



EFFECT OF ORGANIC MATTER ON REMOVAL OF HEAVY METALS IN SOIL WITH ELECTROCHEMICAL PROCESS

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Abstract

This research presents the effect of organic matter (humic acid) as a surfactant on the electrochemical process for removal of Pb, Cd and Zn from mine tailing soil. The soil contained high concentrations of the target metal contaminants (Pb = 13365 mg kg⁻¹, Cd = 15742 mg kg⁻¹ and Zn = 19565 mg kg⁻¹). The electrochemical tests were carried out in a specially designed electrokinetic reactor with two intermediate aqueous collection locations within the soil chamber using tap water and organic matter. Humic acid was added in soil as a surfactant in order to enhance the removal of lead, cadmium and zinc and it was applied at five percent. Humic acid was used with tap water as the pre-mixing agents of the contaminated soil. A constant DC voltage of 20 V (0.625 V/cm) was applied across the working electrodes in all the experiments for a treatment time of 48 h. The concentration accumulation of the metal species in the anode, cathode and the intermediate collection chambers were measured over time, as well as pH, conductivity and ORP. The removal efficiency was reported in percentage as the summation of the cumulative metal mass removed into all collection chambers in aqueous form, normalized to the initial mass of the metal in the soil.

Demir *et al.* [1] studied the effect of *in situ* electrochemical remediation in order to remove heavy metals from contaminated-soil by using only tap water. Their experimental results have indicated that total electrochemical removal of lead, cadmium, and zinc from soil using tap water was 35.59%, 78.09% and 55.09% respectively.

In this study, the total removal efficiency of the metal ions from soil mixed with tap water and humic acid were determined 20.07%, 68.47% and 49.61% for Pb, Cd and Zn, respectively. Comparing the results for two separate experiments, it can be concluded that the addition of humic acid results in the decline of metals mobility. When humic acid is added into soil, removal efficiencies of metals decrease about 15 percent for Pb, 10 percent for Cd and 6 percent for Zn.

Keywords: heavy metal, humic acid, electrochemical remediation, soil pollution

1. INTRODUCTION

Soils can be contaminated with heavy metals due to agricultural, industrial and mining activities. Metal contaminated soils compose an important environmental problem with adverse consequences for the ecosystem functioning. Due to these adverse impacts of heavy metals, the heavy metal-contaminated soils should be remediated. Cadmium, copper, lead, mercury, nickel, and zinc are considered the most hazardous heavy metals and are included on the EPA's list of priority [2-3]. Besides, the remediation of soils contaminated with heavy metals such as Pb, Cd and Zn has been one of the most

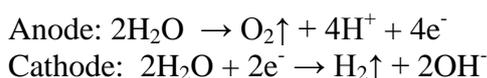
difficult tasks due to its toxicity, nondegradable and strongly sorption of ions to soils.

There is a pressing need to develop effective and economical remediation methods suitable for this class of contaminants. Over the past two decades, researchers concern relating to ecological threats caused by heavy metal contamination of soil and groundwater have led to intensive research of new and promising remediation technologies. Electrokinetic remediation is probably one of the most promising *in situ* soil decontamination methods capable of removing organic, inorganic contaminants and radionuclides, as it has high removal efficiency and time effectiveness in low permeability soils [4-5].

An alternative and effective process to lower the levels of soil pollutants *in-situ* is an electrochemical method, which is also referred to as “electrokinetic” method. Electrokinetic soil processing is also called electrokinetic remediation, electroreclamation and electrochemical decontamination [6].

Electrokinetic method is a process in which a low-voltage direct-current electric field is applied across a section of contaminated soil to move contaminants. When the working electrodes (a cathode and anode) are introduced into wet soil the charged particles and polar molecules (e.g., ions, water, micelles, colloids) are mobilized by the electrical field. Ions and water molecules that they have according to type of ions are moved toward the oppositely charged electrodes. Electromigration, electroosmosis and the electrolysis of water are the main mechanisms that enable the transport of ions. Electromigration occurs in all soils, whereas electroosmosis is only significant in clay soils (low permeability soils) [7].

Electrochemical remediation technique is highly affected by the electrode reactions, which consist typically in the electrolysis of water;



The hydrogen ions produced decrease the pH near the anode. Along with a decrease in pH, desorption of the adsorbed metals on the soil surface is increased. At the same time, an increase in the hydroxide ion concentration causes an increase in the pH near the cathode so metal ions will precipitate on the cathode [5-8].

Since the system can be adjusted to work at constant or variable pH conditions, it has been recommended and used abundantly in treatment of municipal and industrial wastewater.

In order to obtain a successful removal, it is necessary to apply the electric field for quite a long time, even in laboratory experiments. Based on these results, researchers have suggested different enhancement methods, with the aim of obtaining lower concentrations in the soil after remediation and in a shorter duration. Enhancement is

typically based on reagent addition or on a combination of different remediation methods [9]

In recent years, enhanced remediation methods which includes electrokinetic remediation as one of the steps have been studied for the *in-situ* remediation of heavy metal contaminated soils. Cationic, anionic and nonionic surfactants are used to increase the removal efficiency of heavy metals from soil in remediation techniques.

Humic substances, such as humic acid (HA) and fulvic acid (FA), come from the decomposition of plant and animal residues. Humic acids are those parts of humic substances which are not soluble in water under acidic conditions, but become soluble and extractable at higher pH values. Complexation by humic acids is of great interest in environmental studies, as the interaction of these ligands with heavy metals determines to a large extent their bioavailability, toxicity and mobility [10-11].

In this study, humic acid, as a natural surfactant, was preferred to use as enhancing agent and the effect of humic acid on the *in-situ* electrochemical remediation was investigated. It was added in soil as an organic matter in order to observe the effect of removal efficiency of lead, cadmium and zinc from soil. The aim of the present study was to examine whether enhanced the electrochemical soil remediation method is suitable for clean up of Pb-Cd-Zn contaminated soils as well as to evaluate the efficiency of electrochemical treatment in the presence of organic matter.

2. MATERIAL AND METHODS

The contaminated soil used for in this work was obtained from an toxic metals-contaminated site in a mine tailings area located in middle of Turkey. The mining activities in this area have continued for many years. In this study, in order to understand the effect of humic acid as a surfactant, remediation of soil contaminated with heavy metals and added to humic acid was carried out via *in-situ* electrochemical process in laboratory conditions. For this purpose, in order to perform the experiments belong to this study, electrochemical reactor was designed in laboratory and then it was started to tests.

2.1. Soil origin and characterization

Soil sample used in this study were collected from the 0 to 30 cm surface layer of a mine tailings area located in the province of Kayseri, Turkey which has been exposed to approximately forty years of active lead-zinc metal industries. Soil sample carried to the laboratory in plastic bag was air-dried and crushed to pass through a 2mm sieve. Standard soil analyzes were made on homogenized soil samples. The soil sample was analyzed for different physical properties using the corresponding ASTM procedures.

Soil sample was analyzed for pH in a 1:1 (m:v) ratio of soil to water solution suspension after 1 h of contact time [12], electrical conductivity was analyzed in suspension generated for pH analysis using electrical conductivity meter and ORP was determined according to method of ASTM D200-09 [13] developed for soils, particle size analysis was performed by a hydrometric method [14].

Humic acid was applied at five percent (w/w) into soil sample as to be a liquid phase with tap water and with it, tap water was used as the electrolyte solution in the electrochemical reactor. Humic acid was added to artificially spike the soil sample after that it had become slurry. The slurry mixture was then thoroughly mixed manually for 10 minutes until homogeneous. Both before and after the addition of humic acid, organic content of soil sample was determined by the ASTM D2974-87 [15] method. Concentrations of heavy metals were analysed by EPA 3050B method [2].

2.2. Experimental set-up

Figure 1 shows the apparatus of electrochemical experimentst were implemented. The set up was made of acrylic plates that measured 5 mm in diameter and 32 cm length. The electrochemical reactor consisted of two electrode compartments and electrode reservoirs, three soil sections, two interface solution sections, a DC power supply and a multimeter to measure current.

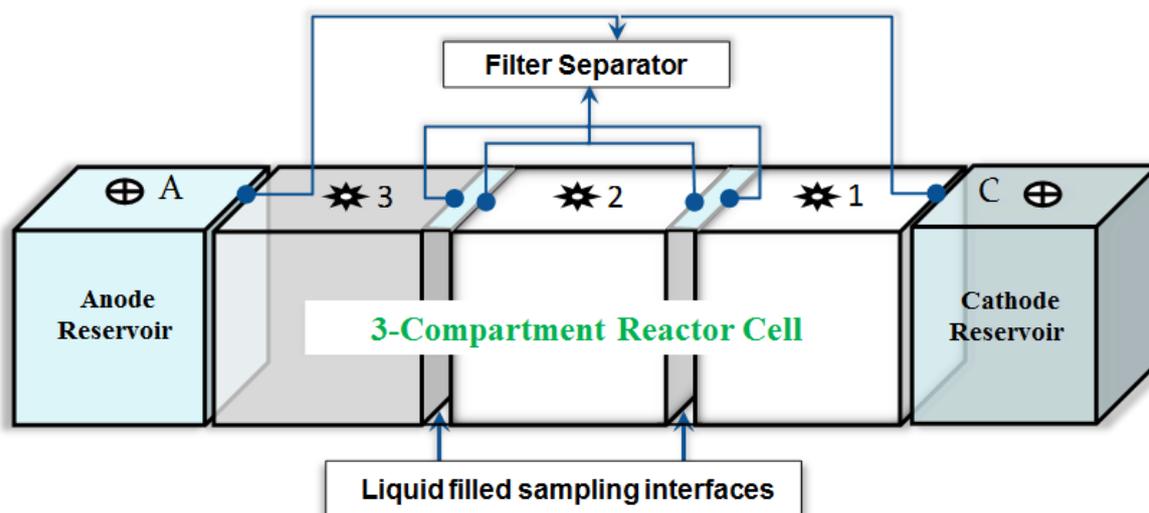


Figure 1. Schematic view of the electrokinetic experiment set

Before soil was placed in three compartments, humic acid was added in soil as a surfactant in order to determine the effect of lead, cadmium and zinc removal from soil by electrochemically. After the addition of HA, soil was placed three separate compartments as equal amounts (335 g) and liquid was filled as electrolyte solution in the reservoir and electrodes were inserted in electrode compartments.

Platinum was used as the electrode material in order to give the potential and current provided from power supply whereas titanium electrodes were used to measure the current and potential passing from the system.

2.3. Electrochemical experimental procedures

All experiments were carried out at room temperature and pressure and they were performed for two days. The electrochemical reactor was conditioned by equilibrating the tap water in the inflow and outflow tubes connected to each electrode chamber. The water levels were kept at the same level in each tube during the entire test periods. Thus, the effect of the hydraulic gradient was eliminated in the transport of ions. Then, platinum mesh working electrodes were connected to a power source and 20 VDC constant potential from the power supply, was applied to the soil samples in all tests for 48 h. This provided a constant voltage gradient of 0.625 VDC/cm between the working electrodes throughout the tests.

During the electrochemical process, 10 mL samples were taken at different time periods for 48 h. The pH, EC, redox potential (ORP) and electric current were measured at the time of sampling throughout each experiment. At the end of the treatment period, soil samples were also collected in triplicate and analyzed for residual metal concentration. All metal concentration measurements were conducted as ppm using Atomic Absorption Spectrophotometer (Perkin Elmer AAS) following the standard procedures.

3. RESULTS AND DISCUSSION

3.1. Soil characterization

The initial physical and chemical properties of air-dried soils used in this study are given Table 1. As shown there, the texture classes of soil was sandy loam (SL) according to U.S. Department of Agriculture Classification system. Since texture classes of soils was determined as sandy loam, in other words because the percentage of clay in the soil was low, atterberg limits was determined as non-plastic. The soil pH was determined a slightly acidic soil (6.1 to 6.8). Before addition of humic acid to the soil, the amount of organic matter was very low because it was between 1–2% by mass; whereas, after addition of humic acid at five percent (w/w) organic matter content of soil was determined between 6-7 % by mass so it has become high (>4%).

Contaminated soil used in this study was obtained from a highly contaminated site containing toxic metals. The initial contents of Pb, Cd and Zn in the soil sample were 13365, 15742 and 19565 mg kg⁻¹, respectively (Table 1). Every type of soils has different range of concentrations depending of the origin of soil that occurred those parent rocks [3] Nevertheless, it is possible to evaluate with the limited values published by Soil Pollution Standards of Turkey for the same metals in soils. Concentrations of Pb, Cd and Zn of the soil used in this study are highly contaminated according to the Soil Pollution Control Standards of Turkey with a maximum allowable limits of 300 mg

kg^{-1} , 3 mg kg^{-1} and 300 mg kg^{-1} for Pb, Cd and Zn, respectively.

Table 1. Characteristics of the studied soil

| Parameters | Values | Test Method |
|-------------------------------------------------|-------------|---------------|
| Water Content (%) | 5.23 | ASTM D 2216 |
| Particle size distribution (%) | | Bouyoucous |
| Sand | 48.96 | |
| Silt | 46.78 | |
| Clay | 4.32 | |
| Atterberg Limits | Non-plastic | ASTM D4318 |
| pH | 6.29 | ASTM D4972-01 |
| Redox potential (mV) | 313 | ASTM G200-09 |
| Electrical conductivity (mS cm^{-1}) | 7.19 | ASTM D2974 |
| Organic Content (%) | | |
| Before Addition of HA | 1.79 | ASTM D2974-87 |
| After Addition of HA | 6.89 | |
| Metal Contents (mg kg^{-1}) | | USEPA 3051 |
| Pb | 13365 | |
| Cd | 15742 | |
| Zn | 19565 | |

3.2. Electrochemical tests

The electrochemical treatment has been recognized as an efficient *in situ* process for the remediation of contaminated soils [7]. Nowadays, several enterprises were implemented to test the capability of electrokinetics in the remediation of soils with mixed metals.

In previous study, before humic acid being added to the soil, tests had been performed only with tap water in the same soil sample contaminated mixed inorganic pollutants by Demir *et. al.* [1]. According to their conclusions, during the electrochemical process, the current of the system increased for half an hour due to the mobilization of ions, then started to decrease due to the precipitation of metals at cathode. At the beginning of the experiment, the measured current was 122 mA while it had dropped to 10 mA at the end

of the experiment.

Throughout the experiment, pH values were analyzed for each solution in the electrochemical cell. As expected, water electrolysis at the electrodes generates an acidic and alkaline medium in the anode and in the cathode, respectively. The pH of solutions around the anode had decreased to about 1.13 while around the cathode it had increased to around 11.31 at the end of the experiment.

The ORP values had increased about 595 mV in the anode compartment, and it had decreased in the cathode compartment to about -167.5 mV for all. The low ORP value in the cathode compartment indicates that it is a reductive environment, hence reduction reactions are predominant. When results of EC values were examined, it had been detected that they increased near the anode whereas they decreased toward the cathode. These findings showed that deposition of metal ions occurred in the cathode compartment diminishing the electrical conductivity.

Their experimental results have indicated that total electrochemical removal of lead, cadmium, and zinc from soil using only tap water was 35.59%, 78.09% and 55.09%, respectively. The removal efficiencies seemed to be influenced by the overall effects of the characteristics of the soils, the initial concentrations and speciation of metal contaminants and the velocity of electromigration.

3.3. Effect of Humic Acids on removal of toxic metals from soil electrochemically

Generally, surfactants are introduced to increase the solubility and mobility of heavy metals during electrokinetic remediation. This is because surfactants have an effect on the electrical double layer interactions and Van der Waals interactions [11]. To examine the effect of natural surfactant on removal of metals from soil electrochemically, humic acid was added to be five percent into the soil and then it was placed in the electrochemical reactor and was started the tests.

During the experiments conducted with tap water and humic acid, while the initial current was determined at 126.2 mA, the current was 1.4 mA at the end of the experiment. Since the constant voltage during this EK process was maintained, the resistance was directly affected by the current in this system. Current is an indication of the amount of mobile ions under electromigration [16]. For this reason, it is possible to say that electromigration is reduced at the end of experiment hence the removal efficiency of toxic metals will also be reduced.

The pH of solutions near the anode reduced to about 1.65 while pH of solutions close to the cathode increased to about 12.24 at the end of 48 h. This result is similar to the previous experiment's conclusion. Due to the high pH near the cathode, the metal ions in soil precipitated as hydroxide salts at the cathode side and metal concentrations had decreased. In contrast, concentrations of metals increased at the anode side because of the low pH.

As observed from ORP results in this experiment, ORP values increased about 594 mV in the anode compartment and it decreased in the cathode compartment to about -43.3 mV for all. The low ORP value in the cathode compartment indicates that it is a reductive environment, hence reduction reactions are predominant. Comparing the results for the only with water in Exp. 1 and 2 (with tap water and humic acid), it can be concluded that pH, EC and ORP's profile were almost the same in both of the experiments.

Figure 2 shows the cumulative mass of the toxic metals in electrolyte for each compartment depending on time during the *in-situ* electrochemical process in Exp.2. At the end of this experiment, the removal efficiency of the metal ions from soil were determined as 20.07%, 68.46% and 49.61% for Pb, Cd and Zn, respectively.

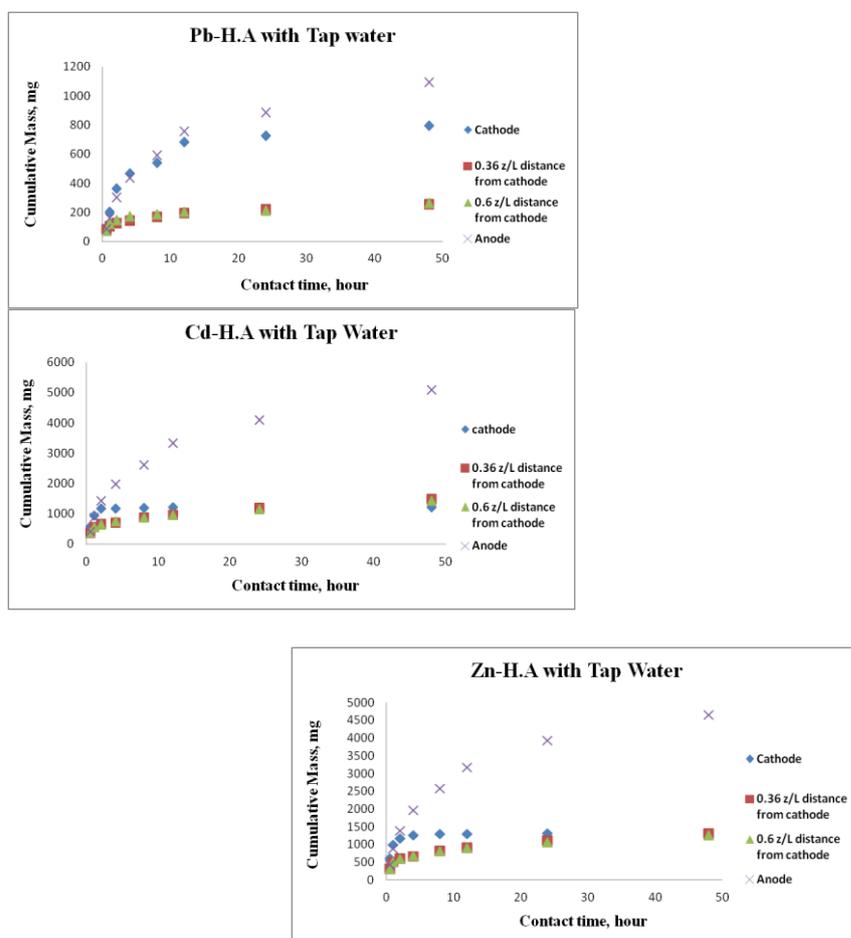


Figure 2. Distribution of aqueous metal concentration over time in EK test of contaminated mine tailing soil mixed with tap water and humic acid

Comparing the results for two separate experiments, it can be concluded that the addition of humic acid results in the decline of metals mobility. When humic acid is added into soil, efficiency of metals removal decrease about 15 percent for Pb, 10 percent for Cd and 6 percent for Zn.

Figure 3 shows the distribution of metal concentration for electrolyte samples taken

from *in-situ* electrochemical set up for each section.

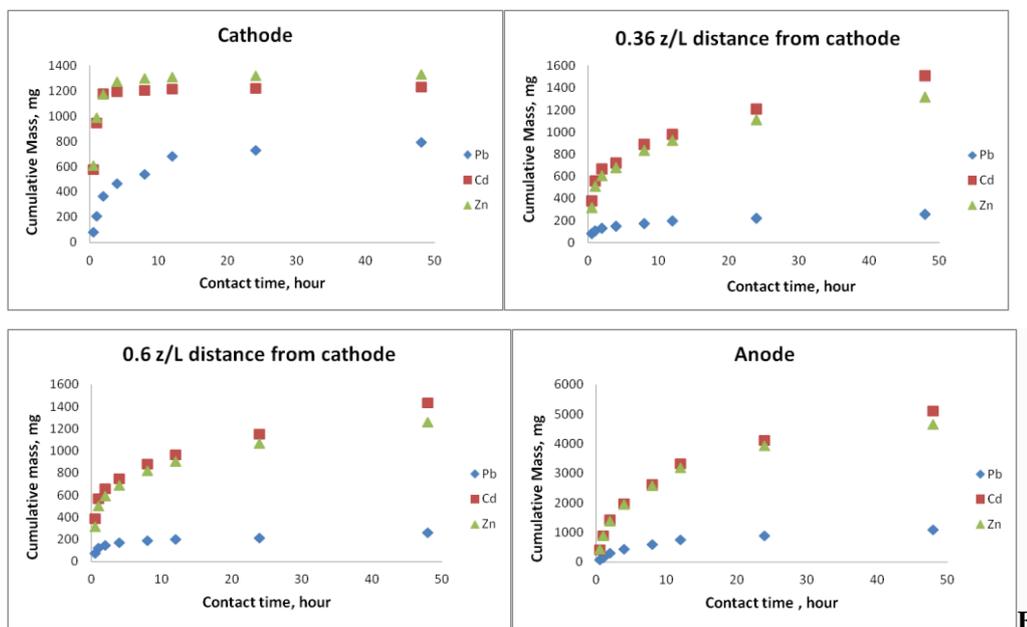


Figure 3. The time-dependent metal concentrations measured in distance from the cathode after the *in-situ* electrochemical experiment performed with mixed tap water and humic acid

As seen from 3rd and 4th graphs in Figure 3, results are quite close to each other. The concentration of Pb transported to solution via electromigration is significantly low compared with those of Cd and Zn. This can be explained by the stronger adsorption of Pb to soil than Cd and Zn. Although the initial concentrations Cd and Zn of soil were different and humic acid was added, they were moved to solution (tap water) through to electromigration almost at the same amount, indicating that there was no sequential extraction or competition between the transport of these two metals.

After 48 hours, the cumulative concentration of Pb, Cd and Zn were determined in the anode compartment as 1092.08, 5104.08 and 4663.86 mg, respectively. Whereas cumulative concentration of those metals were determined in the cathode compartment as 794.78, 1230.31, 1327.09 mg for each metal, respectively.

The concentrations of all the metals in the anode compartment were determined higher than in the cathode compartment. It can be explained that metal ions were precipitated as hydroxide complex in the cathode side but they weren't precipitated in the anode side because of pH at 1.36.

4. CONCLUSION

In this study the electrochemical removal of Pb, Cd and Zn was evaluated by the application of humic acid as surfactants. Comparing the results for earlier experiment carried out with only tap water, it can be concluded that the addition of humic acid into

the soil was decreased mobility of metals hence the removal efficiency of metal has also decreased. Also in this test, Cd was extracted more than Pb and Zn. Removal efficiencies of metals have determined in the order Cd>Zn>Pb in electrochemical reactor.

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