Investigation of a combined continuous flow system for the removal of Pb and Cd from heavily contaminated soil

Aydeniz D. Delil [a, *], Nurcan Köleli [b]

[a] Department of Environmental Engineering, Faculty of Engineering, Mersin University, Çiftlikköy Campus, Mersin, Turkey
[b] Department of Civil Engineering, Faculty of Engineering and Architecture, Arel University, Istanbul, Turkey

HIGHLIGHTS

- The remediation performance of the continuous flow combined treatment system was evaluated for heavily contaminated soils.
- The Cd concentration transferred from the soil column to the solution is greater than the Pb.
- There is a linear relationship between the potential that is applied in electrochemical studies and the removal efficiency.
- Cd ion, compared to Pb ion, is less reduced in the electrochemical cell.

ARTICLE INFO

ABSTRACT

In this study, a combined continuous flow system was designed to remove Pb and Cd from heavily contaminated mine tailing soils. 0.05 M Na_2EDTA was used as a chelating agent to remove Pb and Cd from polluted soil, taken from the vicinity of Kayseri ÇİNKUR, Turkey. The initial concentrations of Pb and Cd were 16381 ± 643 and 34347 ± 1310 mg kg^{-1}, respectively. The electrochemical treatment process was applied to the waste washing solution, which emerged after being extracted from soil column and contained Pb and Cd. Metal ions were transformed to the metallic form by applying the electrochemical treatment process to the washing solution, containing Pb^{2+} and Cd^{2+}.

At the end of the leaching experiment, which was done with a 50 g soil sample in the soil column system, Pb and Cd removal efficiencies from soil were 59.72% and 58.01%, respectively. Then, the soil column solution was subjected to electrolysis through a 48 h period at 10 V. The electrochemical removal efficiency of ions, which moved from column to solution, was 84.46% for Pb and 59.21% for Cd.

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1. Introduction

Soil pollution caused by heavy metals has begun to become an important environmental problem in the world in terms of ground water quality, human health and food safety (Shen et al., 2018).

Heavy metals penetrate into the soil through anthropogenic activities such as mining, fossil fuel combustion, industrial discharge and the use of pesticides and fertilizers in agriculture (Liu et al., 2018; Sarwar et al., 2017). Because of the contamination of soil due to these activities, the need for appropriate remediation methods to eliminate toxic and hazardous substances like heavy metals from soil increased (Al-Hamdan and Reddy, 2008). Soil remediation, aims to control, decrease or remove pollutants that pose a risk to the ecosystem and human health (Hou and Al-Tabbaa, 2014).

In recent years, in-situ and ex-situ new generation combined soil remediation methods have been improved for contaminated areas with complex multi pollutants, such as hydrocarbons and heavy metals (Park and Son, 2017; USEPA, 2007). In general, in-situ remediation technologies are known to cost less, but require more time to achieve the desired reclamation. On the other hand, ex-situ technologies provide higher removal efficiency in a much shorter period of time (USEPA, 2007).

The soil washing process is one of the widely used ex-situ remediation methods due to being effective, having an environment-friendly remediation and a high efficiency to separate toxic metals and organic contaminants from soils (Dermont et al., 2008; Hou et al., 2014a; Son et al., 2011). The main mechanism of

soil washing is the removal of contaminants from the soil using various chemical agents like EDTA (Park and Son, 2017). The re-use of soil after soil washing can support green and sustainable reclamation which attracts attention (Hou et al., 2015).

However, the soil washing method only allows the contaminant to be passed from one medium to another (from soil to solution). In this case, the contaminant has only changed phase, and its complete elimination cannot be provided. For this reason, an alternative and effective treatment method that can be integrated into this method is needed to treat the complex solution containing EDTA and toxic ions that will emerge after the soil washing method.

In this study, the electrochemical method, which is one of the most promising treatment techniques in recent years, has been integrated into the soil washing method. The electrochemical treatment process is based on the movement of pollutants, charged in a medium between two electrodes with the effect of the low voltage direct current (DC) that is applied. This movement is towards the anode for negatively charged pollutants and towards the cathode for positively charged pollutants. The movement of pollutants is largely accomplished through electro-migration, electro-osmosis and electrophoresis transport mechanisms (Acar and Alshawabkeh, 1993; Rosestolato et al., 2015). As a result of the electrolysis of water, hydrogen ions are formed in the anode, and hydroxyl ions in the cathode. The forming H^+ ions move towards the cathode. The movement of the H^+ ions towards the cathode is due to advection (electro-osmotic flow and hydraulic gradient) and diffusion (concentration difference and electrical gradient) (Ottosen et al., 2009). The basic electrode reactions are shown below. According to these reactions, due to H^+ and OH^- formation, the pH decreases in the anode and increases in the cathode.

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

$$Cathode: 4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- \qquad (2)$$
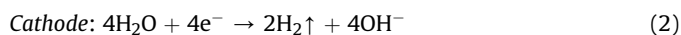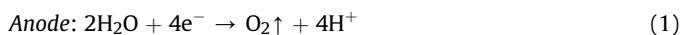
In recent years, combined treatment methods, including the electrochemical process, have been used to remove heavy metals from contaminated soils (Ait Ahmed et al., 2016; Demir et al., 2015; Demir Delil and Köleli, 2018; Son et al., 2012). In addition, within the scope of in-situ soil treatment studies, chelating agents such as EDTA, decreasing the adsorption and the surfactants, decreasing the surface tension, have been used in order to increase the efficiency of the electrochemical method (Bahemmat et al., 2016; Hahladakis et al., 2014, 2016).

In a study conducted by Pociecha and Lestan (2009), a two-stage method was used to treat a soil contaminated with Cu. In the first stage, EDTA was used for the extraction of Cu and the extracted Cu was removed using the advanced electrochemical oxidation method in the second stage. The free Cu ions in the solution were removed by electro-deposition around the cathode (Pociecha and Lestan, 2009).

In another similar study, Pociecha and Lestan applied the electrocoagulation process to remove Pb, Zn and Cd from the washing solution, which occurred after the contaminated soil was washed with EDTA. The removal efficiencies were 95% for Pb, 68% for Zn and 66% for Cd (Pociecha and Lestan, 2010).

Although the treatment studies of the complex solution, formed after the soil washing method, are partially included in literature, this is an area that still needs research. This type of study, which is especially performed in the continuous system, is important for the applicability of the combined treatment method in the field. In this study, the remediation performance of the soil sample contaminated with mining wastes in a continuous flow column system, combined with two different treatment technologies, was evaluated.

For this purpose, Pb and Cd ions in contaminated soil were taken into a solution with a continuous flow column system. After that, they were transformed into metallic form (non-toxic form) by being precipitated through the electrochemical method. This process can be considered as an environment-friendly approach because of both providing metal recovery and the complete elimination of toxic effects.

2. Material and method

2.1. Soil sampling and analysis

The soil sample used in the study was collected at a depth of 0–30 cm from a region in Kayseri, Turkey, where mining waste was stored. The coordinates of the soil sampling area were determined by GPS (38° 42′ 43″ N and 35° 15′ 55″ E). Soil samples carried to the laboratory were air-dried and passed through a 2 mm sieve. Some physical chemical soil analyses were performed according to standard methods. The total metal analysis was performed according to the EPA 3050 method and the concentrations of metals were determined by the PerkinElmer AAnalyst 700 Model Atomic Absorption Spectrophotometer (USEPA, 1995).

In addition, various mineralogical analyzes were done with the soil sample. Chemical components of soil were determined using the X-Ray Fluorescence (XRF). The X-Rays Diffractometer (XRD) analysis was also done with the related soil in order to determine the mineralogical composition of the soil. Changes in the surface of the original and remediated soil were determined by the scanning electron microscopy (SEM) at the Mersin University Advanced Technology Education, Research and Application Center.

2.2. Batch soil washing tests

Soil washing tests were carried out at room temperature with 0.05 M Na_2EDTA, and at 175 rpm for 36 h with a 20:1 liquid:soil (v/w) ratio. In this experiment, 10 g soil was used with a 200 mL washing solution. During the washing process, samples were taken from the solution at certain times (0, 15, 30, 45, 60, 120, 240, 480, 720, 960, 1200, 1440 and 2160 min) and then those samples were filtrated through a Whatman 42 filter paper. Subsequently, the solutions were acidified to become pH 2 with 1:1 HNO_3 for Pb and Cd analysis.

2.3. Column experiments

Column experiments were performed to better understand Pb and Cd mobility and the removal mechanism under dynamic flow conditions. The transport of Pb and Cd from soil to solution was investigated by column experiments in a medium, which is close to natural conditions. For this purpose, 0.05 M Na_2EDTA solution was carried upwards to the column filled with 50 g of soil at 0.3 mL min^{-1} flow rate in natural pH. The samples were collected for 48 h in 40 min interval time with the automatic sample collector, added to the outlet of the pump. In the experiment performed, the glass column length was 7.40 cm, the inner diameter of the column was 2.50 cm and the space volume was 15.7 cm^3.

2.4. Determination of reduction potential

Primarily, optimum reduction potentials were investigated for the electrodeposition of Pb and Cd in waste washing solution. In the solution, containing toxic metal ions formed after the soil was extracted with Na_2EDTA solution, the CH 600A model potentiostat was used to determine the reduction potential of Pb and Cd. For this purpose, the reduction potentials of Pb and Cd were determined

using the Pb granule working electrode in solutions obtained by washing the 20:1 liquid:soil (V:w) ratio.

The reduction potentials were determined at electrode potential of −1.0 V and −0.6 V vs. Ag/AgCl reference electrode.

2.5. Batch electrodeposition tests

Electrodeposition tests were performed in a fixed-bed glass reactor. The electrochemical experiment setup consisted of the granule Pb ($45 \, cm^2$) as the working electrode and Pt ($1 \, cm^2$) as counter electrode and a DC power supply and multimeter.

The experiments were carried out in the washing solution obtained by shaking the 25 g soil sample with 500 mL (20:1 L:S ratio) 0.05 M Na$_2$EDTA at 175 rpm for 24 h. The initial pH of the solution was measured as 8.32, and 1 mL samples were taken in regular intervals. These samples were diluted with deionized water, acidified with 1:1 HNO$_3$ to pH 2 and stored in low temperatures for the use in further analyses with AAS during the electrochemical process. The electrochemical removal efficiency (ERE) of Pb and Cd in the cell were calculated in Eq. (3), where Co is the initial metal ion concentration (mg L^{-1}) and Ce is an equilibrium metal ion concentration in treated solution (mg L^{-1}).

$$ERE \, (\%) = \frac{Co - Ce}{Co} \times 100 \qquad (3)$$

2.6. Combined continuous flow system

In this step, soil washing and electro-deposition experiments performed in discrete were combined and the removal of Pb and Cd in the continuous flow system was investigated. For this purpose, electrochemical cells were added to the system consisting of columns and pumps. In addition, an HPLC pump was placed between the electrochemical cell and the automatic sample collector to ensure that the inlet and outlet flow is equal. A 10 V of constant voltage from the power supply was applied to the solution inside the reactor.

In the combined system, experiments were carried out for about 2 d and the solutions from the column were collected at every 3rd h for 48 h with the automatic sample collector. Then the pH and EC and the metal concentrations of these solutions were determined with AAS.

3. Results and discussion

3.1. Soil properties

Some physical and chemical analysis results performed in soil are shown in Table 1. The physical and chemical properties of the soil usually limit the selection of the treatment process. In other words, a treatment technology is chosen based on soil class (particle size distribution) or soil characteristics.

The soil pH is determined as 7.87 and is slightly of alkaline characteristic. The pH of the soil is very important in the application of soil treatment technologies (Nowack et al., 2006). The resolution of inorganic pollutants is influenced by pH and high pH decreases the mobility of inorganic pollutants in the soil (Alloway, 1995; Abdu and Mohammed, 2016). The amount of organic matter in the soil is determined as 4.75% (>4%) and the soil is rich in organic matter. The lime content of the soil was found to be 11% and it is classified as calcareous. The texture class of the soil was found to be sandy and loamy (SL). The texture class, pH and organic matter content of the soil showed that it is suitable for applying soil washing because

Table 1
Some physical and chemical properties of the soil.

Soil properties	Values	Reference
pH	7.87	Richards (1954)
Electrical conductivity (mS cm^{-1})	3.2	Kacar (1995)
Organic matter (%)	4.75	Kacar (1995)
K$_2$O (mg kg^{-1})	490	Olsen et al. (1982)
Lime (%)	11	Allison and Moodie (1965)
CEC (meq 100 g^{-1})	1.75	Kacar (1995)
Spesific surface area (m^2 g^{-1})	7.05	BET
Sand (%)	48.96	Bouyoucus (1962)
Silt (%)	46.78	Bouyoucus (1962)
Clay (%)	4.32	Bouyoucus (1962)
Texture	Silty loam (SL)	Bouyoucus (1962)
Total Pb (mg kg^{-1})	16381 ± 643	USEPA (1995)
Total Cd (mg kg^{-1})	34347 ± 1310	USEPA (1995)

metal mobility is higher in these types of soils.

Pb and Cd concentrations of soil samples were found to be 16381 ± 643 mg kg^{-1}, 34347 ± 1310 mg kg^{-1} respectively. These values were considerably higher than the amount found in natural soil (Kabata-Pendias and Pendias, 2001; Nowack et al., 2006) because the wastes, which generated as a result of Pb mining and metallurgy activities, were stored formerly in that study area.

XRD analysis was carried out to determine certain mineral compositions of the soil sample. According to the results of the analysis, four types of crystal structures including ankerite, albite, celsian and coesite were found in the soil. At the end of the XRF analysis in soil, Cd and PbO percentages were found to be 4.52 and 2.78 respectively. High Pb and Cd rates indicate that the sample is a waste of mining rather than soil. The low clay content of the soil in the texture analysis is another indicator of this fact.

10000× magnified SEM images after the column experiment with the original of the soil sample are shown in Fig. 1a and b, respectively. When the image in Fig. 2a is examined, it can be seen that the soil sample is initially heterogeneous and has a very porous structure. In addition, dried plant particles were found in the soil sample as a sign of the presence of organic matter. Some differences were observed between the original soil sample and the SEM images of the soil sample washed with EDTA. After the soil's contact with Na$_2$EDTA, the surface properties changed when compared to its initial state, deformation occurred on the surface, and the layer over the soil was lost.

3.2. Batch soil washing

The effect of the concentration of 0.05 M Na$_2$EDTA and the washing time at 20:1 (liquid:soil) ratio on Pb and Cd removal is shown in Fig. 2, respectively.

As shown in Fig. 2. Pb ions, that are transferred into the solution, reached the equilibrium in 2 h and after this point there was not much change in Pb concentration transferred into the solution. At the end of 2 h, the removal efficiency of Pb was calculated as 52%, and at the end of the experiment (36. h) this value was 58%. The tests, carried out with 0.05 M Na$_2$EDTA washing solution, showed that 2 h of contact time is sufficient for metal ions in the solution to reach the equilibrium. In the study carried out by Zhang et al. (2010) it was stated that the 2 h application of soil-solution contact time was sufficient for the metal ions in the solution to reach the equilibrium (Zhang et al., 2010).

However, the results for washing the Cd in the soil show that the Cd concentration in the solution do not reach the equilibrium within 2 h. This result is thought to be due to the fact that the Cd adsorption in soil occurs with the non-linear sorption mechanism (Kantar et al., 2009). The Cd in the solution reached the equilibrium
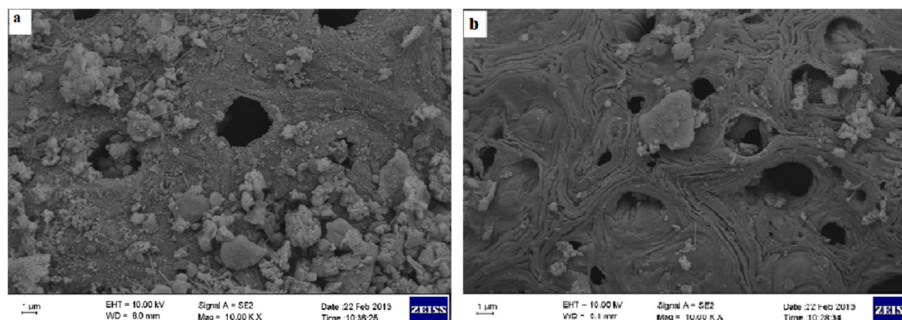
Fig. 1. a) 10000× magnified SEM image of the original soil before being washed b) 10000× magnified SEM image of the soil after column experiment.
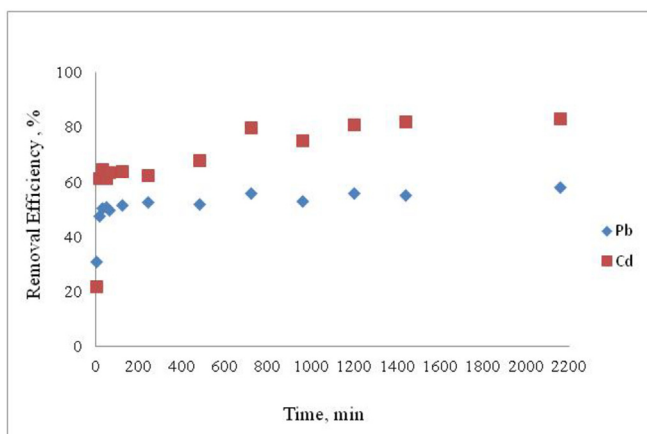

Fig. 2. Effect of washing time on Pb and Cd removal (20:1 liquid:soil ratio).

at the end of 20 h and the removal efficiency of Cd was determined to be 81%. When Fig. 3 is examined, the desorption of the Cd increased depending on time. In the first 2 h, the Cd removal was 64%, and at the end of the experiment the Cd removal was found to be 83%. In this study, since it was aimed to remove Pb and Cd at the same time, the Cd became the determinant of the contact time and subsequent experiments were carried out for 36 h.

3.3. Removal and transport of Pb and Cd from soil column

Column experiments were carried out to better understand the movement of metal ions and the transport with EDTA under dynamic flow conditions in a medium close to natural aquifer. Fig. 3
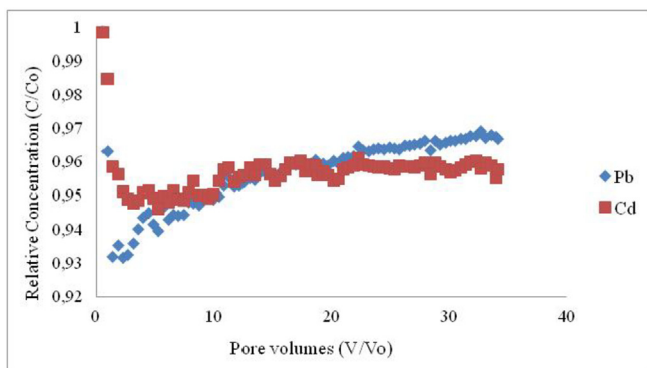

Fig. 3. The breakthrough curve (BTC) of Pb and Cd in soil from column experiments (Soil mass 50 g, 0.05 M Na$_2$EDTA, 0.3 mL min^{-1}, 2 d).

shows the effect of the flow rate on the removal of Pb with Cd in natural pH conditions in the soil column.

In Fig. 3, C: is the remaining metal concentration (mg kg^{-1}) in the soil column; and Co: is the initial metal concentration (mg kg^{-1}) in the soil.

As seen from the breakthrough curve, the C/Co values of the samples, which are removed from the column in the first 40 min, are 1; and the Pb and Cd concentrations carried to the solution are very low. Metal ions in the soil started to pass to the solution after the 80$^{\text{th}}$ min. The concentration of Pb dissolved in solution is 1118 mg L^{-1}, while the concentration of Cd is 1664 mg L^{-1}, at 2.17 pore volume. The concentration of Cd transferred from the soil column to the solution is greater than the Pb. This is because of the fact that the Cd concentration in the soil is initially higher, and the Cd is a element with higher mobile characteristics than the Pb. In literature was reported that the increasing order of desorption can be established as Zn > Cd > Pb (Abdu and Mohammed, 2016; Al-Turki and Helal, 2004; Mouni et al., 2017).

As can be seen from these results, the relative concentrations of Pb and Cd (C/Co) were between 0.93 and 0.96 for both metal ions during the experiment. After the column experiment, the concentration of the Cd in the solution was found to be greater than that of Pb.

In the approximate pore volume of 2, the Pb concentration was 1118 mg L^{-1}, whereas the Cd concentration was 1843 mg L^{-1} in the pore volume of 5.21. However, when the initial Cd concentration of the soil, and Cd is considered to be a more mobile element, it can be said that the transported concentration of Cd to the solution is low compared to Pb. This result can be explained by the fact that the formation constant of the Pb-EDTA ($K_{\text{Pb-EDTA}} = 1.1 \times 10^{18}$) complex formed by EDTA and Pb is higher than that of the Cd-EDTA complex ($K_{\text{Cd-EDTA}} = 2.9 \times 10^{16}$). (Heil et al., 1999; Zhang et al., 2010).

3.4. Determination of electrode potential for reducing metal ions

The voltammograms belonging to Pb and Cd, which are determined with potentiostat, are shown in Fig. 4.

When the voltammogram is examined, it is seen that it is possible to reduce the Cd to −0.6 V and more negative potentials. It can be said that Pb can be reduced to more negative potentials starting with the potential of −1.0 V. According to these results, the potential range of the electrode, to which both metals can be reduced, is between −0.6 V and −1.6 V.

All electrodeposition tests were carried out at cell potentials at 6 V, 8 V and 10 V which correspond to the electrode potential. Metal ions (Pb and Cd) were reduced from the ionic form to the metallic form by the following reactions.
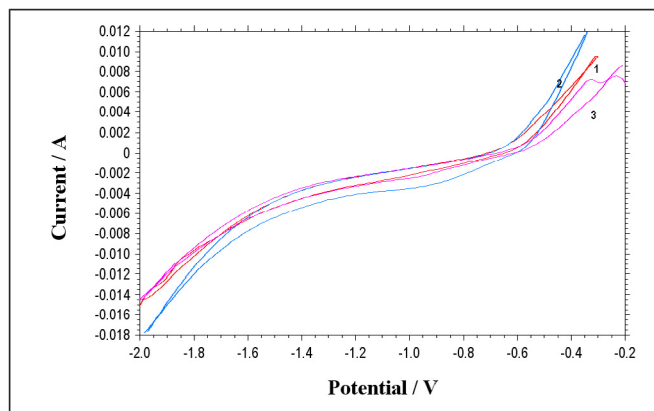
Fig. 4. The cyclic voltammogram (vs Ag/AgCl, scan rate is 20 mV s^{-1}) taken in solution containing 0.05 M Na$_2$EDTA, Cd and Pb ions on working electrode. *1: 0.05 M solution of Na$_2$EDTA. 2: 100 mg L^{-1} Pb involving solution of 0.05 M Na$_2$EDTA. 3: 100 mg L^{-1} Cd involving solution of 0.05 M Na$_2$EDTA.

$$Pb(II) + 2e \leftrightarrow Pb \qquad\qquad (4)$$

$$Cd (II) + 2e \leftrightarrow Cd \qquad\qquad (5)$$

3.5. Batch electrodeposition experiments

The results obtained at the end of the electrodeposition experiments are shown in Table 2. Pb and Cd removal were performed at three different cell potentials (6 V, 8 V and 10 V) in natural pH. After the electrolysis experiments, the Pb removal efficiencies were 88.9%, 99.2% and 99.7% for 6 V, 8 V and 10 V respectively. Cd removal efficiency values were 18.4%, 54.6% and 80.3% respectively. When the results are evaluated, it is seen that there is a linear relationship between the potential that is applied in electrochemical treatment studies and the removal efficiency. The amount of dissolved metal ions increases by increasing the potential or the current density passing through the system, and as a result more metal hydroxide complexes emerge (Faraday's Law). These complexes adsorb strongly the contaminants or precipitate with them and as a result, higher efficiency is obtained (Song et al., 2017).

The maximum removal efficiency for both Pb and Cd ions from the soil solution by electrolysis was achieved at 10 V. Therefore, the optimum potential is determined as 10 V.

3.6. Removal of Pb and Cd with combined continuous flow system

At this step, two different soil treatment technologies were combined to investigate the removal of Pb and Cd from both the soil and the waste washing solution. For this purpose, from the soil

Table 2
pH, EC and removal efficiency values of the solution after electrochemical treatment.

	6 V		8 V		10 V	
	E.B	E.A	E.B	E.A	E.B	E.A
pH	8.32	8.22	8,32	7.95	8.32	7.07
EC	12.07	7.75	12,07	7.86	12.07	7,33
Removal of Pb, %	–	88.9	–	99.2	–	99.7
Removal of Cd, %	–	18.4	–	54.6	–	80.3

E.B: Before Electrodeposition.
E.A: After Electrodeposition.

column 0,05 M Na$_2$EDTA solution was passed at natural pH until the electrochemical cell was filled (contact time:15 h). The initial Pb and Cd concentrations of the solution collected in the cell were determined as 1486 and 1785 mg L^{-1}, respectively. Subsequently, the electrolysis process was started in the electrochemical cell.

The time-dependent change in the metal ion concentration in the solution in the electrochemical cell is shown in Fig. 5. As can be seen, the metal concentrations decreased in the cell due to the electrochemical effect, although there was a continuous flow from the soil column to the cell.

The soil sample used in the study was taken near the Pb mining area, thus, the metal concentration was very high in the soil. The structure of contaminated soil is complex and the behaviour of pollutants in the soil depends on many factors, such as adsorption capacity, clay and organic matter content, which make it difficult to remove the metals from the soil. On the other hand, the soil structure is a dynamic system with an extremely high buffering power. In other words, a cationic pollutant holds very tightly to the soil due to the electrical double layer and the sorption forces (Abdu and Mohammed, 2016; Arenas-Lago et al., 2015). Therefore, the metal ions are carried in low amounts from the heavily contaminated soil.

Besides, since EDTA is not a specific chemical agent used, it can create strong complexes with alkaline surface cations such as Al, Ca, Fe and Mn that are found in the soil structure other than Pb and Cd (Giannis and Gidarakos, 2005). Therefore, the chelating power of EDTA decreased and consequently had a negative effect on the removal efficiency in the soil.

The amounts of metal ions were transported with EDTA from the soil column to the cell for 2 d, and then the amounts of metal ions were subjected to electrolysis and were calculated cumulatively.

The amount of Cd carried from the column to the electrochemical cell increased depending on the time. The cumulative mass was 6598 mg and 14422 mg for Pb and Cd, respectively at the end of 48 h. According to the calculated cumulative mass, the total removal of Pb and Cd from the soil column by EDTA was 59.72% and 58.01% respectively. This result showed that Cd and Pb ions decreased almost at the same amount from the soil column although the initial concentrations of them were different.

The electrochemical removal efficiencies of metal ions in soil washing solution were 84.46% for Pb and 59.21% for Cd, respectively. These results show that Pb is reduced more than Cd in the combined continuous flow system. The removal of metals from the column solution by electrolysis was ordered as Pb > Cd. The reason for the Pb to be removed more effectively than the Cd during
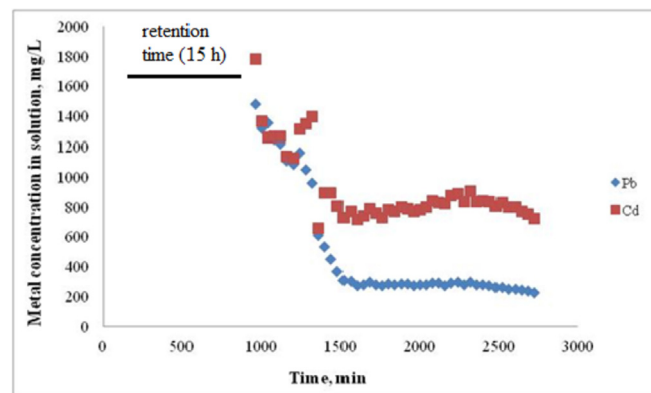
Fig. 5. Changes of Pb and Cd concentration in continuous flow combined system with 0.05 M Na$_2$EDTA (Soil mass 50 g, flow rate 0.3 mL min^{-1}, 2 d).

electrochemical treatment is that it has a high reduction potential (Pb^{2+}/Pb) (Pociecha et al., 2011).

The pH and electrical conductivity (EC) of the samples were collected after the continuous flow combined system was measured. It is observed that there is a decrease in pH of the samples taken from the cell at the beginning and then an increase depending on the time. Before the electrochemical reduction, the initial pH of the solutions leaving the column was 8.47 and then it decreased to 3.5, after the 800th min the pH of the solutions increased. At the end of the experiment, the pH of the solution reached 9.15. The alkaline pH in the solution increased the precipitation of metals. In a study conducted by Figueroa et al. (2016), the initial pH of deionized water in the electrode chambers was about 6, and due to the electrolysis of water, the pH in the anode decreased and stabilized at pH 2, and in the cathode it increased up to pH 12 (Figueroa et al., 2016).

The pH in the electrochemical cell reached the value of 9 after a period of time and this is the proof of the fact that metal ions in the solution are deposited in the cathode. At the beginning of the experiment, the pH of the solution was 3.5, which showed that the reaction in the anode was faster and more efficient than the reaction in the cathode in the initial minutes of the electrolysis. The increase in pH indicates that the reduction reaction in the cathode is more dominant than the anode reaction.

EC is another indication of the amount of mobile ions in soil and reflects indirectly the amount of ions in the solution (Chen et al., 2006). In the study, it is observed that the EC values in the electrochemical cell, unlike the pH, decrease at the initial of the electrolysis and remain constant throughout the experiment. In the column test, where the electrochemical treatment is not included, the EC of the solutions was 10 mS cm^{-1}. The EC decreased to 1.3 mS cm^{-1} in the combined treatment system, where the electrochemical method was included. This result is the evidence of electrochemical reduction.

All these results indicate that ions transported from the soil column to the electrochemical cell were subjected to electroreduction in the electrochemical cell, they were precipitated as hydroxyl (electrodeposition) and were transformed into an insoluble form. Depending on the time and pH, the dissolved ion concentration in the solution and due to it, the EC decreased.

4. Conclusions

The greatest lack of soil washing methods is that it requires excessive water consumption to prepare the washing solution, and the need for additional treatment methods of the complex solution contaminated with metal ions after soil washing. For this reason, it is necessary to use another alternative and effective treatment method that can be integrated into this method for the remediation of the waste solution containing EDTA and toxic ion. The electrochemical treatment of the waste washing solution is partly included in literature, but research is still needed. In this study, the electrochemical method, which has become popular in recent years, was consecutively used in the continuous flow system after the soil washing method. For this purpose, Pb and Cd were transferred to the solution through solid-liquid leaching from the soil. Subsequently, in accordance with the principle of zero waste, Pb and Cd ions in the solution were precipitated in a glass reactor by electrochemical reduction and were transformed into metallic form (non-toxic). In this way, an environment-friendly approach was produced where both metal recovery and toxic effects were completely eliminated.

The results showed that factors such as liquid:soil ratio, contact time, initial metal concentration and soil structure were effective on the removal efficiency. In addition, the reduction potential, pH and contact time were found to be important for the electrochemical method. As the result of the column test shows, the Cd concentration, being transferred from soil to solution, was found to be more than the Pb concentration. The electrodeposition results showed that Cd was less reduced electrochemically when compared to Pb. In this study, it was determined that an alkaline medium has a negative effect on the efficiency of the metal removal from the soil. It can increase the concentration of metal ions carried from soil to solution by applying different alternatives to minimize the negative effects of this situation. The Pb and Cd removal efficiency can be increased by increasing contact time in column tests.

This research, conducted on a laboratory scale, can be planned to provide a different and new approach to soil contamination control by designing a pilot scale facility.

Acknowledgements

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