

Investigation of Electrokinetic for the Removal of Mercury from Contaminated Soil and Sediment

Arash Kiyae¹, Mohammad Reza Tavakoli Mohammadi^{2*}, Ahmad Khodadadi³

- 1- MSc Student of Civil Engineering, Environmental Group, Tarbiat Modares University, Tehran, Iran.
- 2- PhD Student of Mining Engineering, Mineral Processing Group, Tarbiat Modares University, Tehran, Iran.
- 3- Associate Professor of Civil Engineering, Environmental Group, Tarbiat Modares University, Tehran, Iran.

* Corresponding Author: mr.tavakolimohammadi@modares.ac.ir

Received: 07 October 2013 / Accepted: 30 November 2013 / Published online: 5 December 2013

Abstract

Electrokinetic remediation is one of the most promising in situ or ex situ processes for decontamination of heavy metals, anions and polar organic compositions from the soil. In this study, we investigated the efficacy of this method in removing mercury from clayey soil (with kaolin to sand weight ratio of 2:1) and from gold mine tailing dam sediment and determined optimum removal conditions. Total mercury concentration in the soil and sediment samples was 800 and 210 mg / kg, respectively, and duration of the experiments was considered as 32 and 30 days, respectively. The experiments were conducted on the samples with two voltage gradients (1.0 and 1.5 VDC/cm) to assess the effect of voltage gradient when using 0.1 M Na-EDTA, 0.1 and 0.4 M KI solutions and distilled water. The results showed that the best efficiency (99.07%) was reached when the 0.4M KI concentration was used with the 1.0 VDC/cm voltage gradients, leaving a residual concentration of 7.47 mg/kg in the soil after the treatment. In addition, the best efficiency for mercury removal from the tailing dam sediment was achieved in these conditions. The electrical current profiles, pH of the anode and cathode reservoirs, electrical conductivity of the soil and its moisture were then plotted and discussed.

Keywords: Electrokinetic, Mercury, KI, Na-EDTA.

1–Introduction

Nowadays, protection of the environment from various pollutants is a dilemma with which man is involved more than any time before. A significant part of pollutants entering the environment is generated by industry and technology in the current era. Emission of heavy metals in the environment is considered as a serious hazard for the survival of living organisms, due to harmful effects of their emissions. Over the past decades, uncontrolled and severe increase in production and consumption of these metals has led to transfer

of large quantities of them to the nature cycle by water, soil and air due to various natural and anthropogenic sources. Because of their stability and lack of biodegradation, they have extensively appeared in the food chain as a serious threat for plants and animals consuming these nutrients (Fenglian and Wang, 2011; Sengupta, 2002).

Among the four heavy metals of mercury, arsenic, cadmium and lead (considered as the most dangerous heavy metals regarding their low permitted limit in the environment), mercury is the only metal of which

accumulation and concentration along a food chain has certainly been confirmed (Clarkson, 1993). Due to such features as high toxicity, the ability of disturbing the soil ecosystem and high contamination of ground water tables, mercury has been recognized as the most dangerous heavy metal (Lindqvist, 1991). The values in Tables 1 and 2 indicate higher toxicity of mercury compared to the other three elements.

Table 1) Drinking water standard for heavy metals, in ppb (Carr and Neary, 2008).

| Metal | EPA | Canada | WHO |
|---------|-----|--------|-----|
| Mercury | 2 | 1 | 1 |
| Arsenic | 2 | 25 | 10 |
| Cadmium | 5 | 5 | 5 |

Table 2) Waste water standard for heavy metals, in ppb (Carr and Neary, 2008).

| Metal | Discharge to surface waters | Discharge to shaft | Agronomy and irrigation consumptions |
|---------|-----------------------------|--------------------|--------------------------------------|
| Mercury | Negligible | Negligible | Negligible |
| Arsenic | 100 | 100 | 100 |
| Cadmium | 100 | 100 | 50 |
| Lead | 1000 | 1000 | 1000 |

Among the available technologies, drilling and ex situ decontamination of contaminated soils along with sequestering measures are widely used and appreciated, although these methods are not usually affordable or technically easy. In contrast, the emergency in situ procedures such as permeable reactive walls and washing may be more appropriate for many mercury contaminated sites.

2-Electrokinetic method principles

Electrokinetic is the term used for remediation process of contaminated soils using electrical field; it is also called soil electrokinetic procedure, electrical reclamation, electrochemical decontamination and electrical remediation (Van, 1997). This method has been described in detail by Lageman (2005). In this

| Lead | 20 | 10 | 10 |
|------|----|----|----|
|------|----|----|----|

Although various mercury forms have been used in different applications for a long time due to their interesting and unique properties, nowadays these compounds have been substituted because of strict environmental regulations.

However, due to recent and past activities, various forms and quantities of mercury have been released into the environment, which can be a risk for both man and environment. Therefore, different methods have been used or are being developed for mercury removal; some of which are presented in Table 3.

system, low level direct electric current is used to apply several mAs per square centimeter of soil between the electrodes. Thus, the electrical potential of several volts per centimeter soil is applied between the two electrodes. For the effective functioning of this system, it is necessary that the soil pore water be able to maintain the electrical potential between the electrodes (Lindgren, 1991).

The results of applying electric current in soil-water system in saturated or non-saturated conditions are as follows:

- 1- Ionic varieties present in the soil pore water move towards the electrode of opposite charge (electrical migration).

- 2- Charged particles in the soil pore water move toward the electrode with the opposite charge.
- 3- Water mass moves towards the cathode (electro-osmosis phenomenon).
- 4- Electrolysis reaction occurs in the electrodes (Hunter, 1981).

The combination of these phenomena results in the movement of contaminants toward the electrodes. Direction and rate of movement are

dependent upon the charge of ions (both magnitude and type), degree of ion adsorption to soil particles and flow rate of electro-osmosis. Contaminants reaching the electrodes can be eliminated by extraction of the water existing in the soil pores near the electrodes, adsorption of contaminants on the electrodes, precipitation or co-precipitation of contamination in the electrodes or making complex with ion exchange resins (Mattson and Lindgren, 1993).

Table 3) Various technologies of mercury remediation

| Various technologies of remediation | Subdivisions | References |
|-------------------------------------|--|---|
| Out-site excavation and treatment | Physical separation | (Biester et al., 2000; Hempel and Thoeming, 1999) |
| | Thermal treatment | (Hinton and Veiga, 2001; Biester et al., 2000; Matsuyama et al., 1999; Larry and Jose, 1990) |
| | Hydrometallurgical treatment | (Thoming et al., 1999) |
| | Soil vapour extraction coupled with soil heating | (Unger et al., 1995; Johnson et al., 1990) |
| | Permeable reactive walls | (Domenico and Schwartz, 1998; Waybrandt et al., 1998) |
| In-situ recovery | In-situ leaching and extraction | (Hinton and Veiga, 2001; Waybrandt et al., 1998) |
| | Electrokinetic separation | (Lageman et al., 2005; Biester et al., 2000; U.S. Army Engineering Corp., 2000; Sobolev et al., 1996) |
| | Electrochemical remediation technologies (ECRTs) | (Hinton and Veiga, 2001) |
| | Interceptor systems | (Hinton and Veiga, 2001) |
| | Phytoremediation | (Hinton and Veiga, 2001) |
| | Passive remediation-wetlands | (Anonymous, 2000) |
| | Pump and treat | (Hinton and Veiga, 2001) |
| Containment | Impermeable barriers, surface seals and drains | (Domenico and Schwartz, 1998) |
| | Stabilization and solidification | (Hinton and Veiga, 2001; Domenico and Schwartz, 1998) |
| | Sediment capping | (Palermo, 1998) |

Studies on electrokinetic remediation of Hg-contaminated sediments are rare. Cox (1996)

used an iodine/iodide (I_2/I^-) lixiviant solution in cathode for the electrokinetic remediation of

HgS-contaminated sediments. Their ultimate aim was to use the lixiviant solution to oxidize the HgS compounds in the sediment and cause the mercury to be released as a soluble complex(HgI4²⁻). This anion complex would then electromigrate towards the anode reservoir where it could be removed. Cox (1996) explained that the electrokinetic remediation of Hg-contaminated sediments was difficult due to the low solubility of mercury compounds in most natural sediments. Mercury pollution, however, may be in an elemental (Hg⁰) form. Besides HgS, it may also convert into other species such as HgCl₂, Hg(OH)₂, or toxic organic forms like dimethylmercury (CH₃)₂Hg. Hem (1970) found that HgS (cinnabar), Hg(I), HgO, Hg₂Cl₂ and HgCl₂ are thermodynamically stable solid-phase species, and to allow the formation of the HgI₄²⁻ complex, species such as HgS, Hg(I) and Hg₂Cl₂, require oxidation by I₂ or another oxidizing agent, whereas more oxidized species such as HgCl₂ and HgO will readily form HgI₄²⁻ complex in the presence of I₂ alone. HgS has a very low aqueous solubility; however, Gilmour (1971) has found that the insolubility of HgS compounds excludes them from consideration in normal soil-water systems. He further determined that Cl⁻ and OH⁻ inorganic ligands would form complexes with Hg (II), and dominate in normal water systems because they are present at high concentrations and possess high stability constants. Hanke (1993) reported the aqueous solubility of HgCl₂, Hg₂Cl₂, and HgO as 70000, 2.0 and 53 mg/L, respectively, whereas the solubility of HgS was only 10 mg/L. Therefore, if the soils possessing a low amount of sulfide are contaminated due to an accidental spill or industrial release of mercury, there would be a greater tendency for Hg to associate with Cl⁻ and/or OH⁻. According to the investigation by Cox (1996), Hg (II) removal could be accomplished by using an iodide solution (KI) at the cathode to form HgI₄²⁻ complexes that would electromigrate towards

the anode for removal. However, strong oxidizing conditions are not necessary since the initial state of Hg contaminant would be in the form of HgCl₂ and not a relatively insoluble species like HgS.

In this research, in line with other activities performed in this context, the efficiency of electrokinetic method in removal of mercury from the artificially contaminated soil and tailing dam sediment of Takab Gold Mine in West Azerbaijan Province of Iran was investigated.

3–Materials and equipment

3.1–Samples

Two samples were used in this study:

-Soil with a 2:1 weight ratio of Kaolinite to sand (sample 1)

-Sediment taken from the tailing dam of gold mine (sample 2)

Table 4) Samples properties.

| Property | Sample 1 | Sample 2 |
|---------------------------------|----------|----------|
| Liquid limit (%) | 65 | 31 |
| Plastic limit (%) | 18 | 18 |
| Optimum moisture (%) | 25 | 20 |
| pH | 7.92 | 8.83 |
| Electrical conductivity (μS/cm) | 7370 | 1036 |
| Mercury concentration (mg/kg) | 800 | 210 |

The physical and chemical properties of these samples are given in Table 4. Kaolinite is a type of clay that has a great ability to absorb cations. It has very fine grains and a high specific surface, so the experimental contaminant [Hg (II)] formed strong bonds with its negative surface and was highly absorbed in its fine

particles. In other words, the contaminant was not easily desorbed after adsorbing on the surface of particles, and could not be removed from the soil by water washing. Decreased concentration of mercury in the soil showed high efficiency of electrokinetic method in removing the contaminant. The sand passed through sieve No. 40 (0.420 mm), remained on the sieve No. 200 (0.075 mm), was washed with water after being placed in 2% sulfuric acid for 24 hours. This soil was artificially contaminated with 800 mg of Hg (II) per kilogram dry soil. In the second sample taken from around the gold mine's tailing dam, mercury was found with a concentration of 210 mg per kilogram dry soil.

3.2–Chemicals

Mercuric chloride (HgCl_2) was used for contaminating the soil with mercury. One of the extracting materials in the cathode reservoir was potassium iodide (KI), which was used in 0.1M and 0.4M concentrations. Disodium ethylene diamine tetra acetate (Na-EDTA) was used in 0.1M concentration. The cells and sand were washed using sulfuric and nitric acids. All chemicals used were manufactured by the MERCK Company (Germany).

3.3–Characteristics of pilot equipment

The Figure 1 shows the system used in this study. According to this figure, four pilots made of Plexiglas in rectangular cube form with an internal surface area of 16 cm² and a total length of 26.4 cm was made. Each pilot consisted of three parts. The median part was 12 cm long and housed compacted soil, and the electrodes (2 cm in length) and their reservoirs (anolyte and catholyte solutions each 4 cm in length) can be found in the two end parts. For discharging the hydrogen and oxygen gases produced at anode and cathode, respectively, small openings were made in the upper parts of the chambers. Two cylindrical reservoirs with a volume of more than 700 ml were connected to the cell by two plastic tubes. These reservoirs

are storage places for the anolyte and catholyte solutions. In each reservoir, the spout was placed where the volume of liquid within the cylindrical reservoir had a volume of 700 ml and a height of 10 cm. To prevent entrance of soil or electrode particles to other parts, a fiberglass filter layer (1.4 mm thick and 6 micron pore size) was used in the interface of the electrodes and in the middle part of cell. The electrodes used in this study were made of graphite with 15×23×40 dimension.

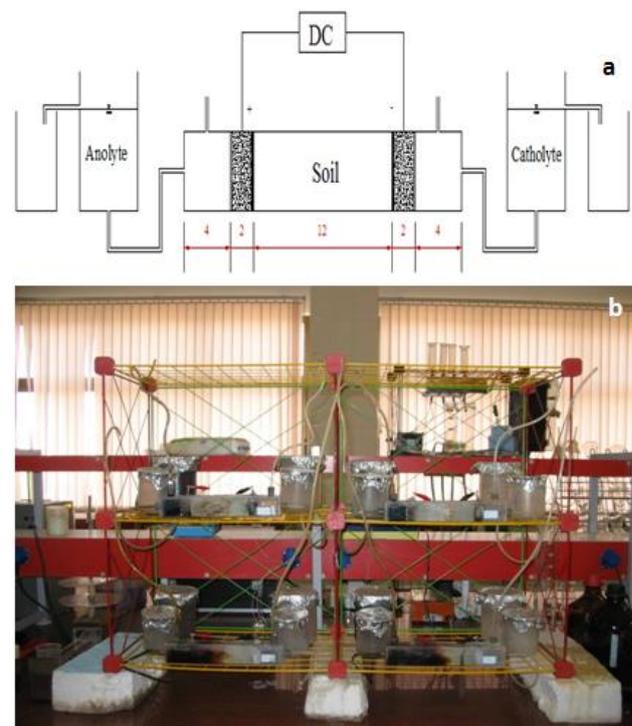


Figure 1) Electrokinetic test setup: a) Schematic (dimensions in cm); b) Laboratory.

Each electrode was in a sealed chamber; one side was connected to soil and the other to the reservoirs. These electrodes were connected to the voltage source by a copper wire (3mm thick). The density of current used and the voltage gradients applied on the soil in this study were 0.5 mA/cm², 1 and 1.5 VDC/cm, respectively. To supply the electric field and measure the voltage and electrical current, a power source with direct current, and 12 and 18 volt constant voltages along with an accurate digital multimeter were used, respectively.

4–Results and discussion

4.1–Mercury removal

The purpose of this study was to evaluate the efficiency of removing mercury from both naturally and artificially contaminated soils

using electrokinetic method to determine the optimum removal conditions. Figures 2a and b show the mercury removal percentage in the soil after electrokinetic remediation with the voltage gradients of 1 and 1.5 VDC/cm, respectively.

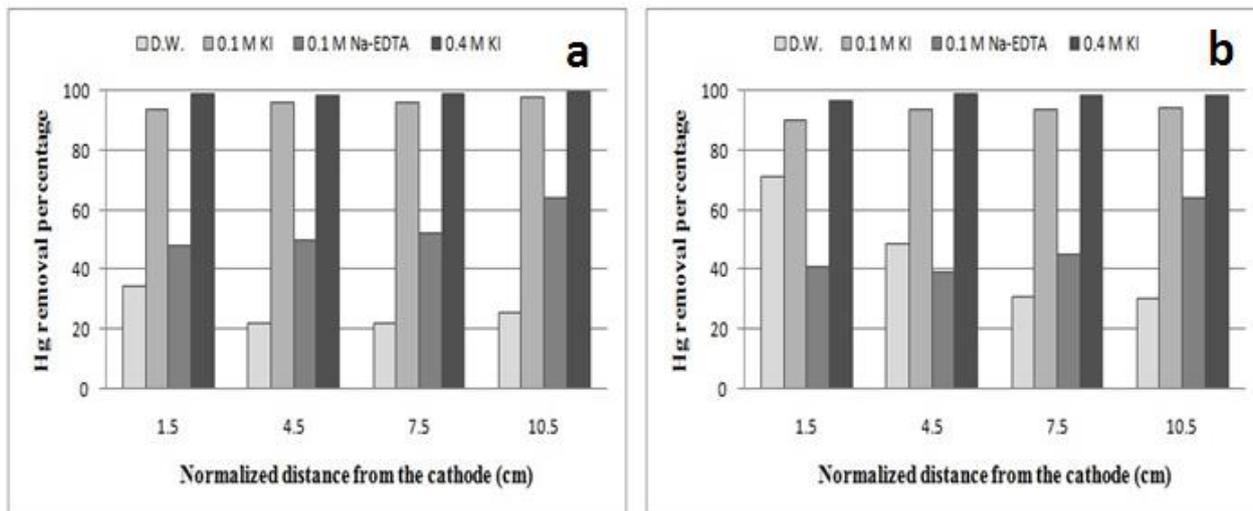


Figure 2) Mercury removal percentage in the soil after electrokinetic remediation a) with the voltage gradient of 1.0VDC/cm. b) with the voltage gradient of 1.5VDC/cm.

Assessment of these diagrams showed that performing this method using distilled water as control in the cathode reservoir has a relatively low efficiency. The reason is the low solubility of mercury compounds in most soils. The results also showed that, due to the positive charge of mercury (Hg^{2+}), the efficacy of its removal was higher in the soil adjacent to the cathode.

The use of 0.1M concentration of Na-EDTA ($\text{Na}_2\text{H}_2\text{Y}$) as catholyte had an efficiency between 48 to 64 percent with the highest efficacy in the soil near the anode. After hydrolysis, $\text{Na}_2\text{H}_2\text{Y}$ was converted into H_2Y^{2-} , HY^{3-} and Y^{4-} , and the value of Y^{4-} increased in higher pHs. By combining $\text{Na}_2\text{H}_2\text{Y}$ with Hg^{2+} and its hydrolysis, HgH_2Y , HgHY^- and HgY_2^{2-} are formed, the percent of which is dependent on the environment pH. In this study, due to low soil pH within the cell, mercury removal efficiency was not very high. Also, due to positive charge of the anode and negative charge of some of the complexes formed,

efficiency of removal in the soil near the anode was higher than in the other parts.

The use of a 0.1M solution of KI in the cathode reservoir as catholyte gave an efficiency between 93.62% and 97.26%. 0.1M potassium iodide (KI) salt in combination with $\text{Hg}(\text{II})$ formed a stable complex of HgI_4^{2-} . Then it was moved toward the anode (positive pole), cleaned out of the soil and decontaminated. Unlike mercury, this high efficiency was due to complete solubility of HgI_4^{2-} complex in the soil. Upon the appearance of iodide (I^-) in the soil, mercury was removed from the soil matrix and moved toward the anode.

Experimental results with 0.4M KI catholyte showed higher efficiency than with 0.1M KI catholyte. The removal of mercury was in the range of 98.51-99.55% in this situation. This increase in recovery was due to higher concentration of iodide in the pilot, and increased likelihood of its combination with mercury. Thus, a higher level of mercury was converted into HgI_4^{2-} , which was followed by

increased removal efficiency. In this situation, the efficiency of removal near the anode (with positive charge) was higher due to higher attraction near the anode.

The removal efficiencies (from the cathode to the anode) in the cell number 1 that were tested as a control with distilled water as catholyte

solution were 71, 49, 31 and 30%, respectively. Due to increased gradient applied to the soil (1.5 VDC / cm), efficiency of 71% for the soil samples in the vicinity of the cathode was reached. However, the efficiency of the two soil samples near the anode was, however, low because of distance from the cathode (negative pole) and low solubility of mercury.

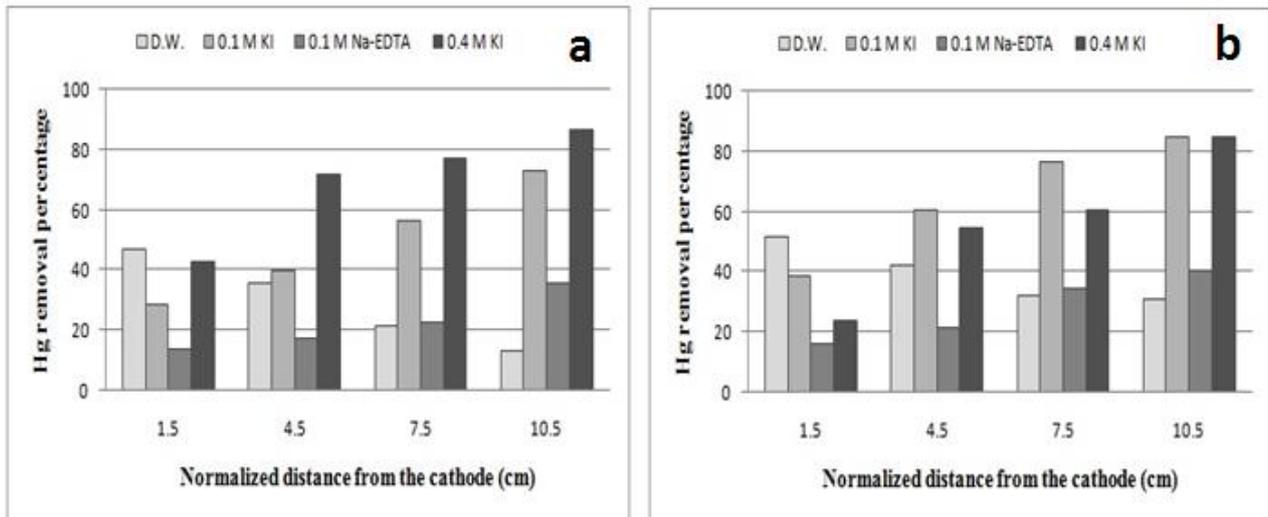


Figure 3) Mercury removal percentage in the sediment after electrokinetic remediation a) with the voltage gradient of 1.0 VDC/cm– b) with the voltage gradient of 1.5 VDC/cm.

The use of Na-EDTA as catholyte also did not bring about a good return. In this case, the removal efficiencies from the cathode to the anode were respectively 41, 39, 45 and 64%. The reason for higher efficiency of soil near the anode was the negative charge of some complexes formed and higher attraction force near the positive pole (anode).

Removal of mercury using a 0.1 M KI washing solution and the voltage gradient of 1.5 VDC/cm had a very good yield. The efficiencies obtained in different parts of the soil were in the range of 90-94%. In this situation, the best efficiency for the soil sample was obtained near the anode too, due to higher ion attraction force. The experiments with 0.4 M KI solution also resulted in mercury removal with the efficiencies of 96.7, 99, 98.7 and 98.3%, respectively, from the cathode to the anode.

Figures 3a and b show the mercury removal percentage in the sediment after electrokinetic

remediation with the voltage gradients of 1 and 1.5 VDC/cm, respectively.

Figure 3a shows that the potassium iodide (KI) solution was more efficient than distilled water and 0.1 M Na-EDTA solution and the average percentages of Hg removed from the sediment were 49.5 and 69.6 with using 0.1 and 0.4 M KI solutions, respectively. This indicates that the effect of increasing of KI concentration is major for Hg removal from the sediment with the voltage gradient of 1 VDC/cm. Figure 3b like figure 2a presents the same mercury removal from the sediment; with this difference that using lower KI concentration had a better effect than the other. This figure also indicates that electrokinetic treatment of Takab sediment using 0.1M KI purging solution and voltage gradient of 1.5 VDC/cm has the best efficiency (65.2%). Since mercury compounds are insoluble in most natural soils, electrokinetic remediation of Takab tailing dam sediment using distilled water as catholyte has low

efficiency. The reaction of mercury with Na-EDTA ($\text{Na}_2\text{H}_2\text{Y}$) produces three compounds of HgH_2Y , HgHY^- and HgY^{2-} , and pH is an important function in the formation of these compounds. In this study, due to lack of the formation of enough negatively charged compounds, mercury removal was low. In the reaction of mercury with KI, instant and soluble complexes of HgI_4^{2-} are formed, which are then transported toward the anode by ionic migration.

4.2–Electrical current results

Figures 4a and b show the current variations measured for the soil in 1 and 1.5 VDC/cm voltage gradients, respectively. As these diagrams show, in the experiments conducted with distilled water and Na-EDTA as catholyte, the current was first descending; however, after 4 to 5 days, the electric current oscillation was very low up to the end of the experiments. In the experiments conducted with 0.1 and 0.4M KI solutions, the electric current was first ascending, and after 2 to 3 days, it was dramatically reduced, so that after 4 to 6 days, the electric current oscillation was low up to the end of the experiments.

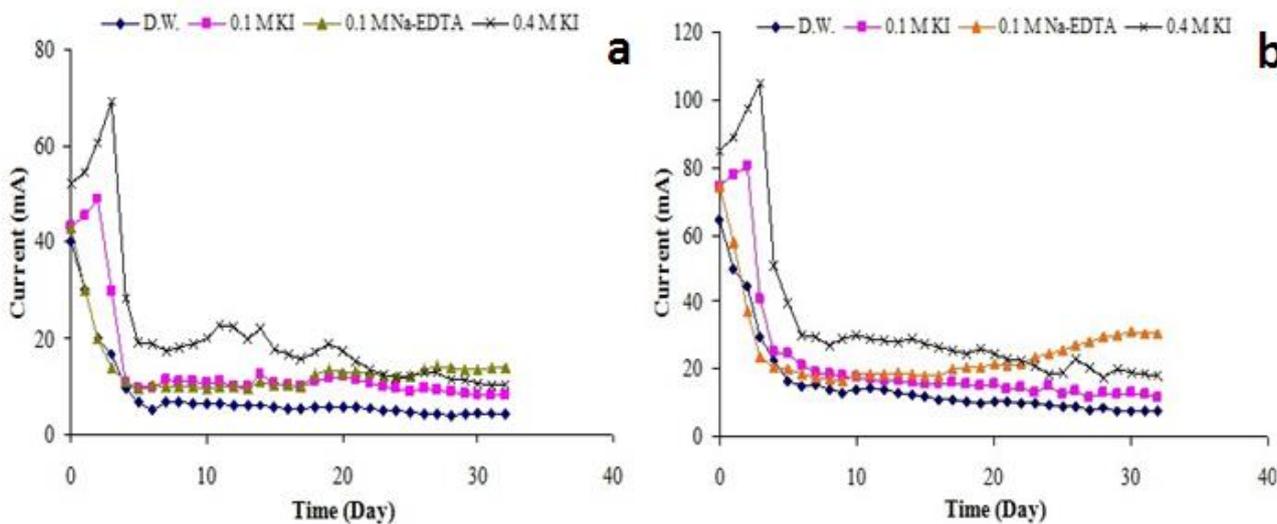


Figure 4) Current variations in the soil: a) with the voltage gradient of 1.0 VDC/cm. b) with the voltage gradient of 1.5 VDC/cm.

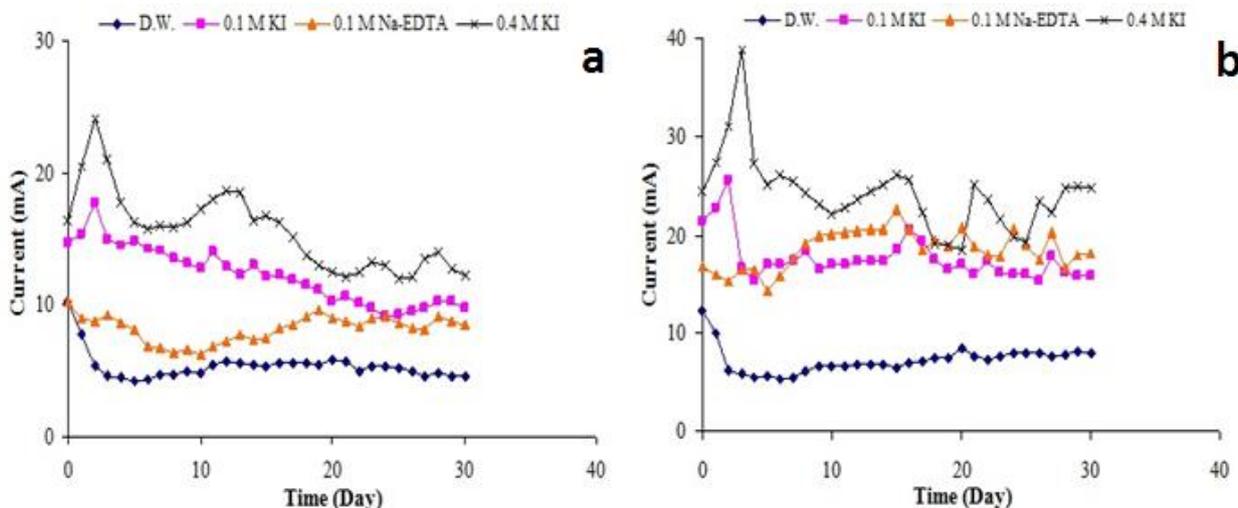


Figure 5) Current variations in the sediment: a) with the voltage gradient of 1.0 VDC/cm. b) with the voltage gradient of 1.5 VDC/cm.

Figures 5 and b show the current variations measured for the sediment in during the whole period of the electrokinetic remediation in 1 and 1.5 VDC/cm voltage gradients, respectively. In cells using distilled water and 0.1 M Na-EDTA solution as catholyte, the behavior of current in the sediment is as described.

When water is added, the salts associated with the dry soil particles dissolve into the water and produce an ionic solution. As the voltage gradient is applied, the initial current is high as a result of strong ionic concentration. As time passes, the electric current decreases because of the cations and anions electromigrate towards the respective electrode. In addition, the products of electrolysis reactions may contribute to the neutralization of migrating ions. In particular, H^+ ions migrating toward the cathode could be neutralized by the OH^- ions migrating towards the anode, thereby, forming water and diluting the number of ions in the solution.

In the cells using KI solution, as the solution begins to migrate into the soil, it supplies

additional ions and causes further salt dissolution to occur, thereby increasing the electric current. The use of a higher concentration KI solution will increase the number of ions in the pore solution, and thus increases the current. The use of a higher voltage gradient affects ion movement because the ions that were previously electro-statically fixed in the test using the lower voltage gradient may become mobile when the electric potential is increased. It is also likely that the higher voltage gradient will increase the rate of electrolysis, and the time-dependent pH changes could affect the current by causing changes such as greater salt dissolution, soil degradation or salt precipitation.

4.3–Reservoir pH profiles

The Figure 6 shows the pH of the cathode and anode reservoirs in soil decontamination using electrokinetic method with a voltage gradient of 1 VDC /cm.

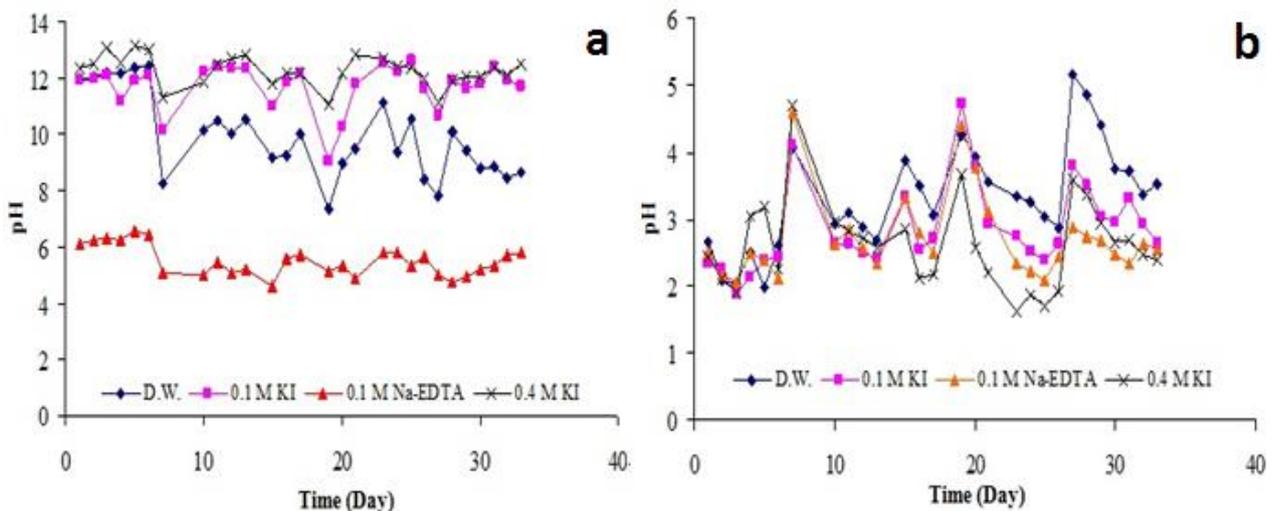


Figure 6) pH variations of the reservoirs with the voltage gradient of 1.0 VDC/cm in soil remediation: a) Cathode. b) Anode.

The trend observed in these diagrams indicates similarity of pH change behavior in all the 4 cells. At the start of operations, due to the presence of a large number of ions in the soil, the electric current through it was high.

Therefore, there was higher electrolysis of water and thus higher H^+ and OH^- . As a result, pH at the cathode reservoir in the beginning of the experiment was higher than later on. In contrast, pH of the anode reservoir was lower at the

beginning of the experiment than later on in the experiment. Sudden changes in pH were due to the exchange of solutions in the anode and cathode reservoirs, which occurred place once a week.

An important point in Figure 7 is lower pH profile of Na-EDTA relative to the other three

solutions because of the acidity of Na-EDTA. In addition, due to passage of higher flow from the cell containing 0.4M potassium iodide than the cells containing 0.1M potassium iodide and distilled water, its pH profile was also in a higher position.

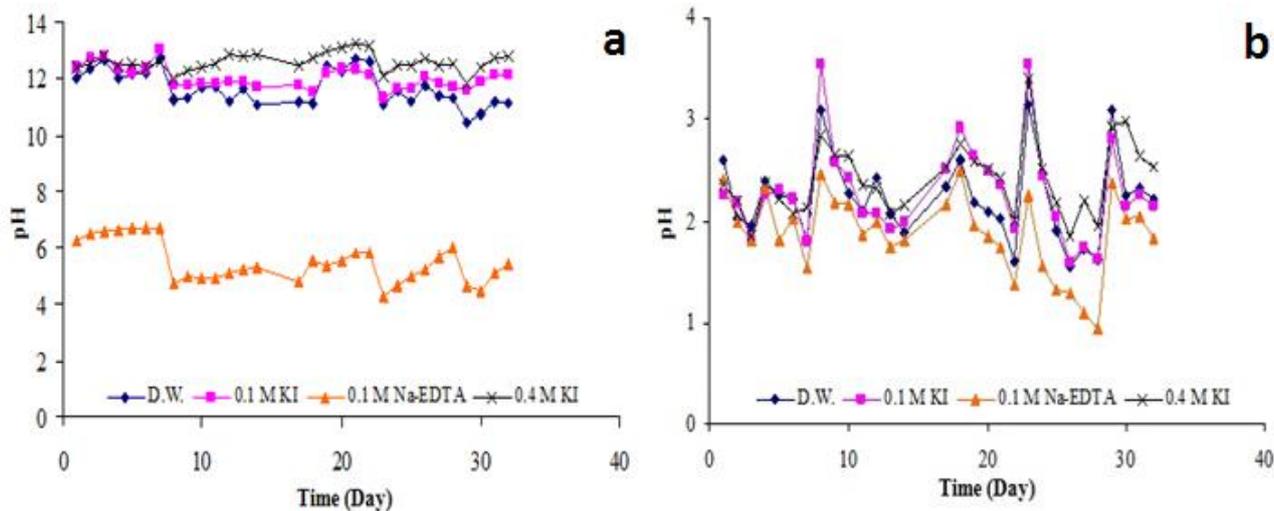


Figure 7) pH variations of the reservoirs with the voltage gradient of 1.5 VDC/cm in soil remediation: a) Cathode. b) Anode.

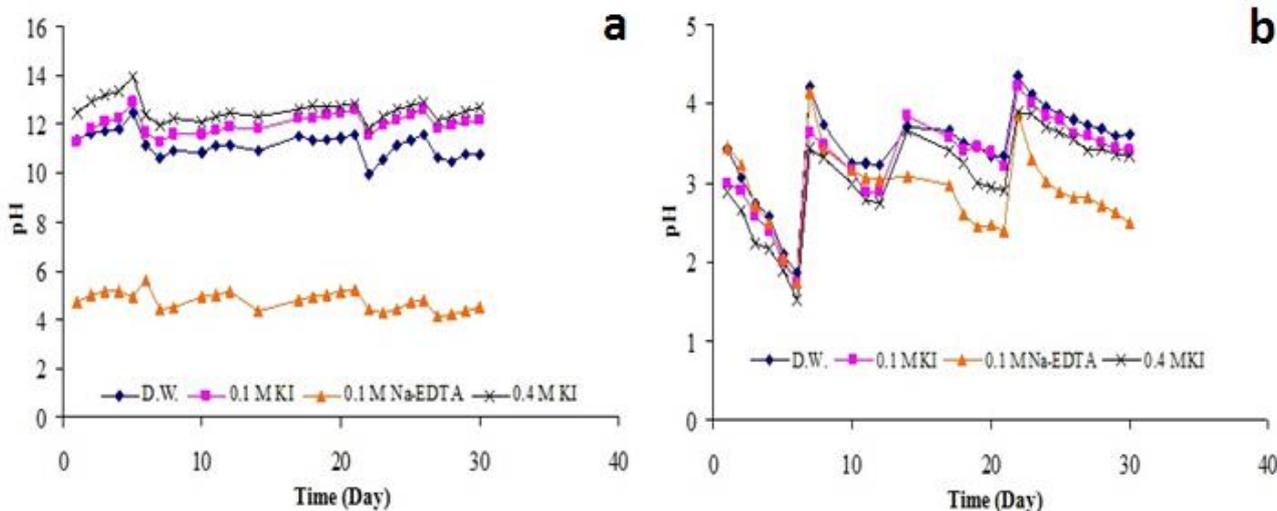


Figure 8) pH variations of the reservoirs with the voltage gradient of 1.0 VDC/cm in sediment remediation a) Cathode. b) Anode.

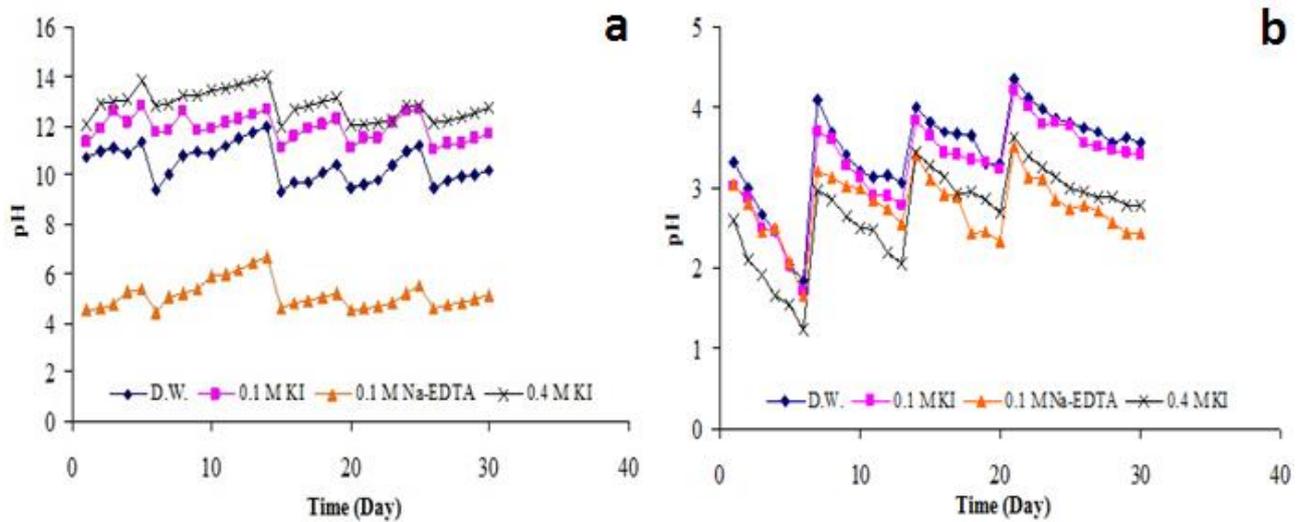


Figure 9) pH variations of the reservoirs with the voltage gradient of 1.5 VDC/cm in sediment remediation a) Cathode. b) Anode.

Therefore, in general, it was concluded that the higher the flow from the cell, the higher the cathode pH and the lower the pH of distilled water in the anode. In other words, pH profiles of the cathode and anode reservoirs were, respectively, higher and lower than the other pH profiles, respectively.

Figure 7 also shows pH changes of the anode and cathode reservoirs with 1.5 VDC/cm voltage gradients. The reason for higher pH of the cathode and lower pH of the anode solutions relative to the experiment with 1 VDC/cm voltage is the higher electrical potential applied on the cells and the resulting increased electrical current. It can also be observed that after 19 days, pH profile of the anode solution in the cell using Na-EDTA is lower relative to the other three cells due to increased flow in this cell and its decrease in the other cells.

Figures 8 and 9 present the pH values measured in the cathode and anode reservoirs during the electrokinetic experiments with the voltage gradients of 1 and 1.5 VDC/cm, respectively.

As shown, the pH of cathode reservoir is basic in all cells, except in those using Na-EDTA as

extracting agent, because this agent is basically a weak acid and the pH of these two cells is around 6 in the cathode reservoir. In addition, the pH of anode reservoir in all cells is acidic. In the beginning of electrokinetic remediation, because the sediment was not treated and the electric current through the sediment was high, the electrolysis rate was high and therefore the pH in cathode and anode reservoirs was higher and lower, respectively, than during the continuation of the tests. Hence, for increasing the efficiency of treatment, the anolytes and catholytes were replaced once a week; therefore, a breakage in the diagrams is observed.

4.4–Soil and sediment pH profiles

The pH values of the soil samples extracted from the cells after decontamination with the voltage gradients of 1 and 1.5 VDC /cm are shown in Figures 10a and b. As can be seen, the pH behavior is similar in the cells with the decontamination solutions of distilled water and 0.1M and 0.4M KI, but a different behavior is seen in the cell using a 0.1M solution of Na-EDTA due to the acidic nature of the material.

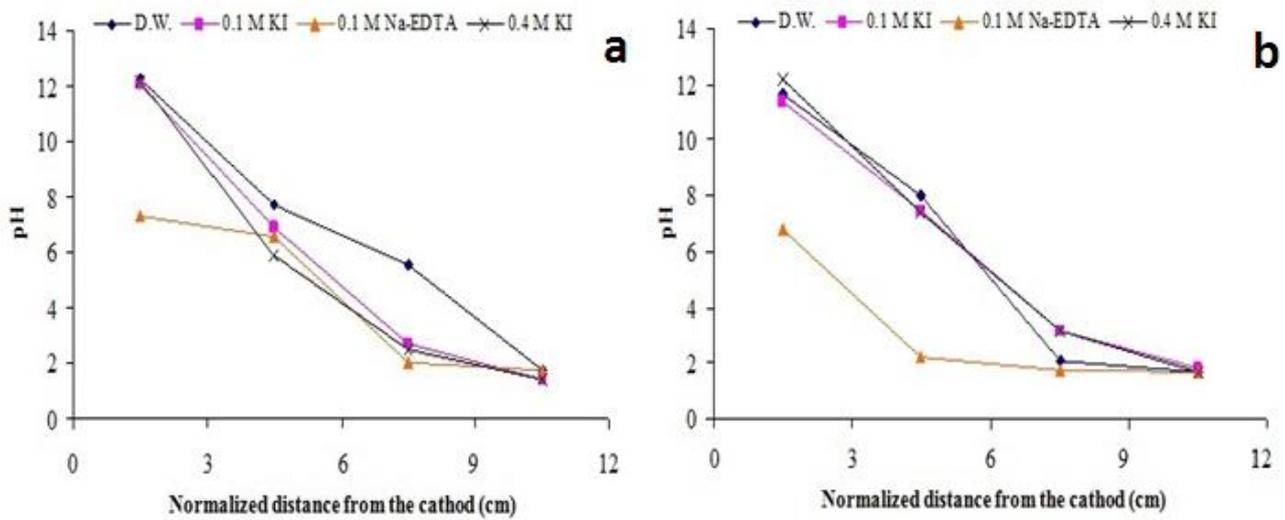


Figure 10) Soil pH variations a) with the voltage gradient of 1.0 VDC/cm. b) With the voltage gradient of 1.5 VDC/cm.

The pH values of the sediment samples extracted from the cells after decontamination with the voltage gradients of 1 and 1.5 VDC/cm are shown in Figures 11a and b. Initially, before conducting the electrokinetic treatment, the pH of Takab tailing dam sediment was 8.83.

As shown in Figures 11a and b, the pH distribution within the sediment in all tests is

similar in the region between the cathode and anode electrodes, where the pH values are around 8-12. Since the sediment has buffer capacity, 16.8% of the sediment consists of CaO that was added to gold ore in the process, and the electrolysis reaction products (H⁺ and OH⁻) did not affect the sediment pH; thus, this item had a low variation.

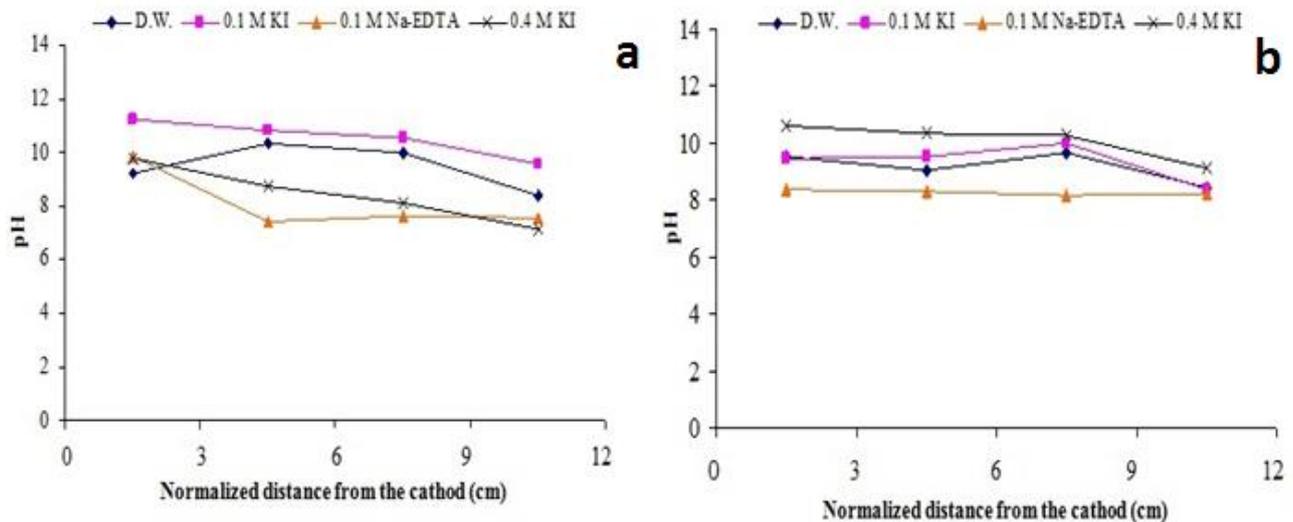


Figure 11) Sediment pH variations a) with the voltage gradient of 1.0 VDC/cm. b) With the voltage gradient of 1.5 VDC/cm.

4.5–Water content profiles of soil and sediment

The percent of contaminated soil after decontamination with 1 and 1.5 VDC/cm voltages gradients is presented in Figures 12a and b.

Although the initial soil moisture content was 30 percent, as shown in the mentioned figures, the percentage of moisture in nearly all the samples has become higher than 30 percent after decontamination. According to the soil pH diagrams and these diagrams, it can be deduced

that the lower the soil pH, the higher the moisture in the sample. In addition, during the extraction, the samples adjacent to the cathode were considerably harder. It is noteworthy that

the difference in moisture content of decontaminated samples was higher in the cell with higher voltage gradient.

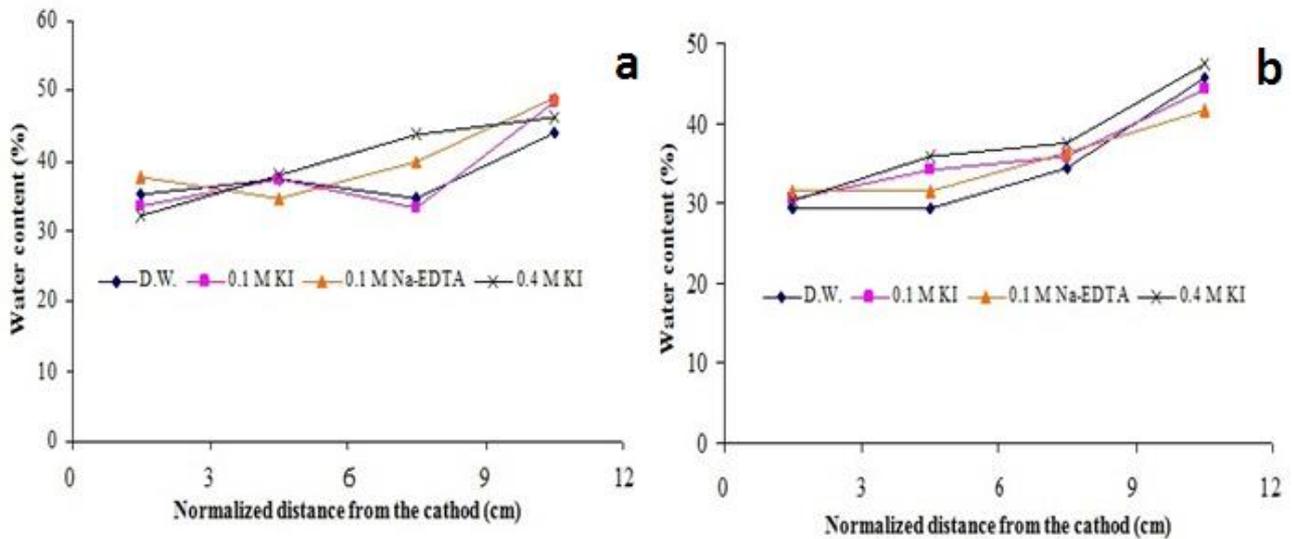


Figure 12) Soil water content variations a) with the voltage gradient of 1.0 VDC/cm. b) With the voltage gradient of 1.5 VDC/cm.

Figures 13a and b show the water content in the sediment samples after electrokinetic

remediation with the voltage gradients of 1 and 1.5 VDC/cm, respectively.

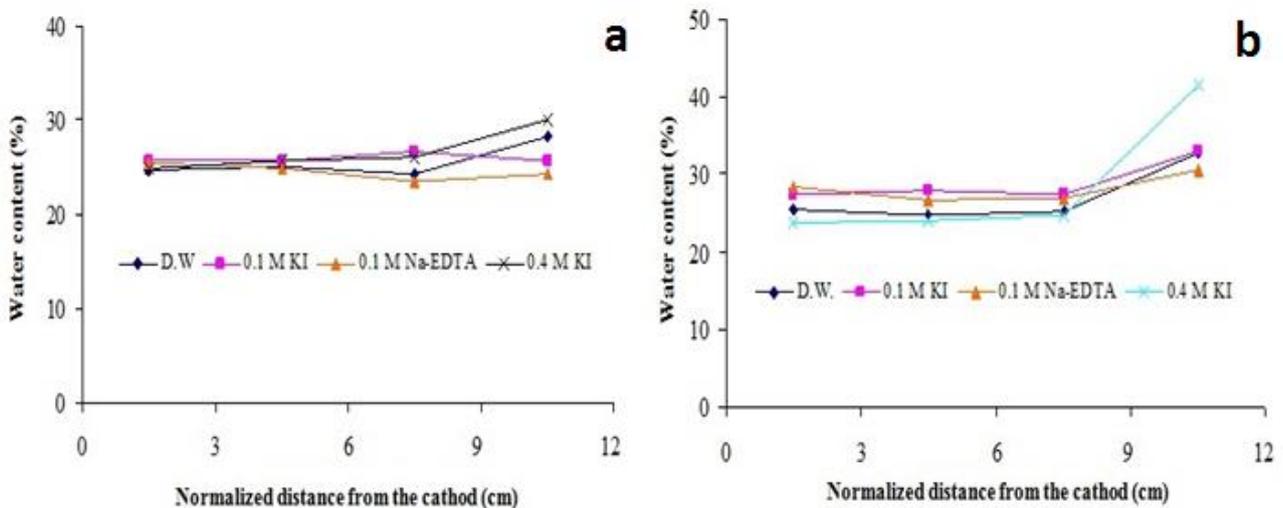


Figure 13. Sediment water content variations a) with the voltage gradient of 1.0 VDC/cm. b) With the voltage gradient of 1.5 VDC/cm.

Before treatment, the clayey soil was placed in the cells with the initial water content of 25 percent. Except for the two samples near the anode, the other samples had water content similar to the initial amount.

4.6–Electrical conductivity profiles

Electrical conductivity of soil confirms the existence of water-soluble salts in the soil. Its low value shows removal of ions from the soil during the decontamination process, leading to the increase the soil’s electrical resistance. Increased value of this parameter also indicates accumulation of ions and salts in the soil sample; however, this is not necessarily an

indication that the soil has not been decontaminated. In this study, the amount of soluble salts was determined by the 1:2 (V:V) soil to water extraction method presented by Dellavallem (1992).

Figures 14a and b further show the values of this parameter after decontamination of soil by the voltage gradients of 1 and 1.5 VDC/cm.

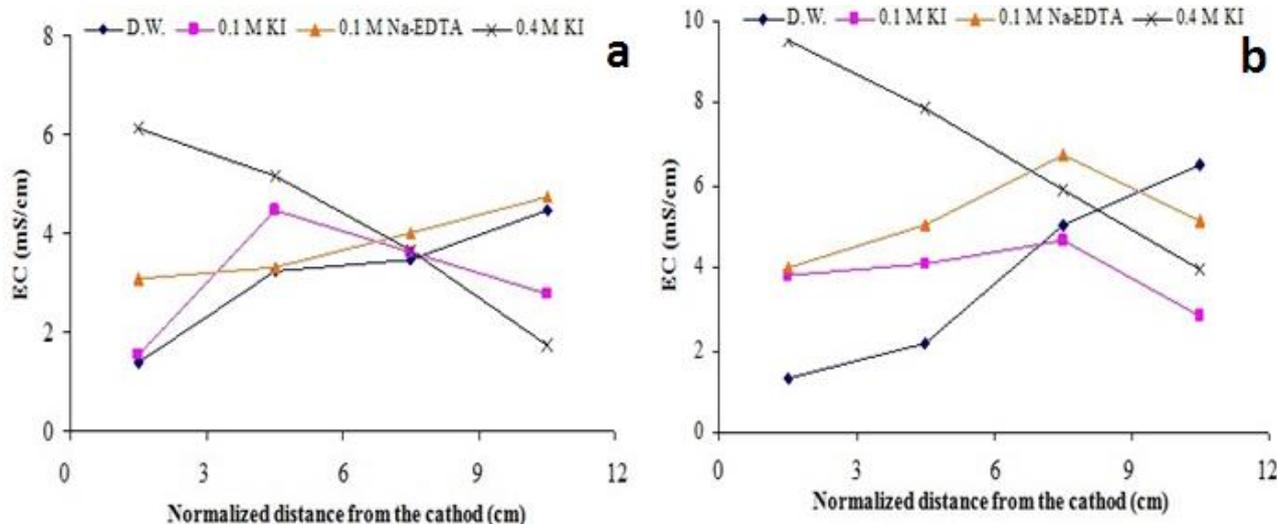


Figure 14. Soil electrical conductivity variations a) with the voltage gradient of 1.0 VDC/cm. b) With the voltage gradient of 1.5 VDC/cm.

As the diagrams show, the lowest value of the electrical conductivity of soil was reached when the highest efficiency of mercury removal was achieved in the cathode reservoir by the 0.4M solution of KI as catholyte and the voltage gradient of 1 VDC/cm.

Figures 15a and b present the electrical conductivity of the sediment samples measured upon completion of the electrokinetic tests.

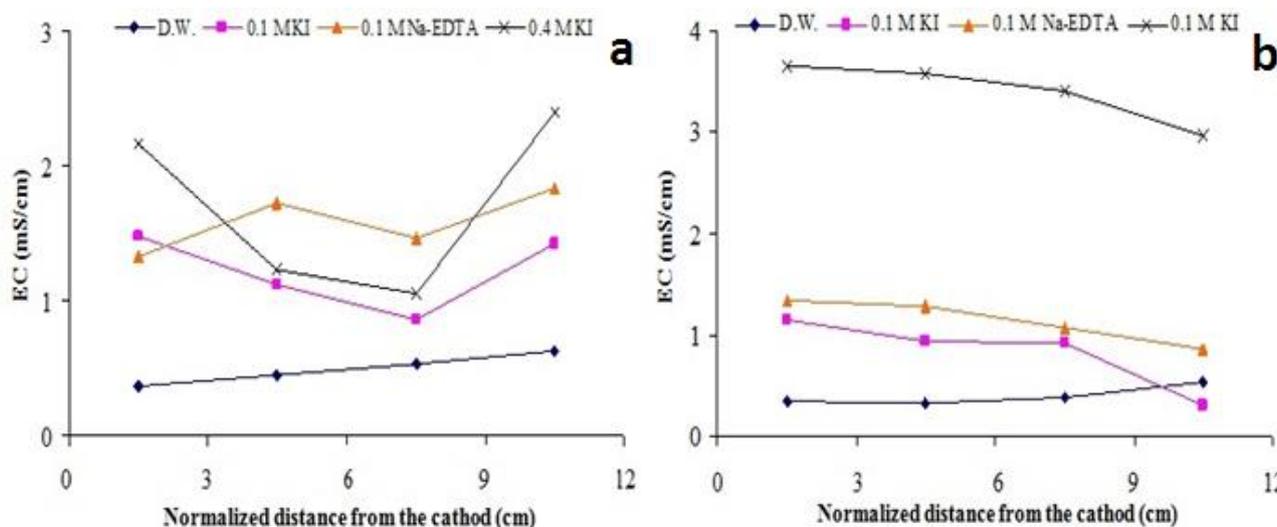


Figure 15) Sediment electrical conductivity variations a) with the voltage gradient of 1.0 VDC/cm. b) With the voltage gradient of 1.5 VDC/cm.

As shown, the initial electrical conductivity of the soil was 1036 μ S/cm, which was decreased

in the cells using distilled water in the cathode reservoir, though it was increased in the other

cells using KI and Na-EDTA as purging solutions.

5–Conclusions

- In decontamination of samples, except for the cells using distilled water as catholyte, the voltage gradient of 1 VDC/cm was more efficient than 1.5 VDC/cm. The highest efficiency was observed when using distilled water anolyte, 0.4M KI catholyte and 1 VDC/cm voltage gradient.

- As mercury compounds in the majority of soils are poorly soluble, the use of KI in mercury removal from the samples resulted in the formation of soluble HgI₄²⁻ complex and increased the rate of mercury removal from the soil.

- In using Na-EDTA as catholyte, due to lack of sufficient complex formation with negative charge, mercury removal efficiency was not high as compared to the KI solution.

- The reason for unsuccessful treatment of mercury in the sediment may be due to the presence of CaO and organic compounds in it. Because metals are soluble in low pH conditions in sediment, the presence of CaO causing acidic condition was not dominated in the sediment.

Acknowledgments:

The authors would like to thank Dr. S. Javanshir and an anonymous reviewer for their kind and careful comments that made the manuscript improved. They also wish to thank Tarbiat Modares University for providing the possibility of conducting this research.

References:

- Anonymous. 2000. Constructing a solution to a mercurial problem. *Environmental Science and Technology*: 34, 241A-241A.
- Biester, H., Schuhmacher, P., Muller, G. 2000. Effectiveness of mossy tin filters to remove mercury from aqueous solutions by Hg(II) reduction and Hg⁰ amalgamation. *Water Research*: 34, 2031-2036.
- Carr, G. M., Neary, J. P. 2008. *Water Quality for Ecosystem and Human Health*, 2nd Edition, United Nations Environment Programme Global Environment Monitoring System (GEMS)/Water Programme.
- Clarkson, T. W. 1993. Mercury: major issues in environmental health, *Environmental Health Perspectives*: 100, 31–38.
- Cox, C. D., Shoesmith, M. A., Ghosh, M. M. 1996. Electrokinetic remediation of mercury-contaminated soils using iodine/iodide lixiviant. *Environmental Science and Technology*: 30: 1933–1938.
- Dellavalle, N. B. 1992. Determination of specific conductance in supernatant 1:2 soil: water solution, *Handbook on Reference Methods for Soil Analysis*, Soil and Plant Analysis Council, Inc., Athens, 44–50 pp.
- Domenico, P. A., Schwartz, F. W., 1998. *Physical and chemical hydrogeology*. John Wiley and Sons, Inc., New York.
- Fenglian, Fu., Wang, Qi. 2011. Removal of heavy metal ions from wastewater: a review. *Journal of Environmental Management*: 92, 407–418.
- Gilmour, J. T. 1971. Inorganic Complexes of Divalent Mercury in Natural Water Systems. *Environmental Letters*: 2, 143–152.
- Hanke, K. R., Kuhnel, V., Stepan, D. J., Fraley, R. H., Robinson, C. M., Charlton, D. S., Gust, H., Bloom, N. S. 1993. *Critical Review of Mercury Contamination Issues Relevant to Manometers at Natural Gas Industry Sites*, Gas Research Institute, GRI-93/0117, Chicago.
- Hem, J. D. 1970. *Chemical Behavior of Mercury in Aqueous Media*, Mercury in the environment, USGS Paper 713, U.S. Geological Survey, Reston, Va., pp. 19–25.
- Hempel, M., Thoeming, J. 1999. Remediation techniques for Hg-contaminated sites, In: R. Ebinghaus, R. R. Turner, L. D. de Lacerda, O. Vasiliev and W. Salomons (Eds.), *Mercury Contaminated Sites, Characterization, Risk Assessment and Remediation*, Springer Publishing, New York, pp. 113–130.
- Hinton, J., Veiga, M. 2001. Mercury contaminated sites: a review of remedial solutions, *Proc. NIMD (National Institute for Minamata Disease) Forum 2001*, Mar. 19-20, Minamata, Japan.

- Hunter, R. J. 1981. Zeta potential in colloid science, Academic Press, London.
- Johnson, P. C., Kemblowski, M. W., Colthart, J. D. 1990. Quantitative analysis for the cleanup of hydrocarbon contaminated soils by in-situ soil venting. *Ground water*: 28, 413-429.
- Larry, R., Jose, L. 1990. Final Best Demonstrated Available Technology (BDAT) background document for mercury containing wastes, U.S. Environmental Protection Agency, Washington, pp. 1-5.
- Lindgren, E. D. 1991. Electrokinetic remediation of contaminated soil, Presented at the Environmental Restoration '91 Conference Pasco, Washington. September 8 through 10.
- Lindqvist, O. 1991. Special issue of first international on mercury as a global pollutant. *Water, Air, and Soil Pollution*: 56, 1-8.
- Matsuyama, A., Iwasaki, H., Kigaki, K., Yabuta, H., Sano, T., Akagi, H. 1999. Study on the remediation technology of mercury-compound contaminated soil by low temperature thermal treatment, In: R. Ebinghaus, R. R. Turner, L. D. de Lacerda, O. Vasiliev and W. Salomons (Eds.), *Mercury Contaminated Sites, Characterization, Risk Assessment and Remediation*, Springer Publishing, New York, pp. 421-440.
- Mattson, E. D., Lindgren, R. E. 1993. Electrokinetic extraction of chromate from unsaturated soils, Presented at Emerging Technologies in Hazardous Waste Management V., September 27 through 29.
- Palermo, M. R. 1998. Design considerations for in-situ capping of contaminated sediments. *Water Science and Technology*: 37, 315-321.
- Reddy, K. R., Chaparro, C., Saichek, R. E. 2003. Iodide-enhanced electrokinetic remediation of mercury-contaminated soils. *Journal of Environmental Engineering*: 129:1137-1148.
- Lageman, R., Clarke, R. L., Pool, W. 2005. Electro-reclamation, a versatile soil remediation solution. *Engineering Geology*: 77, 191-201.
- Sengupta, A. K. 2002. Environmental separation of heavy metals: engineering processes, Lewis Publishers.
- Sobolev, I. A., Barinov, A. S., Prozorov, L. B., Kuptsov, V. M. 1996. Remediation of Hg Contaminated Soil. *International Congress on Environmental Geotechnics*: 2, 1083-1088.
- Thoming, J., Sobral, L., Wilken, R. D. 1999. Electroleaching: a mobile clean-up process for mercury contaminated materials, In: R. Ebinghaus, R. R. Turner, L. D. de Lacerda, O. Vasiliev and W. Salomons (Eds.), *Mercury Contaminated Sites, Characterization, Risk Assessment and Remediation*, Springer Publishing, New York, pp. 441-456.
- U.S. Army Engineering Corp., 2000. In-situ electrokinetic remediation for metal contaminated soils, USEAC Environmental Technology, Website: <http://aec-www.apgea.army.mil:8080/prod/usaec/et/restor/insitu.Htm>.
- Unger, A. J. A., Sudicky, E. A., Forsyth, P. A. 1995. Mechanisms controlling vacuum extraction coupled with air sparging for remediation of heterogeneous formations contaminated by dense non-aqueous phase liquids. *Water Resources Research*: 31, 1913-1925.
- Van, C. I. 1997. Electrokinetic, Ground Water Remediation Technologies Analysis Center. Technology Overview Report, To-97-03.
- Waybrandt, K. R., Blowes, D. W., Ptacek, C. J. 1998. Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. *Environmental Science and Technology*: 32, 1972-1979.