

Assessing effect of electrode configuration on the efficiency of electrokinetic remediation by sequential extraction analysis

D. Turer^{a,*}, A. Genc^b

^a Department of Geological Engineering, Hacettepe University, Beytepe Campus, 06532 Ankara, Turkey

^b Department of Environmental Engineering, Zonguldak Karaelmas University, 67100 Zonguldak, Turkey

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Abstract

The electroremediation experiments were conducted on artificially polluted soils by introducing a single metallic contaminant (Pb, Zn and Cu) and multiple metallic contaminants (Pb + Zn + Cu). Based on sequential extraction results, it was observed that the removal efficiencies of lead, zinc and copper vary depending on types of contamination. When the soil was contaminated only by lead, the removal efficiency was found to be 48%. However, the removal efficiency of lead decreased to 32% when the soil was contaminated by the combination of lead, zinc and copper. Similar results were observed for zinc and copper. The corresponding removal efficiency values for zinc and copper were 92% and 37%, and 34% and 31%, respectively.

Effects of electrode geometry on the removal efficiency of metals were investigated by constructing a multiple anode arrangement. In this arrangement, the electrokinetic unit consists of three cylinders, which lie one inside the other, and the soil was placed in the middle cylinder. The central cylinder was the cathode well and the outer cylinder was the anode well, where eight identical anode electrodes were placed in octagonal with respect to the cathode electrode. By using this electrode arrangement in removal of metals from the soil contaminated with the combination of three metals (Pb + Zn + Cu), the removal efficiencies of lead, zinc and copper were found to be 29%, 18% and 18%, respectively. As it can be seen, these numerical values are much lower than the values that were obtained when the traditional two-plate electrode arrangement used in the electroremediation experiments (32%, 37% and 31%).

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1. Introduction

Electroremediation is a developing technology that is intended to separate and extract heavy metals, radionuclides and organic contaminants from saturated or unsaturated soils. This technology involves passage through soil of direct current between appropriately distributed electrodes. The applied current transports dissolved charged ions due to electromigration towards the oppositely charged electrode. Concurrently, electro-osmosis moves the pore water in response to electric field towards to the cathode because

of the negative surface charge of the soil. Several laboratory, pilot scale, or in situ studies have widely demonstrated the efficiency and the feasibility of the electrokinetic remediation technique for the removal of heavy metals from soils [1–5]. A comprehensive review of the literature on electroremediation of soils was presented by Page and Page [6].

During the electroremediation of soils, the electrolysis reactions that occur at the electrodes can produce large changes in the pH of the pore fluid. These reactions generally generate hydrogen and hydroxide ions at the anode and the cathode, respectively. Thus, pH is acidic near the anode and alkaline near the cathode. It is observed from the experimental studies that metals usually accumulate at the pH-shift in the soil and this accumulation is often attributed to precipitation of

* Corresponding author. Fax: +90 312 299 2034.

E-mail addresses: dturer@hacettepe.edu.tr (D. Turer), aytengenc@yahoo.com (A. Genc).

metal hydroxide [1,3]. Metal ions in soils can exist in different chemical forms depending on environmental conditions. They can exist as solid precipitates, dissolved solutes in the soil pore fluid, adsorbed/sorbed complexes on the particle surface and bonded species on organic matters in the soil. The distribution of metal ions among various forms is commonly referred to as metal speciation in the solid phase of soil. According to the sequential extraction technique, it is possible to fractionate the metals, which are present at different forms (exchangeable, sorbed, carbonate bound, organically bound and residual fractions) in soils, by using appropriate chemical reagents and extraction conditions [7]. Numerous studies have been carried out to investigate the speciation of heavy metals in naturally and artificially contaminated soils [8–13]. These studies have revealed that pH, soil structure, types of pollutants and contamination levels affect the distribution of heavy metals in the different fractions of soils. Among these factors pH has been regarded as the most important variable, which regulates the mobility of ions, i.e., as pH decreases the mobility of metal ions increases, and vice versa.

Reddy et al. [14] analyzed transport mechanisms of heavy metals (Cr, Ni and Cd) from artificially contaminated soils in the presence of electric field by using the sequential extraction method. They reported that higher rates of metal ions migration occurred when the metals existed in exchangeable fraction. A similar observation was also reported by Kim and Kim [15] who used a tailing soil in the electroremediation experiments. They reported that the metal ions (Cd, Cu, Pb and Zn) that were present in the exchangeable fraction of the soil were more sensitive to the electric field than the metals that were in more strongly bound fractions, i.e., organic and residual fractions. Suer et al. [16], on the other hand, concluded that metal ions were removed from all soil fractions during electroremediation and it is even possible to mobilize the metals in the residual fraction with the treatment of electric field.

In this work, the electroremediation experiments were carried on artificially contaminated soil samples. The removal efficiencies of lead, zinc and copper in different soil fractions are investigated by using the sequential extraction method. The effect of single contaminant versus multiple contaminants in the soil on the removal efficiency has been analyzed. In addition, a circular electrode arrangement has been tested in the electroremediation experiments and the comparison of removal efficiency values for this arrangement and the plate electrodes are presented.

2. Properties of soil used in electroremediation experiments

The silty, clayey soil samples were collected from an area, which is away from possible rural pollution (Zonguldak–Koroglu, Turkey). Particle size distribution of the soil determined by sieving for the particles bigger than 75 μm (the ones left on sieve #200), and the size distribution

of the particles smaller than 75 μm were found using hydrometer. The results of the analysis showed that 55% of the soil samples used in electrokinetic experiments was smaller than silt size. In order to determine bulk soil mineralogy, the samples were grinded and XRD was applied to the samples without any further treatment. The result of the XRD showed that the soil have 48% clay minerals, 30% quartz and 21% feldspar. For determining clay mineralogy, 2–3 g of grinded sample was stirred in 200 ml water in order to put the clay minerals in suspension. Forty-five minutes later, the clay minerals at the surface of the water were collected using a pipette and placed on lamellas and left to dry. The lamellas as air-dried, as glycolated and after heating at 500 °C were analyzed by XRD. The results of XRD analysis showed that 55% of the clay minerals in the soil are vermiculite, 32% of it, illite and 13% of it, kaolinite.

3. The preparation of artificially contaminated soil samples

The soil was sieved and the fraction that is smaller than 4 mm was used in the experiments. Heavy metal ions were introduced into the soil as $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ salt solutions. For example, in the preparation of the contaminated soils with lead, 1 kg of soil was added to 1 l of 1000 ppm Pb^{2+} solution. The soil mixture was then mixed for an hour and allowed to settle down for more than 2 days. After draining the excessive water, the soil was used in the electroremediation experiment. Five grams was taken from the prepared soils for the determination of the initial concentration of lead. The same procedure was repeated in the preparation of soil samples that were contaminated with zinc and with copper. In the case of multiple metallic contaminants, i.e., the soil was contaminated with lead, zinc and copper, 3 kg of soil sample was added to 3 l of 5000 ppm Pb^{2+} , Zn^{2+} and Cu^{2+} solution. The mixture was stirred for 4 h and allowed for settle down for 6 days.

4. Electroremediation experiments

Two different setups (a rectangular and a circular) have been used (Figs. 1 and 2) in the electroremediation experiments. These setups consist of a dc power supply (500 V and 5 A), an electrokinetic unit, electrodes, connection cables and two water tanks (10 l). Both of the electrokinetic setups are made up of plexiglass and have three compartments: anode, soil and cathode.

The rectangular electrokinetic unit has 10 cm \times 10 cm \times 20 cm dimensions. The sidewalls of the anode and the cathode compartments have holes in order to provide electro-osmotic water flow due to application of electric field. In addition, the surfaces of these sidewalls were covered with filter paper to prevent soil passage into the electrode compartments. Both anode and cathode compartments were open at the top to

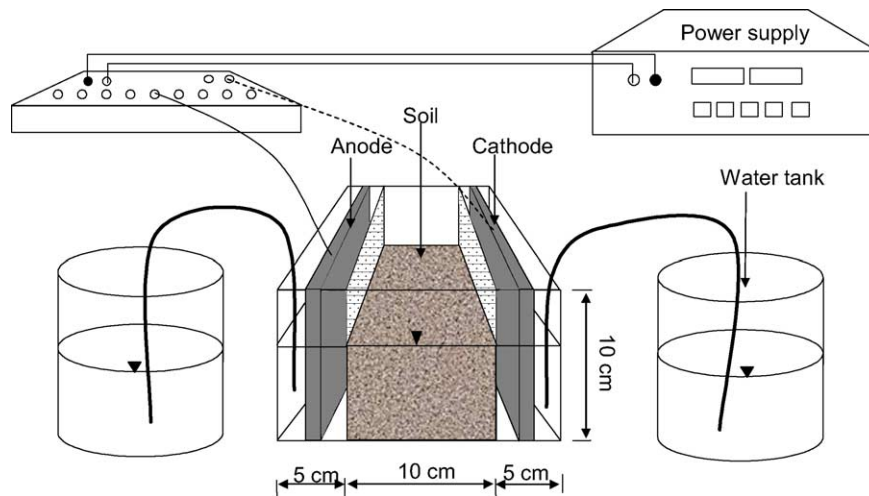


Fig. 1. Rectangular electrokinetic experimental setup.

vent the electrolysis gases. In this unit, two identical graphite plates, which have dimensions of $8\text{ cm} \times 12\text{ cm} \times 1.5\text{ cm}$, were used for the anode and the cathode electrodes (Fig. 1).

The second electrokinetic unit consists of three cylinders, which lie one inside the other with 5 cm, 25 cm and 35 cm diameters. The central cylinder was selected as the cathode compartment to minimize the extent of the basic environment by the cathode and the outer cylinder was selected as the anode compartment to maximize the spread of the acidic environment generated by the anodes. The sidewalls that connect the anode and the cathode to the soil compartment have holes with 3 mm diameter. Nine identical graphite rods with $12\text{ cm} \times 1.5\text{ cm} \times 1.5\text{ cm}$ dimensions were used as electrodes and eight of them were the anodes. In this unit, the anode electrodes were placed in octagonal with respect to the cathode electrode (Fig. 2).

The electroremediation experiments had been started with packing the contaminated soil samples into the electrokinetic unit and filling the anode and the cathode compartments with tap water (100% saturation). In all experiments, the water lev-

els in the anode and the cathode compartments were kept at a constant value, which was 8 cm in height. In order to investigate sensitivity of metals at different fractions (exchangeable, sorbed, bound to carbonates, bound to organics and residual) of soils to electric field, a high potential difference was applied to electrodes. It is thought that, in this way, it is possible to identify the fractions that are not responding to the electric field. Therefore, a constant potential difference of 250 V was applied to the electrodes during the experiments and maintained for about 30 h. The current passed through the electrodes and pH in the electrode compartments were recorded every hour. In all experiments, the maximum current was observed at the beginning, which was around 120 mA. The current decreased to the values around 50 mA towards to the end. At the beginning of each experiment, pH was equal to 6 in the both compartments. Depending on the electrode reactions, the pH in the anode compartment dropped to as low as 2 and the pH in the cathode compartment increased to 11.

Upon the completion of each electroremediation experiment, the soil was removed and analyzed to determine the extent of metal removal from the soil as a function of distance

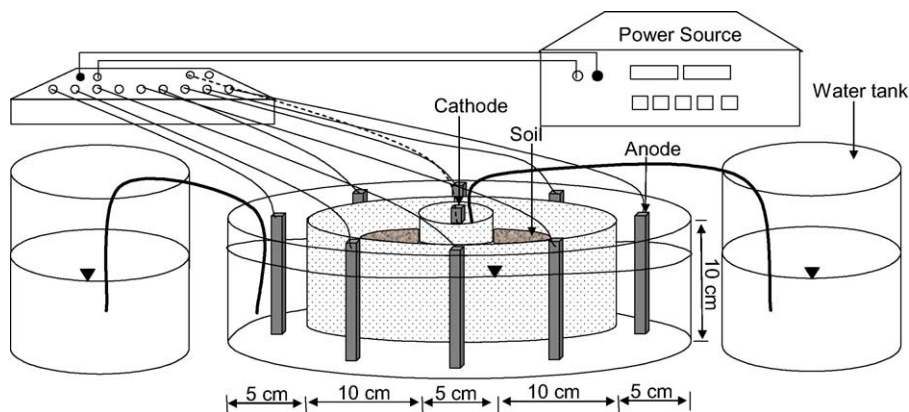


Fig. 2. Circular electrokinetic experimental setup.

from electrodes. The soil was divided into four sections as 0–2.5 cm, 2.5–5 cm, 5–7.5 cm and 7.5–10 cm depending on distance from the anode. From each section, about 5 g were taken and dried for sequential extraction analysis.

5. Application of sequential extraction procedure

Sequential extractions were performed on contaminated soils before and after electrokinetic experiments to provide an understanding of the distributions of the contaminants in the soils. In the sequential extraction analysis, the procedure that was suggested by Sposito [17] was followed. According to the procedure, 2 g of dried soil sample was placed in a centrifuge tube and the following steps were applied:

- 25 ml of 0.5 M KNO_3 was added and shaken for 16 h (exchangeable fraction);
- 25 ml of distilled H_2O was added and shaken for 2 h (sorbed fraction);
- 25 ml of 0.5 M NaOH was added and shaken for 16–21 h (organically bound fraction);
- 25 ml of 0.05 M Na_2EDTA was added and shaken for 6 h (carbonate bound fraction);
- 25 ml of 4 M HNO_3 was added and heated (70–80 °C oven) for 16–21 h (residual fraction).

After each step, the sample was centrifuged and filtered through a Whatman #42 and saved for atomic absorption spectrometric analysis. Sposito [17] described adsorption mechanisms of metals on soils by using a surface complexation model. According to this model, some metal ions are surrounded by waters of hydration and are not directly bounded to the soil surface. These ions accumulate at the interface of the charged surface in response to electrostatic forces (exchangeable fraction). On the other hand, some metal ions are directly bound to the soil surface, no water of hydration are involved. This form is distinguished from the exchangeable state by having ionic and/or covalent character to the binding between the metal and the surface. This adsorbed mechanism is often termed specific adsorption. In this study, the specifically adsorbed fraction will be shown in shortly as the sorbed fraction.

6. Results and discussion

The removal efficiencies of Pb, Zn and Cu were investigated depending on types of soil contamination and electrode geometry by performing electroremediation experiments. The removal efficiency of a metal is expressed by the ratio of the amount remaining in the soil after the application of electric field to that initially. The total amount of metals in a soil section is obtained by adding the amounts of metals in all fractions.

6.1. Removal efficiency and types of soil contamination

After applying 250 V difference between the electrodes for a duration of 30 h, the distributions of Pb, Zn and Cu in different fractions (exchangeable, sorbed, bound to carbonates, bound to organics and residual) of the soils that were contaminated with a single metal are presented in Fig. 3(1a–c), respectively. In the same graph, when no voltage was applied to the electrodes, the distributions of Pb, Zn and Cu in different fractions of the soils are represented with the columns assigned as Pb_0 , Zn_0 and Cu_0 . The analysis of Pb_0 , Zn_0 and Cu_0 columns show that the amount of the metals incorporated to sorbed fraction is very small for all of the metals. It can be observed that Pb was mostly in the exchangeable and bound to carbonates fractions (Fig. 3(1a)). Zn, besides the exchangeable and bound to carbonate fractions it can also be seen mostly in the residual fraction of the soil (Fig. 3(1b)). Cu was predominantly existed in the exchangeable fraction and the rest was equally distributed among bound to carbonates, bound to organics and residual fractions (Fig. 3(1c)). When the soil is contaminated with the combination of three metals, it can be observed that there are only small changes in the distribution pattern of Pb and Cu among different fractions of the soil (Pb_0 and Cu_0 columns in Fig. 3(2a and c)), however, the difference in Zn distribution calls for attention (Zn_0 column in Fig. 3(2b)). In the presence of three metals, the highest amount of Zn was observed in the exchangeable fraction, it is almost 85% of the total amount. This value was only 16% when the soil was contaminated with only Zn. In addition, the amount Zn in the carbonate fraction changed dramatically. In the presence of three metals, 4% of the total amount of Zn was observed in the bound to carbonate fraction whereas it was 32% for the single contamination. From these results, it can be said that the presence of Pb and Cu interfere the sorption mechanism of Zn and that three metals compete each other to fulfill different fractions of soil.

Fig. 3(1a–c and 2a–c) illustrate that after the application of the electric field, the distribution of the metals in different fractions didn't change very much but the amounts of the metals that were retained in each fraction changed significantly. From the analysis of these graphs it can be concluded that, as the distance from the anode increases total amounts of the metals retained in the soil also increase. As it can be seen in Fig. 3(1c), when the distance from the anode was 8.75 cm the amount of copper retained in the soil section was even more than the initial Cu_0 . This can be explained as the migration of metal ions towards to the cathode with the help of electrical field. If the duration of the electrical field were longer than 30 h, it is expected that the amount of copper retained in the soil toward the cathode would also decrease.

Depending on the results obtained from Fig. 3(1a–c), the removal efficiencies of Pb, Zn and Cu (single metallic contamination) with respect to the distance from the anode were presented in Fig. 4(a). As it can be seen, more than 80% of the initial Pb, Zn and Cu were removed from the soil with the application of electric field in areas close

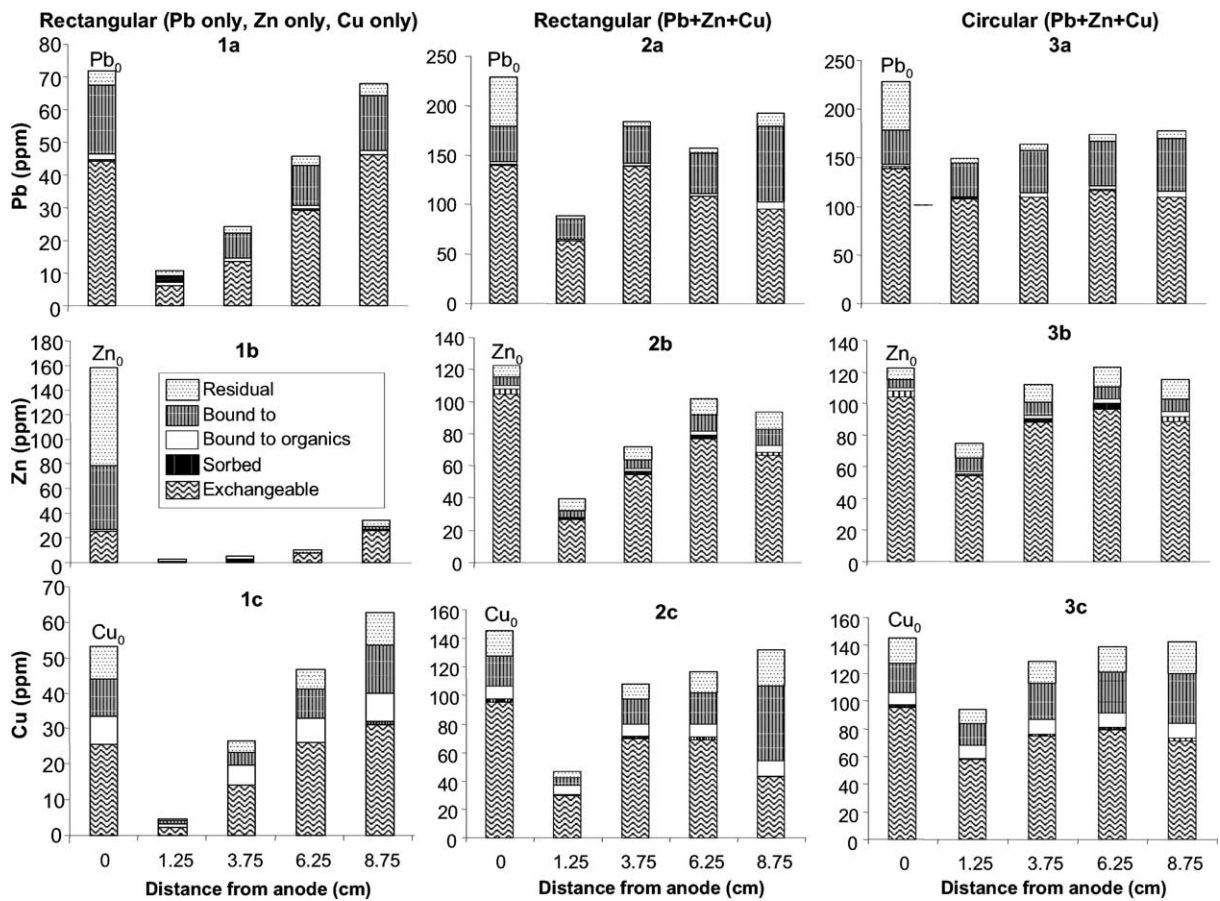


Fig. 3. Distribution of metals before and after the application of electric field.

to the anode (0–2.5 cm). However, as the distance from the anode increases, the removal efficiency for each metal changes dramatically. Among three metals, the most effective removal efficiency for all distance from the anode was achieved for zinc. In areas close to the cathode the precipitation of Cu was appeared, and therefore, the overall removal efficiency of Cu was lower than Zn even though copper and zinc have numerically very close mobility values [18]. The mobility of lead was the lowest among the studied metals, and therefore, lower removal efficiency was expected. When the soil in the electrokinetic unit was

taken as a whole the overall removal efficiencies for lead, zinc and copper were evaluated as 48%, 92% and 34%, respectively.

In the same way, the removal efficiency values for each metal were evaluated according to the results shown in Fig. 3(2a–c) when the soil was contaminated with the combination of three metals. These results are depicted in Fig. 4(b) and the corresponding overall removal efficiencies of lead, zinc and copper were evaluated as 32%, 37% and 31%, respectively. Even the increase in Zn amount in exchangeable fraction, on which electrokinetic remediation was expected

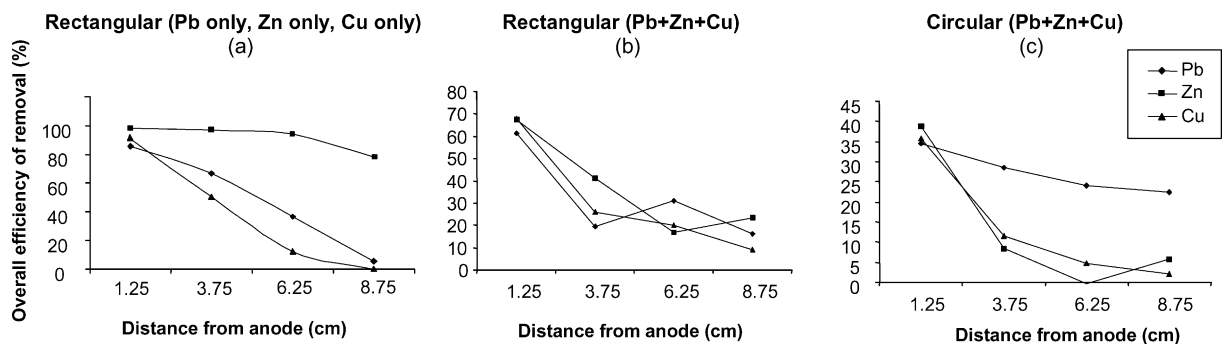


Fig. 4. Overall removal efficiencies for each metal.

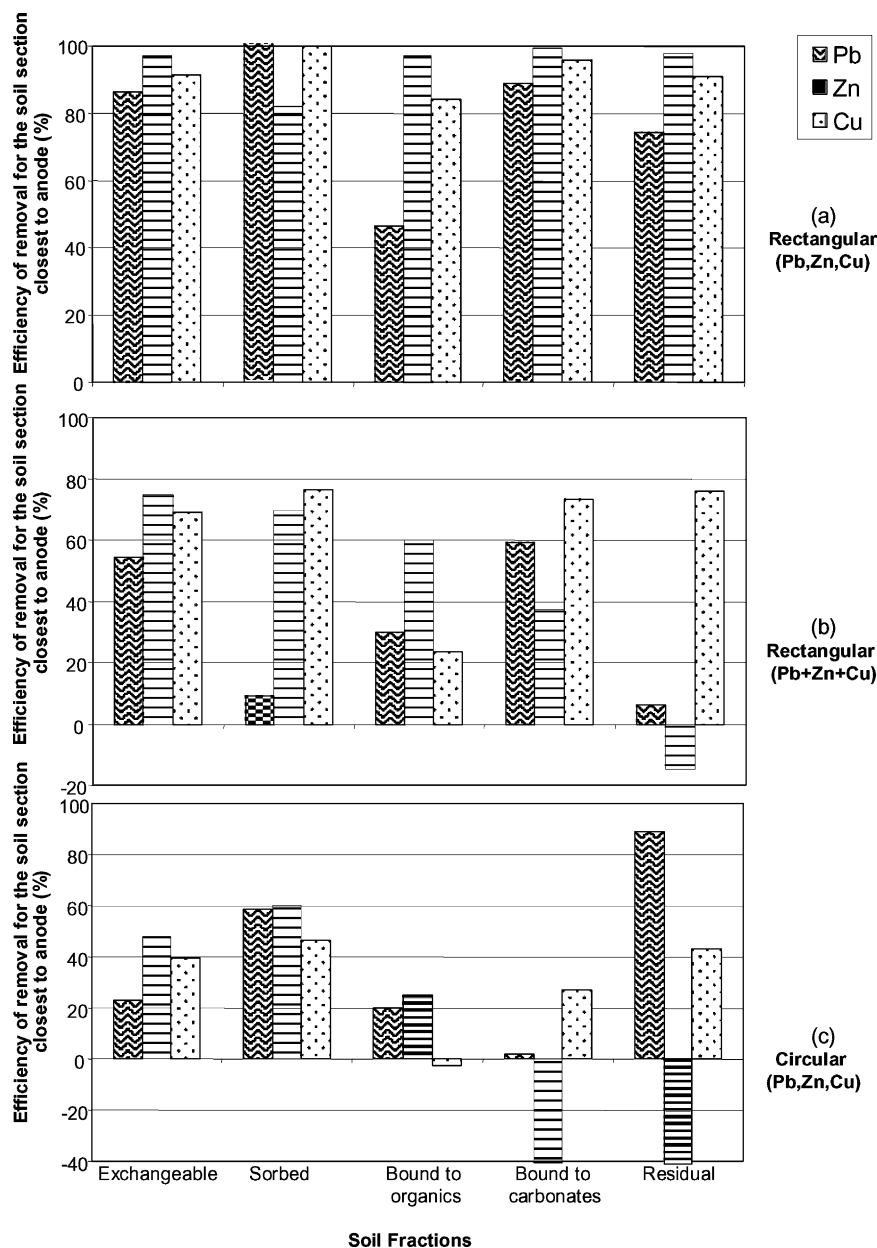


Fig. 5. Removal efficiencies of metals for each fraction in soil sections closest to the anode.

to be the greatest, didn't change the general trend of decrease in removal efficiency.

Because of applying electric field for a short period of time (30 h) during the experiments it is thought that the soil section closest to anode is the most representative section to check the efficiency of electrokinetic remediation among different fractions of soil. Therefore, the experimental results for this section are redrawn in Fig. 5. It is found out that remediation was working effectively for all of the soil fractions for the soils contaminated with a single metal (Fig. 5(a)). For Zn and Cu, it worked especially well for all soil fractions, for Pb however, the organically bound fraction showed comparatively low efficiency. For the case of the soils polluted with multiple contaminants (Pb + Zn + Cu), the removal efficiency

of Pb drops to very low levels for the sorbed and residual fractions (Fig. 5(b)). For Zn, besides the drops in efficiencies for all fractions, the residual fraction does not respond electric field at whole. Cu in all of the fractions responds better than other metals to the removal process except for the bound to organic fraction. In Fig. 5(b and c) some negative values of removal efficiencies are obtained for the bound to carbonates and residual fractions of soil. For example, -20% is shown for the residual fraction of Zn contaminated soil in Fig. 5(b). This means that the amount of Zn ions in the residual fraction increases 20%. This increase shows that there is a redistribution of metal ions in different fractions of soil as well as the migration of metal ions towards the cathode. According to the results of Fig. 5, among three metals an appreciable

amount of increase in the bound to carbonates and residual fractions of soil was observed only for Zn, which can be explained as a result of hydroxide precipitates or formation of new complexes.

6.2. Removal efficiency and electrode geometry

The circular electrokinetic unit (Fig. 3(3a–c)) showed the same kind of trends with the previous experiments, but it did not improve the removal efficiency, it rather decreased (Fig. 4(c)). The general trend of decrease in the removal efficiency as distance from the anode increases is also seen in this electrokinetic unit. The removal efficiency drops below 40% for all soil sections, and for all heavy metals. The highest removal efficiency comes from the section closest to anode, as expected. When the fractions of soil at the section closest to anode were analyzed, it can be seen that the removal efficiency for all metals at all fractions is lower than 60% except for Pb in the residual fraction, which is 89% (Fig. 5(c)). The overall removal efficiencies for lead, zinc and copper were evaluated as 48%, 92% and 34%, respectively, when the soil in the electrokinetic unit was taken as a whole.

In both electrokinetic units, the distance between anode and cathode electrodes was 14 cm, and 250 V potential difference was applied to the electrodes. For the rectangular electrokinetic unit, 118 mA was recorded as the current passed through electrodes at the start of the experiment and this value dropped to 53 mA at the end of the experiment. For the case of circular electrokinetic unit, the corresponding current values were 105 mA and 48 mA. According to these numerical values, it can be concluded that there is not very much difference in the current pass through the electrodes for both electrokinetic units. However, the current density, i.e., current per unit area, in the rectangular electrokinetic unit, is independent of location since the cross-sectional area is always constant. In the circular electrokinetic unit, on the other hand, the cross-sectional area is a function of radius, and therefore, the current density is changing in radial direction. Moreover, in the rectangular electrokinetic unit, two graphite plates were used as the electrodes and the generated electrode field can be assumed uniform. In the case of the circular electrokinetic unit, however, the graphite rods were used as the electrodes and these may develop spots of inactive electric field between electrodes of the same polarity. Therefore, the generated electric field is expected to be non-uniform and to change in radial direction. It is thought that the main cause for the decrease in the removal efficiency is the development of inactive electric field areas in the soil.

Another reason for the decrease in the removal efficiency using circular electrokinetic unit could be because of the pH. During the experiments the pH in the anode and the cathode compartments were recorded every hour. The pH in the anode compartment at the rectangular electrokinetic unit was dropped from 6 to 2 after 3 h of electric field application and it stayed there until the end. However, this value was never observed in the anode compartment of the circular electroki-

netic unit. The pH was 6 at the start and no change had been observed for 5 h and then it decreased to 5 and stayed there until the end. Therefore, the variations of pH in the compartments of both electrokinetic units were quite different from each other, which is a result of dimensional difference of the two electrokinetic units. According to the electrode dimensions, which were given in the experimental section, the surface area of the electrodes that were contact with water can be calculated. In the rectangular electrokinetic unit, the surface areas of the anode and cathode electrodes were the same and it was equal to 152 cm². In the circular electrokinetic unit, however, the total surface area of the anode (384 cm²) was eight times that of the cathode (48 cm²). In addition, the amount of water in the anode and cathode compartments for the two electrokinetic units was different. For the case of rectangular electrokinetic unit the volume of water in both compartments was 400 cm³. On the other hand, for the circular electrokinetic units, it was 3770 cm³ and 157 cm³ in the anode and in the cathode compartments, respectively. These differences show clearly that the response time in the change of pH in the anode compartment of the circular electrokinetic unit will be slower than that of the rectangular one. It is known that as pH decreases the mobility of metal ions increases [12]. Therefore, it is expected that if the pH in the anode compartment of the circular electrokinetic unit were controlled by the addition of some chemical agents such as acetic acid then the removal efficiency values obtained at the rectangular electrokinetic unit could be attained for the circular electrokinetic unit. In that case the use of circular electrode configuration would have the advantage of decontaminate more soil than the rectangular electrode configuration by using the same amount of electricity.

7. Conclusions

The variation of metal concentrations in different fractions of the soil after the application of the electric field was investigated by using sequential extraction analysis. It was observed that by the application of electric field not only metal ions migrate toward the cathode but they also redistribute in different fractions of soil.

The experimental results show that the removal efficiencies of lead, zinc and copper from the soil vary depending on the type of contamination. When the soil was contaminated by each of the metal separately, the removal efficiencies of Pb, Zn and Cu in the soil section closest to anode were evaluated as 48%, 92% and 34%, respectively. On the other hand, if the soil was contaminated with Pb, Zn and Cu together, lower removal efficiencies for the same section were obtained for each metal (32%, 37% and 31%).

Effects of electrode geometry on the removal efficiency were studied by constructing a circular electrode arrangement in the electroremediation experiments. The corresponding overall removal efficiencies of lead, zinc and copper from the soil by using the circular electrode arrangement were 29%,

18% and 18%, respectively. These values are lower than the ones obtained when the plate electrodes arrangement were used (32%, 37% and 31%). The presence of inactive electric field areas in the soil could be the main cause for the decrease in the removal efficiency values obtained for the circular electrode arrangement.

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