH of 6 was used in both the anode and cathode compartments and other conditions are preserved as (EX-1). In the third experiment (EX-3) tap water at pH of 8 was used in the electro-kinetic cell but other conditions were also kept as in (EX-1). All experiments were executed to study the effectiveness of increasing pH on the removal efficiency. In (EX-4), diluted date vinegar of pH 4 was used as purging solution instead of tap water. Vinegar was used for the buffering of existing hydroxide ions and maintaining the pH at 4. Vinegar was also used to boost the propagation of hydrogen ions throughout the soil bed which may increase the reactivity of these factors. To maintain the pH in tap water at 4, 6, and 8 in all experiments, nitric acid (HNO_3) was added at to the cathode compartment, whereas sodium hydroxide (NaOH) was added to anode compartment. In case of the loss of purging solution due to evaporation, this loss has been compensated the addition of purging solution to the anode and cathode compartments. In the end of each experiment, the soil section and (DPF) were taken out from the cell. Soil section was divided to five parts and every part was weighed and preserved in a glass container. From every section of the soil, 5 g of dry soil was taken and mixed with 12.5 ml of distilled water. The mixture was shaken completely by hand for many minutes and the solids were then permitted to settle for 1 hour, pH and EC of the soil were measured.

2.7. Chemical Analysis

Lead contaminant in different soil sections was extracted by performing acid digestion in accordance with (Haswell 1991). In this procedure, the soil samples were crushed and approximately 1g of a representative sample from each section was weighed accurately in a 250 ml beaker 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 a hot sandy bath until the brown vapor disappeared and the sample arrived to the dry state. The last step takes about (45-60) minutes. The sample was left to cool in the beaker, then 5 ml of concentrated hydrochloric acid (HCl) was added and then heated in a hot sandy bath for about (5-10) minutes. The beaker was cooled and 5 ml of concentrated hydrochloric acid was added and 50 ml of hot distilled water was also used to wash the sides of the beaker from the remains of dissolved sample. The mixture was heated again to reach the boiling points for (2-3) minutes. Then the sample was filtered with No.42 filter paper in a 100 ml volumetric flask. The precipitate was washed with distilled water and was added to the previous washing water to be filtered and completed the volume to 100 ml (Haswell 1991). Finally, the concentration of lead was determined by the Atomic Absorption Spectrophotometer (model Shimadzu AAS-7000).

3. Results and Discussion

3.1. Effect of pH

Figures (2), (3) and (4) show the total lead concentration, pH and the EC variation in each section of the treated soil; by using tap water at pH 4, 6, and 8, respectively. The initial concentration of lead throughout the soil was 1000 mg/kg and the final concentration of lead was reduced; varying from 240-345 mg/kg near the anode to 340-435 mg/kg near the cathode. Increasing in lead concentrations were observed near the cathode and a maximum lead desorption and mobilization from the soil was at pH value of about 4. Hence, the best removal efficiency was 76% at pH 4. Figure (2) indicates that the transport of lead ions occurred from anode to the cathode and the amount of lead ions transported increases with the decreasing of pH in solution, because when soil pH decreases the soil cation exchange capacity (CEC) decreases and hence the tendency for metal ions to become adsorbed on to the soil particles also decreases **(**Mirsal 2008**)**. Under acidic conditions, the edge hydroxyl groups in clay mineral may take up H cations to produce the positively charged hydroxyl aluminum with a charge of +2, while the removal of H cations from these groups under alkaline conditions produces a negatively charge species with a charge of -2 (White 1997)**.** In soil, an ion exchange reaction between the hydrogen ion and the adsorbed metallic ion surfaces on the clay particles may also occur. In addition, the hydroxide ion produced in the cathode may be neutralized by the hydrogen ion migration which is produced in the anode. However, the cathode region may show a high pH by the surplus of low mobility hydroxide ions, which react with the lead ion and may precipitate it in soil (Acar & Alshawabkeh 1993).

Figure (3) and (4) explain the pH and EC variations along the treated soil for same tests. The generated hydrogen and hydroxyl ions are transported through specimen in opposite directions by electro-migration, diffusion and advection. The advance of base front is slower than the advance of the acid front because of the electro-osmotic flow and also because the H^+ ions have higher ionic mobility than OH^- ions (Acar & Alshawabkeh 1993).

In figure (5), it could be noticed that at the beginning of the experiments there was a slight increase in current with time. The pH of purging solutions also affects the current with changes in the physiochemical properties; such as mineral dissolution chemical precipitation/dissolution etc. In low pH of influent solution, current reaches its maximum value due to higher solubility of minerals and their migration (Hamed & Bhadra 1997).

3.2. Vinegar as an Enhancing Conditioner

Figures (6), (7) and (8) give the variation between the vinegar and tap water, which were used as purging solutions at pH of 4. These figures show the lead concentration, EC, and pH along the soil specimen after the completion of the electro-kinetic treatment. As can be seen from these figures, the migration of lead occurred toward the anode in case of vinegar (EX-4), which has an opposite direction to the migration direction observed in tap water (EX-1). This means that vinegar-lead complexes might become negatively charged and began to migrate back toward the anode (Hossieni *et al.* 2011). As a result of this conflict, lead was accumulated in the soil sections near the anode. Figure (6) indicates that the best removal efficiency of lead when the vinegar is used as a purging solution (EX-4); hence, it reached to 79.5%, compared with only 76% in tap water at pH 4. This performance may because the vinegar has worked as a strong chelating agent. Other conditions may have been thermodynamically favorable for the vinegar to make complex compounds with lead which may improve the lead removal efficiency (Shukla *et al.* 2003; Hossieni *et al.* 2011).

In figures (7) and (8), it is noticed that the pH is decreasing slightly along the soil specimen from the anode to the cathode, and the pH in the vinegar test (EX-4) was approximately below 5.7 along the soil specimen. Therefore, the vinegar test had a pH profile which is approximately similar to those previously described in (EX-1) of tap water with pH 4. It seems that the electrolysis reaction at the anode and the subsequent electro-migration and electro-osmotic flow of H^+ ions resulted in the migration of an acidic front across the soil specimen (Reddy and Chinthamreddy 2003). These results are in agreement with the finding reached by the same author (Mutter *et al.,* 2014), who found that 92% of lead can be successfully removed from a calcareous sandy soil (having 89% sand) by the use of an organic chelating reagent (0.2M EDTA, pH 4) as a purging solution.

3.3. Effect of Palm Fiber

According to the present experimental work, date palm fibers (DPF) have successfully prevented the reverse electro-osmotic flow, which has a negative effect on the direction and magnitude of lead migration during electro-kinetic process. (DPF) were effective in adsorbing lead metal from the aqueous solution. Due to the high adsorption capacity of (DPF), small amount of lead ions were adsorbed by (DPF); because the competition of the salts ions already existing in the soil samples (table 1) with lead ions (Shukla *et al.* 2003). However, the amount of lead ions adsorbed by (DPF) was in the range of 45 to 90 mg/kg in tap water treatment (EX-1 to EX-3) to 98 mg/ kg in the vinegar treatment (EX-4).

3.4. Removal Efficiency of Lead

Figure (9) shows the results of lead removal efficiencies for all the experiments. The removal efficiencies were calculated based on the initial and residual contaminant masses in the soil. The removal efficiency of lead (R %) was calculated by the following equation:

$$R \% = \frac{Initial\ conc. - Residual\ conc.}{Initial\ conc.} 100$$

Where, R% is the Removal Efficiency.

The best lead removal efficiency obtained was 79.5% when the vinegar of pH 4 was used as a purging solution (EX-4), compared with other removal efficiencies (76%, 70% and 65.5%) in tap water of different pH (4, 6 and 8 respectively). This because date vinegar is a liquid containing about 4% acetic acid, 0.2% ethanol and 6% soluble sugar (Matloop & Hamza 2013), which are all organic compounds and behave as chelating agents and can desorb lead cations from soil colloids and improve lead removal from soil (Shukla *et al.* 2003; Hossieni *et al.* 2011; Mutter *et al.* 2014). As a reminder and due to this fact, both acetone and ammonium acetate and also ethanol have been used since the fifties of last century and are still being used by most soil laboratories in extracting cations and in the determination of soil cation exchange capacity and other chemical properties (USDA 1954).

4. Conclusions

The salient conclusion of this work is that the removal efficiency of lead increases with the decreasing pH of purging solutions; because in high pH values, the tendency of metal ions to become adsorbed on to the soil particles also increases. The lead removal efficiency at pH 4 was greater when the vinegar was used as a purging solution than tap water of same pH (79.5% and 76%, respectively); because vinegar contains acetic acid, ethanol, sugar and other organic compounds and hence may behave as a strong organic chelating agent. In addition, vinegar is readily available, environmentally benign and does not interact or has any negative impact on soils. Vinegar, and as in most organic compounds, can also reduce pH in calcareous soils (the type which is used in this study) and improve soil conditions for better microbial activities, nutrients availability and also soil aggregates stability and structure. Date palm fibers were found to be an effective eco-friendly bio sorbent material in preventing the electro-osmosis mechanism in sandy soils; especially when the accumulative electro-osmotic effluent becomes high in such process. However, electro kinetic process by using both available date palm products appears to be as a suitable solution for the remediation of heavy metals contaminated soils in Iraq.

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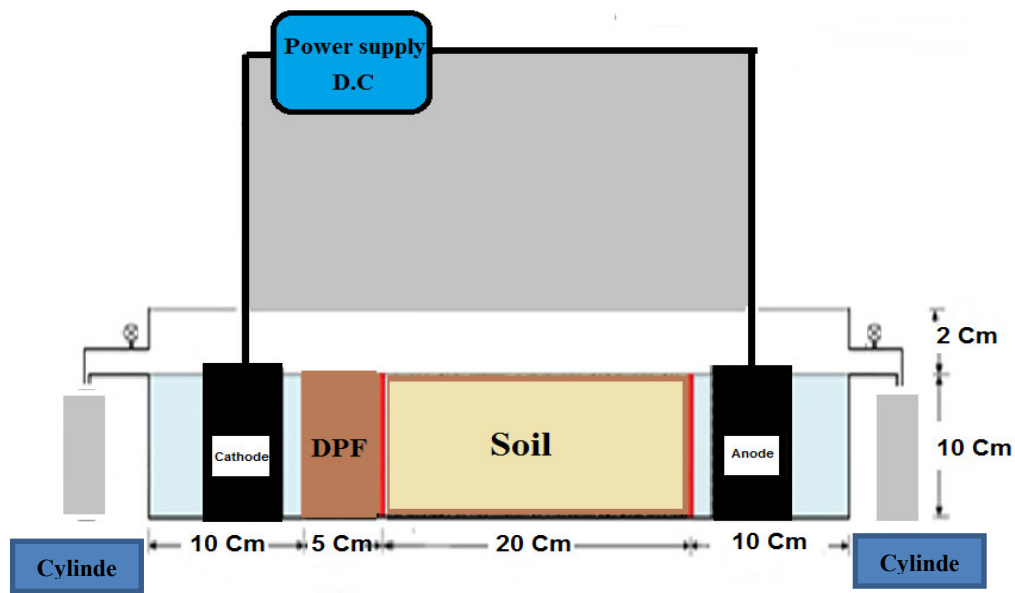
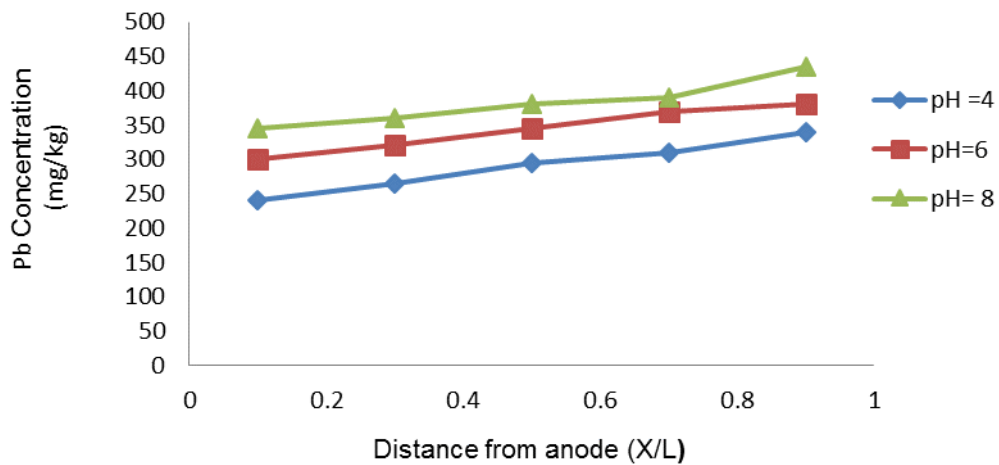Figure1. Schematic diagram of the electro-kinetic reactor

Figure 2. Pb concentration (mg/kg) versus distance from anode at different pH of purging solutions
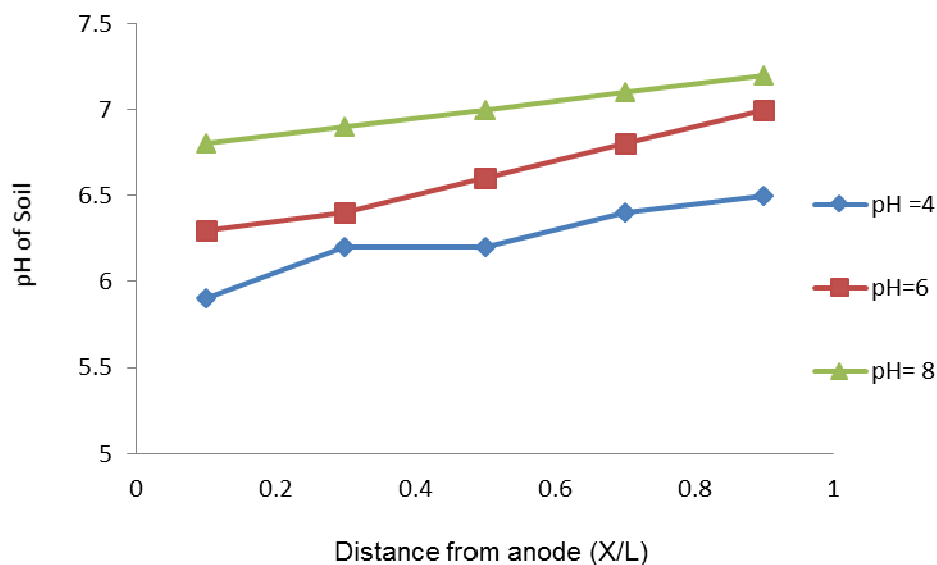
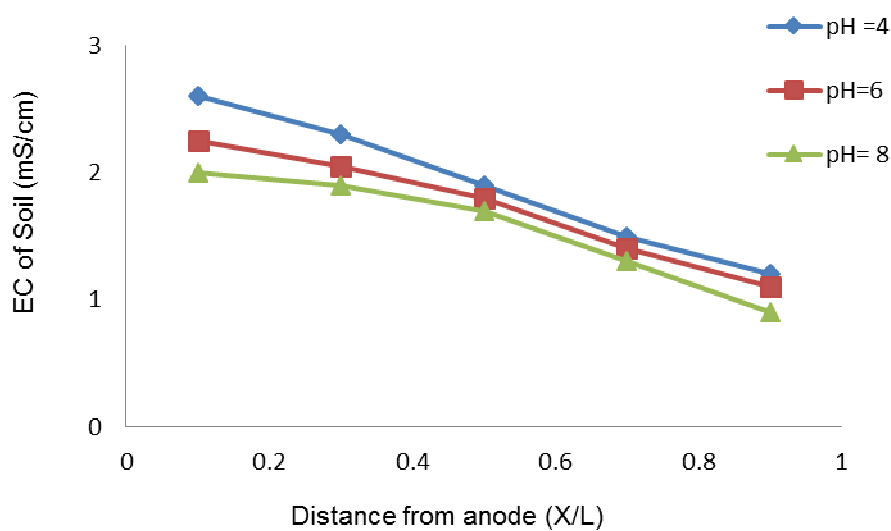Figure3. pH of the treated soil versus distance from anode at different pH of purging solutions

Figure 4. EC of the treated soil (mS/cm) versus distance from anode at different pH of purging solutions
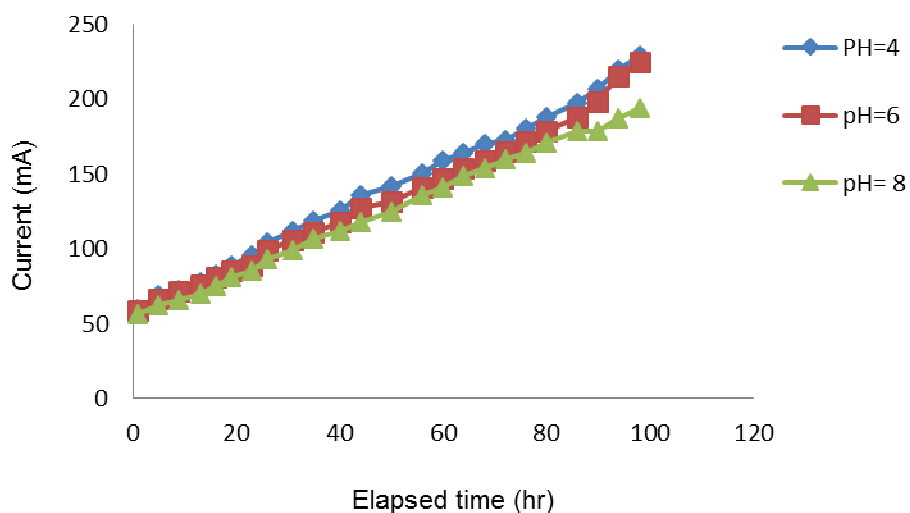
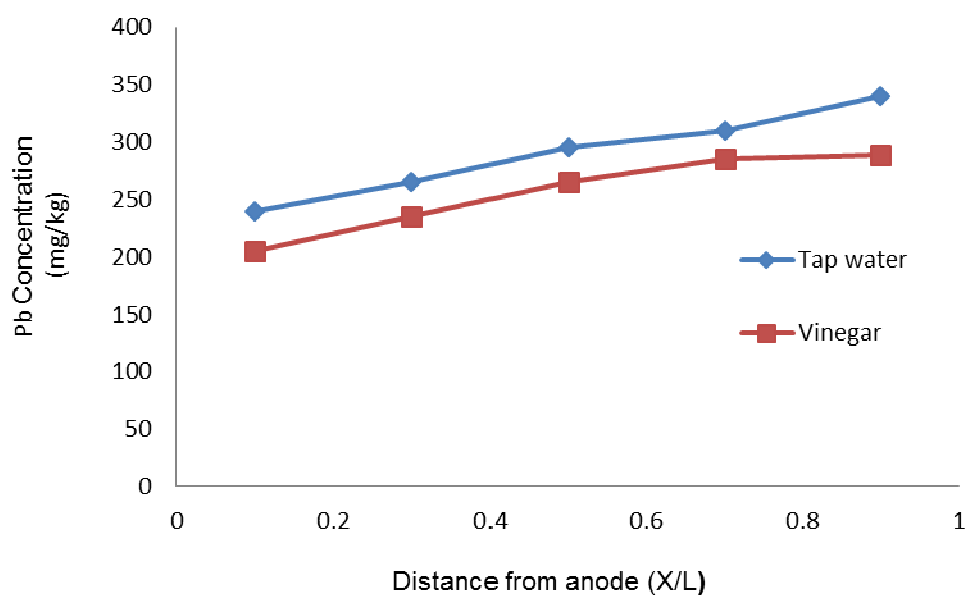Figure 5. The Current(mA) respect to time (hr) at different pH of tap water

Figure 6. Pb concentration (mg/kg) versus distance from anode at different purging solutions
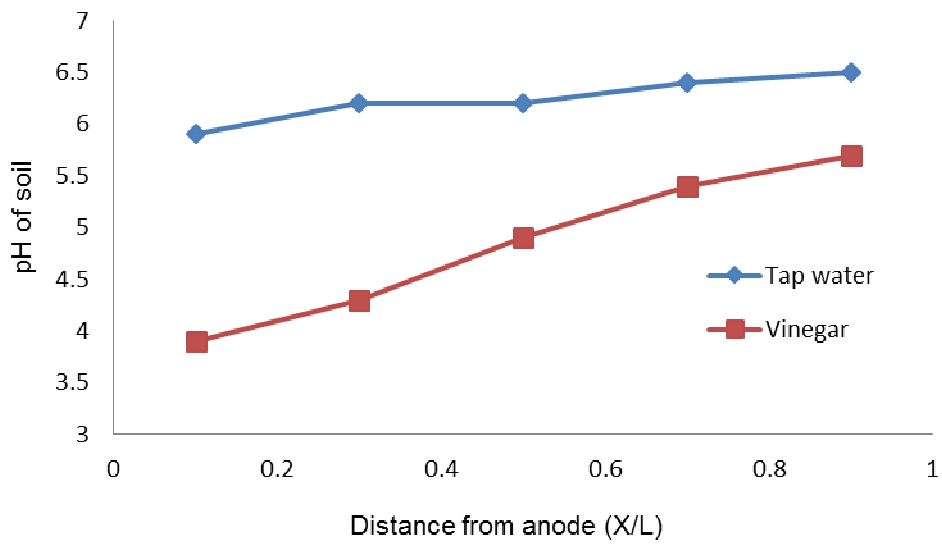
Figure 7. The pH of soil versus distance from anode at two types of purging solutions
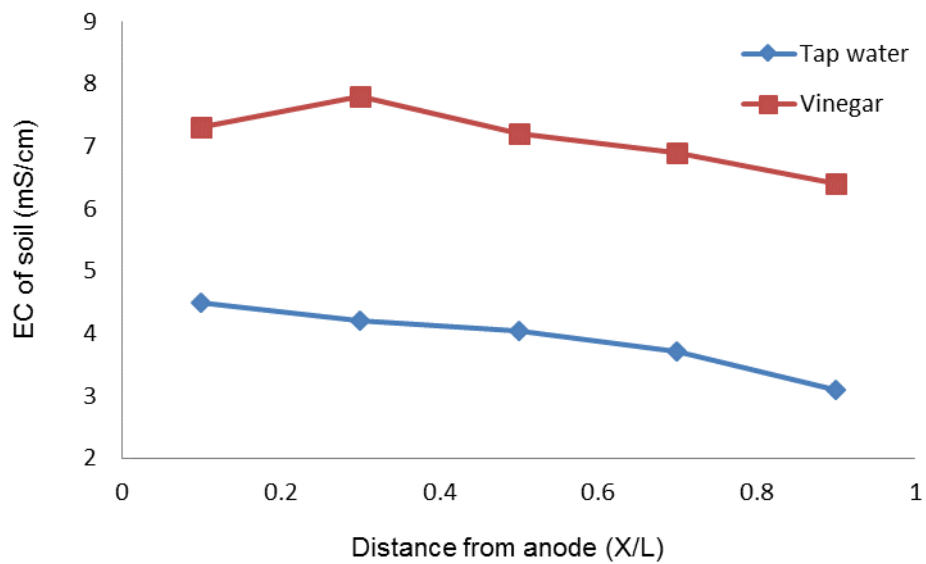

Figure 8. EC of treated soil (mS/cm) versus distance from anode at two types of purging solutions

Figure 9. Removal efficiency of lead

Table1. Composition and properties of the soil

Property	Value
Particle size distribution Sand (%) Silt (%) Clay (%) Soil classification (USDA)	 70 19 11 Sandy soil
Atterberg limits (ASTM D 2487) Liquid limit (%) Plastic limit (%) Plasticity index (%)	 28 8 20
Specific Gravity Porosity (%)	2.6 27.8
Cation Exchange Capacity (meq/100g)	12.3
Initial pH	7.7
CaCO3 (%)	6.0
Electrical Conductivity EC (µS/cm)	510
Organic Content (%)	0.7

Table 2. Experiment Conditions and Purposes.

Exp. NO.	duration of Process (days)	Initial lead Conc. (mg/kg)	PH of Purging solution	Type of Purging Solution	Experiment Purpose
EX-1	5	1000	4	Tap water	Baseline Exp.
EX-2	5	1000	6	Tap water	Effect of PH
EX-3	5	1000	8	Tap water	Effect of PH
EX-4	5	1000	4	Vinegar	Vinegar Effect