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Simultaneous Application of Electrokinetic and Washing Solvents for the Decontamination of Zn and Pb from tailings of Angouran lead and Zinc Mine

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Abstract

Mining activities have led to the accumulation of large quantities of mineral tailings containing potentially hazardous metals, contaminating the surrounding soil. This study investigated the effectiveness of electrokinetic remediation combined with washing solvents for the decontamination of zinc and lead from mine tailings. Samples were collected from various locations within the Angouran mine in Zanjan, Iran, and analyzed for total metal concentration using the standard ICP method. Electrokinetic tests were conducted using different washing solutions-hydrochloric acid, nitric acid, acetic acid, and sulfuric acid-each at a concentration of 0.1 M and mixed with soil in a 1:2 solution-to-solid ratio. A voltage of 1.5 V/cm was applied throughout the experiments. To mitigate heavy metal precipitation near the cathode, the same chemical solutions were used in the cathode chamber. The results demonstrated that distilled water resulted in the lowest removal efficiency for zinc (16%) and lead (11.5%), while hydrochloric acid showed the highest removal efficiencies of 64% for zinc and 45% for lead. These findings indicated that electrokinetic remediation, particularly when using hydrochloric acid as a complexing agent, was an effective method for removing significant quantities of zinc and lead from contaminated soil.

1. Introduction

There is a high demand for large amounts of fuels, industrial chemicals, various fertilizers, pesticides, and drugs, which has resulted in millions of tons of hazardous tailings in many locations worldwide. These pollutants pose a significant threat to the quality of water, soil, and ecosystems. Therefore, it is crucial to implement effective measures to address and mitigate their impact [1-3]. Mine tailings, animal manures, waste, and sewage, as well as leaks and penetration of petrochemical, oily, and acidic materials into the ground, are the primary causes of soil contamination [4-6]. The mining industry is a significant economic activity contributing to the global economy. Although mining is critical to economic growth, it has significant environmental consequences that cannot be overlooked. The mining industry has a wide range of environmental effects on both small and large scales [7-9]. Waste generated due to mining activity poses a serious issue due to the large amounts generated, even up to 65 billion tons per year, and is often associated with the risk posed by its storage and environmental management, which contain heavy metals, combustible materials, hazardous waste, and contaminating gases in varying concentrations. Zinc (Zn), chromium (Cr), arsenic (As), lead (Pb),

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Corresponding author: amirhosseinkarimi@shahroodut.ac.ir (A.H. Karimi) cadmium (Cd), and mercury (Hg) are among the hazardous metals discovered at contaminated sites.

Several measures have been implemented in recent decades to reduce the problems caused by mining activities, which has resulted in the development of novel methods for the remediation of contaminated soils, such as bioremediation, phytoremediation, soil cultivation, extraction of contaminant vapors, solidification and stabilization, thermal contamination removal, soil washing, biological remediation, and electrokinetics [10,11]. It should be noted that these methods are not universal, and the method chosen depends on the location and properties of the contaminated site, the type of contamination, and the contaminant's properties.

Electrokinetic remediation is a promising method for cleaning soils, particularly fine-grained soils contaminated with organic and inorganic materials [12-14]. Compared to other soil remediation methods, electrokinetics is relatively safe, effective, simple, and cost-effective [15,16]. Electrical migration, electrophoresis, diffusion, and electroosmosis are contaminant transport processes that can be used in electrokinetic remediation [17,18]. When an electric current is applied to the soil, electrolysis reactions or water decomposition will occur at the electrodes. Because of the oxidation phenomenon, electrolysis reactions at the anode generate oxygen gas and hydrogen ions, whereas they generate hydrogen gas and hydroxide ions at the cathode [19]. The electrolysis reactions at the electrodes are depicted in Equations 1 and 2:

$$2H_2O \rightarrow O_2+4H^{+}+4e \quad (1)$$

$$4H_2O+4e^{-} \rightarrow 2H_2+4OH \quad (2)$$

Given the electrolysis reactions at the electrodes, it produces an acidic front at the anode and a basic front at the cathode, resulting in decreased and increased pH at the anode and cathode, respectively. Ions are also attracted to one another and produce water when they collide.

The pH level in the soil sample changes due to the presence of electroosmotic (EO) flow and ionic migration. The pH of the soil sample rises as it moves from the anode to the cathode. The increased pH level of the soil sample on the cathode side caused by water electrolysis results in heavy metal deposition, which reduces the efficiency of electrokinetics. To overcome this limitation, solutions other than distilled water can be used near the electrodes to reduce the pH, preventing heavy metal deposition and, in some cases, causing their release from the soil. The electrokinetic process is heavily influenced by soil pH and electrolysis reaction [20]. The solutions used must create the proper pH conditions in the soil and interact with the metals in the soil to cause them to be removed. In general, the efficiency of organic and inorganic matter removal is affected by chemical processes in the electrodes, soil mechanical properties, soil moisture, pore fluid properties, contaminant compounds, voltage and current intensity applied, electrolyte type, and electrokinetic test conditions [21]. Some researchers have combined the electrokinetic method with other remediation techniques to enhance remediation efficiency. For example, Alyani [22] investigated nitrate removal from fine-grained soil using the electrokinetic technique in conjunction with a granular activated carbon-permeable reactive barrier. Soil washing is a method of removing contaminants from soil that uses either a physical or chemical technique. The water used in this process can be pure or contain additives like acids, bases, surfactants, solvents, or separating agents that aid in separating contaminants from soils and sediments [23]. Organic compounds, heavy metals, pesticides, and petroleum products are among the contaminated target groups of this process. Soil washing can occur in or ex situ. During in-situ soil washing, chemical solutions are injected into or sprayed on the contaminated area to mobilize contaminants. After mixing the extraction solution with the contaminants, the contaminant solutions are collected and discarded using suction filtration methods. Lower-permeability oils are deemed unsuitable for in-situ washing, necessitating the excavation of contaminated soil. According to published research some researchers have made significant efforts to use soil washing techniques in the electrokinetic method to increase metal removal efficiency [24,25]. Giannis demonstrated that soil pH and leaching solutions are the most important factors in dissolving and excreting cadmium metal from soil under electric field, and that this method could remove 85 percent of cadmium from contaminated soil [26].

In the field of electrokinetic remediation, significant advancements have been made in improving the removal efficiency of heavy metals from contaminated soils. Cai et al. [27] conducted a pivotal study that examined the role of electrode materials in electrokinetic processes. Their research demonstrated that the choice of electrode material can drastically influence the efficiency of lead removal from soils. This finding is crucial as it underscores the need to select appropriate materials to optimize the remediation process, a consideration that is also relevant to the current study where we aim to enhance the electrokinetic removal of lead from mine tailings.

Building on these advancements, Hussein and Alatabe [28] explored the integration of renewable energy sources into electrokinetic remediation. They successfully utilized solar energy to drive the electrokinetic process, achieving removal efficiencies as high as 90.7% in sandy soils. Their work not only highlights the potential for sustainable energy solutions in environmental remediation but also sets a benchmark for the levels of efficiency that can be attained. In our research, while we focus on the application of traditional DC power sources, the insights from Hussein and Alatabe inspire considerations for future studies where renewable energy could be incorporated to reduce operational costs and environmental impact.

Furthermore, the enhancement of electrokinetic remediation through chemical methods has been explored by Faisal and Hussein [29]. They introduced an acidic injection well technique that significantly improved the electrokinetic removal of copper from contaminated soils. This method highlights the potential for chemical pre-treatments or in-situ adjustments to soil pH to enhance the mobility of heavy metals, thereby improving the overall efficiency of the remediation process. Our study takes inspiration from this approach by investigating the effects of different washing solvents on the mobility and removal efficiency of lead and zinc during electrokinetic remediation. The insights provided by Faisal and Hussein [29] demonstrate the importance of optimizing both the physical setup and the chemical environment within the remediation system.

These studies collectively inform the design and execution of the current research. By incorporating lessons learned from the impact of electrode materials, the potential for renewable energy integration, and the use of chemical enhancements, our work aims to push the boundaries of what is achievable in the remediation of lead and zinc from mine tailings. The combination of these strategies holds promise for developing more efficient, cost-effective, and environmentally sustainable remediation techniques.

Kalumba and Mudenge [30] explore the potential role of electrokinetics technology in the dewatering of tailings and the recovery of valuable minerals. Their research highlights the dual functionality of electrokinetic methods, which can simultaneously dewater tailings and extract metals, making it a highly efficient approach for managing mine waste. They discuss how electroosmosis and electromigration processes can be harnessed to achieve these outcomes, with particular emphasis on the benefits of integrating these processes to enhance both environmental sustainability and economic viability in mining operations.

This study is particularly relevant to the current research, which also investigates the application of electrokinetics for metal recovery. However, while Kalumba and Mudenge [30] focus on the broader implications of combining dewatering with metal extraction, our research narrows down to the specific effects of different acid-based washing solvents on the electrokinetic removal of zinc and lead from mine tailings. By focusing solely on the remediation aspect, our work aims to optimize the efficiency of metal extraction under controlled conditions, without addressing the dewatering process. This distinction highlights a more targeted approach to understanding the interactions between chemical agents and electrokinetic forces in heavy metal remediation.

When compared to the study by Faisal and Hussein [29], which investigated the effects of electrokinetic technology under the influence of washing and buoyancy forces with different purging solutions on the removal of zinc, lead, and nickel from contaminated soil, our research presents a distinct approach. Faisal and Hussein [29] introduced the concept of buoyancy forces and utilized EDTA as a purging solution to enhance metal mobility under inclined conditions. In contrast, our research does not incorporate buoyancy forces or chelating agents like EDTA. Instead, it focuses on directly comparing the effectiveness of various acids—such as acetic, hydrochloric, nitric, and sulfuric acids—as purging solutions, offering a more straightforward assessment of these acids' influence on metal removal efficiency.

This study aimed to investigate the effectiveness of electrokinetic zinc and lead removal from mine tailings using various purging and washing solutions. This study included two series of experiments. The soil was saturated with distilled water and various solutions were used as washing solutions (purging solutions) in the first series. In contrast, the soil was washed with different acids at a fixed concentration of 0.1 M in the second. The distribution of zinc and lead was also investigated during the experiment.

Despite the advancements in soil remediation techniques, significant challenges remain, particularly in addressing the limitations of conventional methods when dealing with fine-grained soils contaminated with heavy metals. Existing studies have demonstrated varying levels of success using electrokinetic remediation independently or in conjunction with chemical agents. However, there is limited understanding of the synergistic effects when electrokinetics is combined with specific washing solvents, especially in the treatment of mine tailings. This study seeks to fill this gap by systematically evaluating the effectiveness of using hydrochloric acid, nitric acid, acetic acid, and sulfuric acid as washing agents in electrokinetic remediation. Our research aims to provide new insights into the optimization of electrokinetic processes, particularly in enhancing the removal efficiency of zinc and lead from contaminated soils, thereby contributing to more effective and sustainable soil remediation strategies.

2. Materials and methods

2.1. Study Area and Sample Collection

The Angouran mine and the Angouran production plant in Zanjan province are Iran's largest producers of lead and zinc (Figure 1). Located in Mahneshan city, 135 kilometers west of Zanjan, Iran, the Angoran mine contains significant mineral reserves. The mine holds eight million tons of zinc reserves in the open sector, four million tons of high-grade zinc reserves in the underground sector, and substantial lead reserves distributed across both sectors.

We used Angouran mine tailings to test the efficiency of electrokinetics in removing the zinc and lead contaminants. As a result, the area was visited, the sources of contamination were thoroughly investigated, and the necessary samples were collected from the tailing (Figure 2).

2.2. Soil Characterization

The soil samples were collected from the Angouran mine tailings. The samples underwent analysis to determine the concentration of various elements using the standard Inductively Coupled Plasma (ICP) method. The tailings were found to contain different concentrations of toxic and hazardous metals, with zinc and lead being the primary contaminants (as shown in Table 1).

The mineral composition of the soil was determined through X-ray diffraction (XRD) analysis, as illustrated in Figure 3. Table 2 presents the minerals of the tailing soil. The main minerals of tailing are gypsum, calcium aluminum oxide, calcium carbonate and quartz. The soil pH was measured according to the EPA 9045D method, yielding a pH value of 6. The electrical conductivity (EC) of the soil was measured using a CLEAN company CON 500 EC meter, following the procedure of Peng and Tian [31].

The cation exchange capacity (CEC) of the soil was determined using the US EPA 9081A method, resulting in a CEC value of 8.8 meq/100 g, which is relatively low, indicating a potential for enhanced remediation efficiency. The CEC of the studied sample is low, as shown in Table 3. Additionally, the point of zero charge (PZC) was determined using the Vakros [32] method providing insight into the surface charge properties of the soil particles.

Soil moisture content was calculated based on the weight loss after heating the samples to 105°C.

Table 1. Properties of Angouran Tailings

Characteristics of tailing	Value
pH	6
*EC (µs)	2377
**CEC (meq/100g)	8.8
***PZC (pH)	5.2
Moisture (%)	3.18
Fe (g/kg)	35.6
Pb (g/kg)	28.2
Zn (g/kg)	10.38
Cu (g/kg)	0.18
Mn (g/kg)	0.116
Mo (g/kg)	0.047
Ag (g/kg)	0.041
Cd (g/kg)	0.038
Cr (g/kg)	0.034
Ce (g/kg)	0.014
Ni (g/kg)	0.011

*EC=Electrical Conductivity
**CEC = Cation Exchange Capacity
***PZC= The point of zero charge

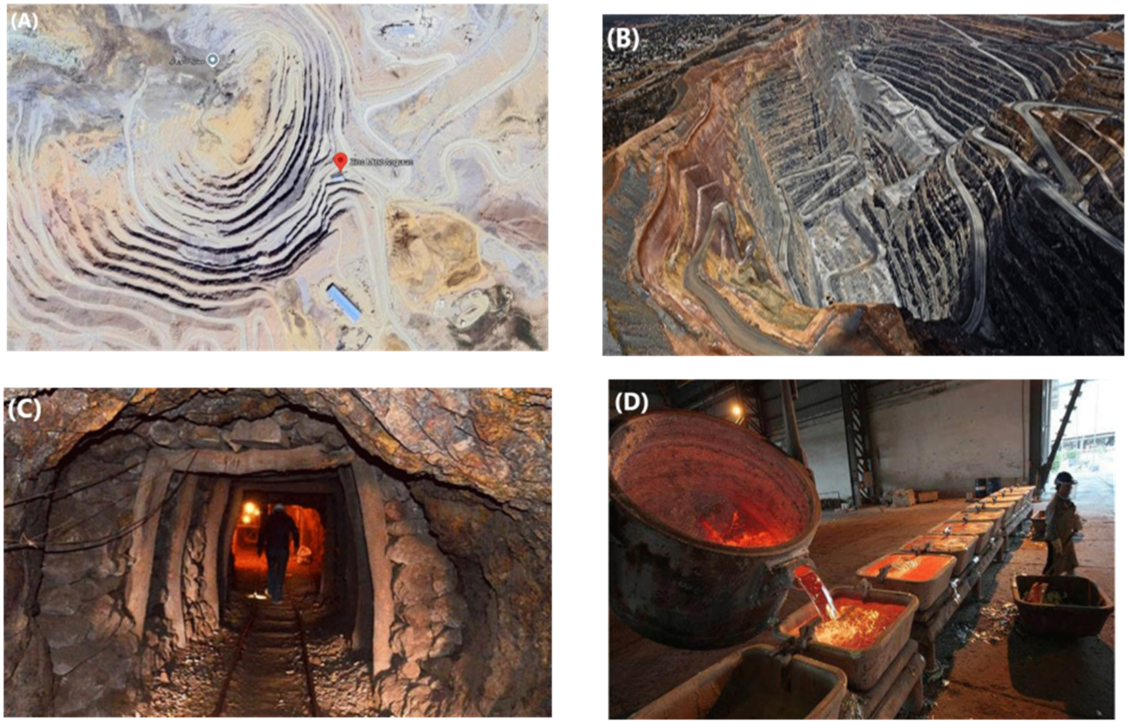

Figure 1. Overview of the Angouran lead and zinc mineral processing plant, showing the location of the sampled soil used in this study (A) photo by google earth (B) perspective mine (C) mining tunnel (D) mine products

(a) (b)

Figure 2. Images depicting (a) the soil sample before treatment and (b) the soil sample after molding and electrokinetic (EK) treatment.

Table 2. The main minerals of Angouran tailing

Compound Name	Chemical Formula	Score	Semi Quant [%]
Gypsum	$Ca (SO_4) (H_2O)_2$	46	20
Calcium Aluminum Oxide	$Ca_4 (Al_6O_{12}) (SO_4)$	22	35
Calcium Carbonate	$CaCO_3$	17	4
Quartz	SiO_2	41	41

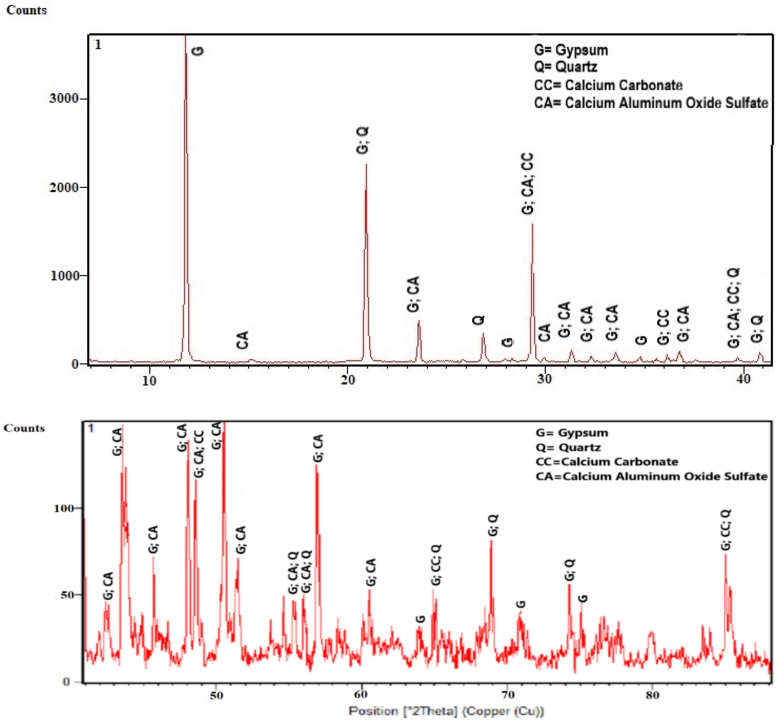

Figure 3. XRD pattern of the soil sample within the 0-90° 2θ range, identifying the mineral phases present before treatment.

Table 3. Soil CEC classification

CEC Classification	CEC (meq/100g)
Very Low	6>
Low	6-12
Middle	12-25
High	25-40
Very High	40<

2.3. Experimental Setup

2.3.1. Description of Electrokinetic Cell

The electrokinetic experiments were conducted using the setup illustrated in Figure 4. The experimental cell consisted of three Plexiglas sections. The central chamber, designated for soil, was a cylindrical compartment measuring 20 cm in length and 7 cm in diameter. The anode and cathode reservoirs, each measuring 7 cm by 5 cm, were positioned at either end of the soil chamber and separated by perforated steel mesh plates. These mesh plates facilitated the connection between the electrolyte and soil chambers, enabling the flow of the electrolyte solution from the anode through the soil chamber and into the cathode reservoir, driven by electroosmotic flow.

Stainless steel electrodes were placed within the anode and cathode reservoirs. A filter paper barrier was employed to prevent soil particles from migrating into the electrolyte chambers. To maintain a consistent electrolyte solution and prevent pH gradient formation, a peristaltic pump was used to circulate the solution within the anode and cathode tanks. The electroosmotic flow, a crucial parameter in the electrokinetic soil remediation process, was monitored using a calibrated tube attached to the cathode chamber to measure the effluent.

2.4. Experimental Procedure

Electrokinetic test conditions are shown in Table 4. This study included two series of experiments. The soil was saturated with distilled water in the first series, and different acids with concentrations of 0.1 M were used to wash the contaminants effectively. In the second ones, the soil was saturated at 0.1 M with organic and inorganic acids such as acetic acid, hydrochloric acid, nitric acid, and sulfuric acid. For purging solutions, the same acids were used. The soil was saturated with acids in a 1:2 ratio (acid to soil). In this study, three inorganic acids (hydrochloric acid, nitric acid, and sulfuric acid) and one organic acid (acetic acid) were selected for the experiments. The inorganic acids were chosen due to their strong acidic nature and high dissociation constants, which make them effective in dissolving metal contaminants and altering soil pH. The organic acid, acetic acid, was included to evaluate its performance as a milder alternative to inorganic acids, with the potential for reduced environmental impact while still forming stable complexes with metal ions for efficient extraction. All experiments were carried out in 24 hours at 1.5 V/cm. Following the completion of the experiments, the soil sample was divided into four equal parts, and the concentration of zinc and lead heavy metal and its pH were measured for each separated part. The tests were conducted twice and the averages of the results were used.

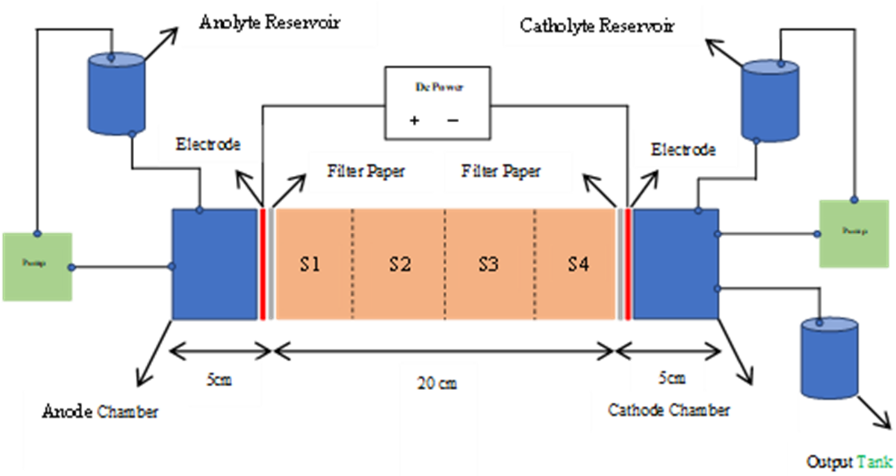

Figure 4. Schematic representation of the experimental setup used for electrokinetic treatment, showing the placement of electrodes, reservoirs, and the soil sample.

Table 4. Experimental conditions for each experiment

Series No.	Test	Voltage (V/cm)	Saturation Solution	Anolyte	Catholyte
1	1(A)	1.5	DW	DW	DW
	1(B)	1.5	DW	DW	Acetic Acid 0.1 M
	1(C)	1.5	DW	DW	Hydrochloric Acid 0.1 M
	1(D)	1.5	DW	DW	Nitric Acid 0.1 M
	1(E)	1.5	DW	DW	Sulfuric Acid 0.1 M
2	2(A)	1.5	Acetic Acid 0.1 M	DW	Acetic Acid 0.1 M
	2(B)	1.5	Hydrochloric Acid 0.1 M	DW	Hydrochloric Acid 0.1 M
	2(C)	1.5	Nitric Acid 0.1 M	DW	Nitric Acid 0.1 M
	2(D)	1.5	Sulfuric Acid 0.1 M	DW	Sulfuric Acid 0.1 M

3. Results and Discussion

3.1. Electroosmotic flow and concentration variations of zinc

A porous medium is a solid frame or matrix permeated by an interconnected network of pores (voids) filled with a fluid (liquid or gas). In the field of micro- and nanofluidics, the term electroosmotic flow (usually interchangeable with electroosmosis or electrokinetic flow) is defined as the migration of bulk ionic liquid due to the interaction between an applied electric field tangentially along a charged surface and the excess net charge density in the electric double layer of such a charged surface. Therefore, electrokinetic flow in porous media is referred to as the motion of bulk ionic liquid flowing through a porous medium due to the interplay of an applied electric field and the excess charge density in the electric double layer of the charged porous structure. EO flow transported pore water through soil particles during electrokinetic remediation. This procedure is critical for removing contaminants from soil or tailing samples and transporting them via electrical migration. The main factors influencing EO flow are pore water properties (particularly pH), the intensity of the electric field used, and soil permeability. Pore water significantly impacts soil solution chemistry and zeta potential, influencing EO velocity. In previous experiment, EO flow generally occurred from the anode to the cathode, causing the volume of the anode reservoir solution to decrease while the volume of the cathode reservoir solution to increase [33]. The EO flow indicates the amount of effluent water. The more effluent water there is, the more water flows through the soil, increasing the efficiency of electrokinetic remediation. The cumulative electroosmotic flow changes in the first and second series of experiments are described in Figures 5(a) and 5(b). According to these two figures, the flow direction of the acids used as washing and purging solutions was normal. That is, the flow is directed from the anode to the cathode. In general, Potential toxic metals (PTMs) such as zinc and lead may migrate towards the cathode via the electrical migration mechanism and electroosmotic flow. When comparing Figures 5(a) and 5(b), it is clear that as washing solutions (second series) are used, the amount of cumulative electroosmotic flow (The volume of the solution exiting the cathode chamber) changes is greater than when acids are used as purging solutions (first series). This is due to the pH of soil pore water, which significantly influences EO flow. Each acid used decreased the soil pH while increasing the EO flow. Among the acids used, hydrochloric acid produced the most EO flow, indicating that any substance that produces more EO flow will be more efficient when compared to the remediation percentage. Hydrochloric acid caused a reaction with the contaminant, preventing it from settling. Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, and distilled water have the highest water effluent from the cathode chamber.

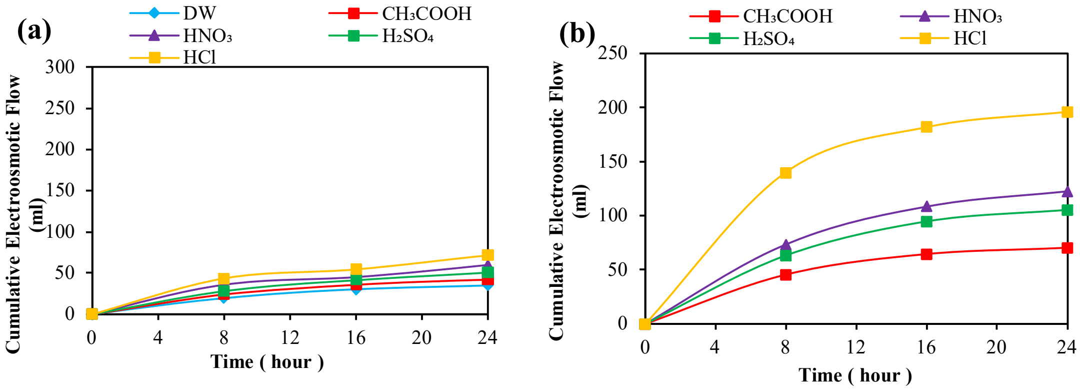

Figure 5. Cumulative electroosmotic flow variation observed during (a) the first series of experiments and (b) the second series of experiments.

Figures 6 and 7 show the ratio of residual zinc and lead concentration in the soil at the end of the experiment to their initial concentration in the first and second series of experiments, respectively. Zinc and lead are a positively charged metal and tend to move towards the negative pole, i.e., the cathode. As shown in these figures (6 and 7), more Zn and Pb was remediated in the sections near the anode reservoir. Due to high pH and Zn accumulation, the Zn and Pb remediation percentage decreased in sections near the cathode reservoir. Electrochemical remediation is generally affected by contaminant concentration, soil type, pH, and organic matter content. Since the contaminant ion was cationic, it must move towards the negative pole, i.e., the cathode. What is apparent in the figures of the concentration investigation is that a higher cleaning percentage is observed in sections close to the anode. The concentration ratio of more than one in sections relative to the cathode can be attributed to the accumulation of mobile contaminant ions and the increase in the absorption of these ions due to the rise in pH of the environment. As shown in Figures 6 and 7, inorganic acids are more capable of removing heavy metals than the organic acetic acid. According to our findings, the highest and lowest percentages of zinc metal remediation in the first series of experiments were observed with hydrochloric acid (25.5%) and distilled water (16%), respectively. Also, the highest and lowest percentage of lead metal remediation in the first series of hydrochloric acid and distilled water tests were 17.9% and 11.5%, respectively. According to the second series of experiments, hydrochloric acid and acetic acid had the highest and lowest percentages of remediation of zinc metal, with 64% and 27%, respectively. Also, the highest and lowest percentage of lead metal remediation in the second series of hydrochloric acid and distilled water tests were 45% and 19%, respectively.

Figures 8 and 9 explain the changes in electroosmotic flow volume versus the change in final concentration (percentage of zinc and lead removal in each series of tests) in the first and second test series. As shown in the figures, for a given series, different catholytes or saturated solutions lead to varying volumes of EO flow. Furthermore, when the results of the two series are compared, it is clear that using saturation solution (in the second series tests) causes more EO flow, resulting in more average removal through the soil sample. As a result, the greater the electroosmotic flow volume, the more zinc and lead are removed.

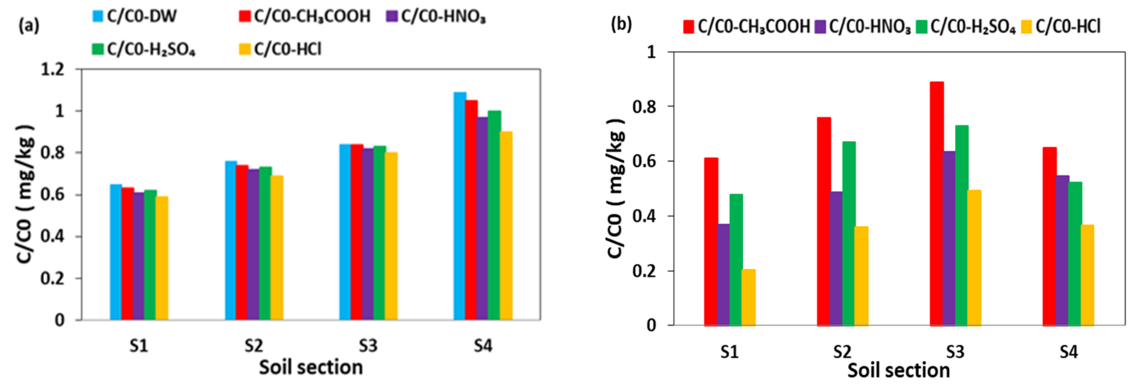

Figure 6. Variation in the concentration of zinc (Zn) in the soil over time for (a) the first series of experiments and (b) the second series of experiments.

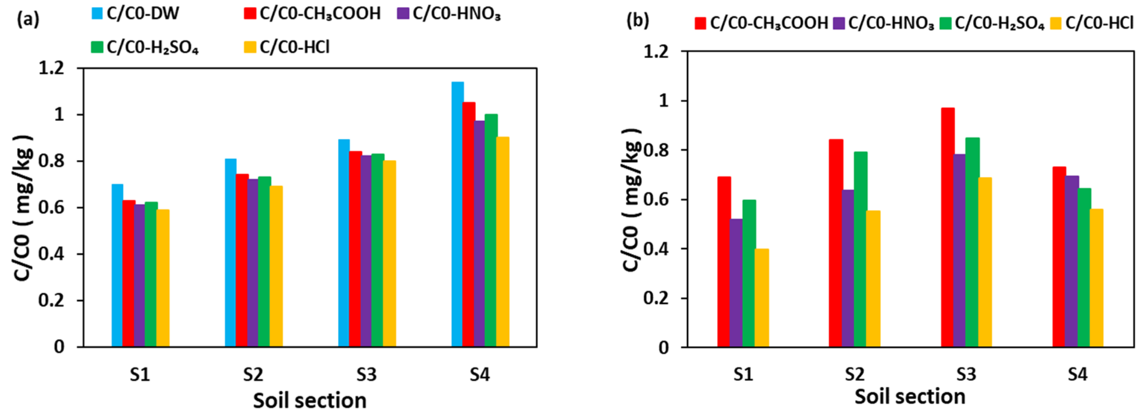

Figure 7. Variation in the concentration of lead (Pb) in the soil over time for (a) the first series of experiments and (b) the second series of experiments.

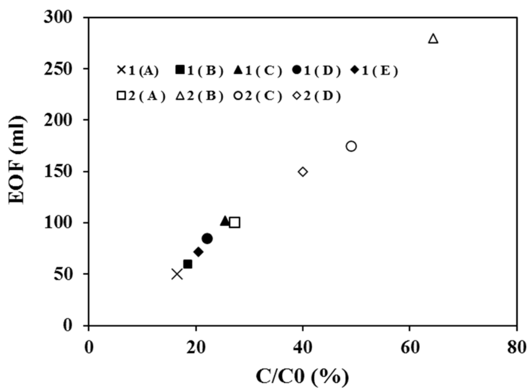

Figure 8. Changes in the concentration ratio (C/C0) of zinc metal relative to the initial concentration over time during electrokinetic treatment.

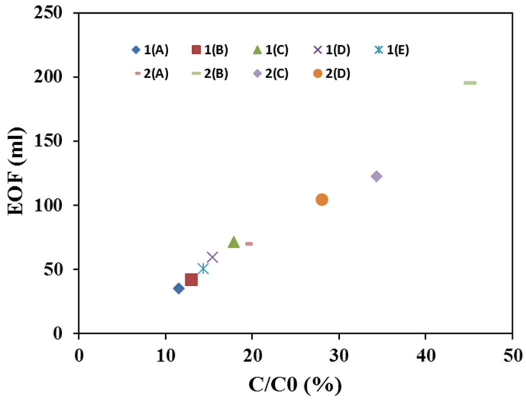

Figure 9. Changes in the concentration ratio (C/C0) of lead metal relative to the initial concentration over time during electrokinetic treatment.

3.2. pH variations in anode and cathode reservoirs and soil profile

Figure 10 shows the pH values measured at the anode and cathode reservoirs. The pH of the anode reservoir was decreased, while the pH of the cathode reservoir was increased, based on the results shown in these figures. This is due to the production of hydrogen ions (H^+) in the anode reservoir and hydroxide ions (OH^-) in the cathode reservoir. These modifications were observed in both series of experiments. The pH changes along the soil profile are depicted in Figures 11(a) and 11(b). The pH of the soil has changed throughout the soil. Ions formed by hydrogen and hydroxide entered the soil due to water electrolysis and altered the soil pH. Hydrogen ions move at twice the velocity of hydroxide ions, leading to a more pronounced development of the acidic zone compared to the basic zone. However, due to the short process time, the soil profile had few pH changes. As shown in Figures 11(a) and 11(b) the soil increments became more basic as one moved closer to the cathode reservoir.

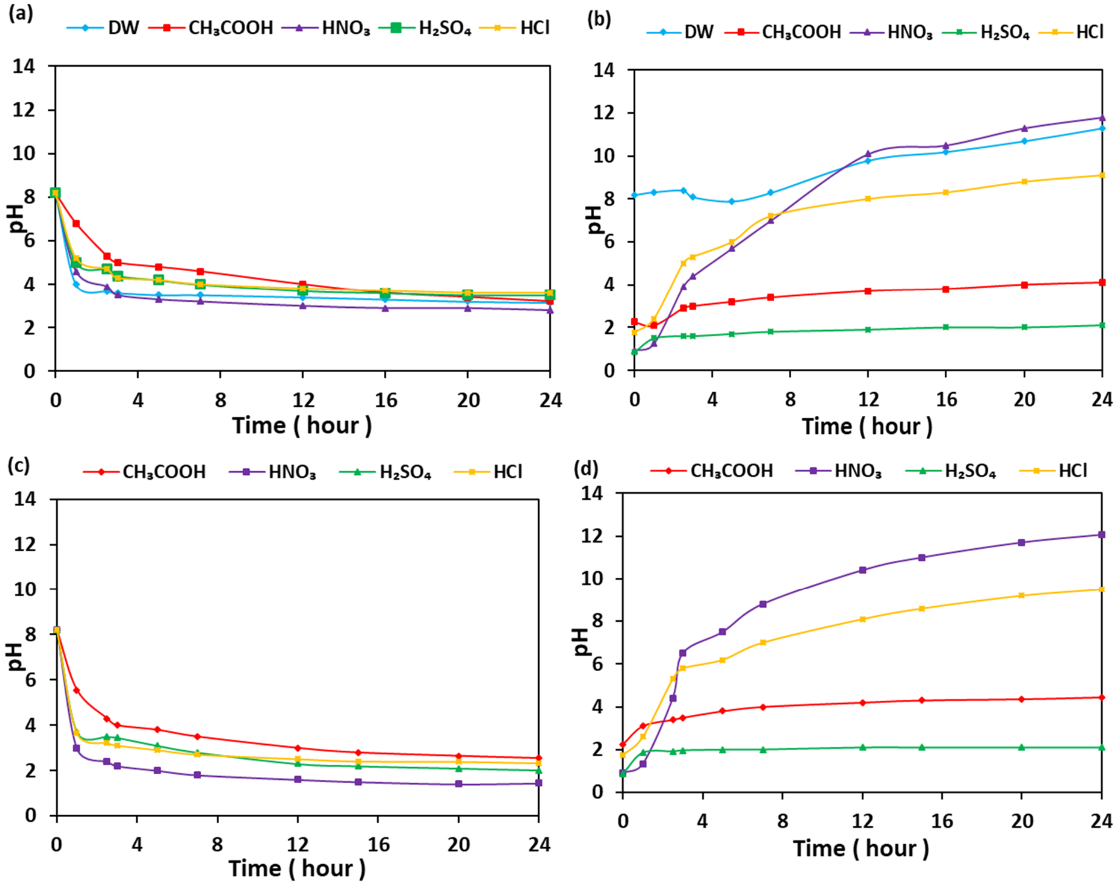

Figure 10. pH variation observed at (a) the anode and (b) the cathode in the first series of experiments, and at (c) the anode and (d) the cathode in the second series of experiments.

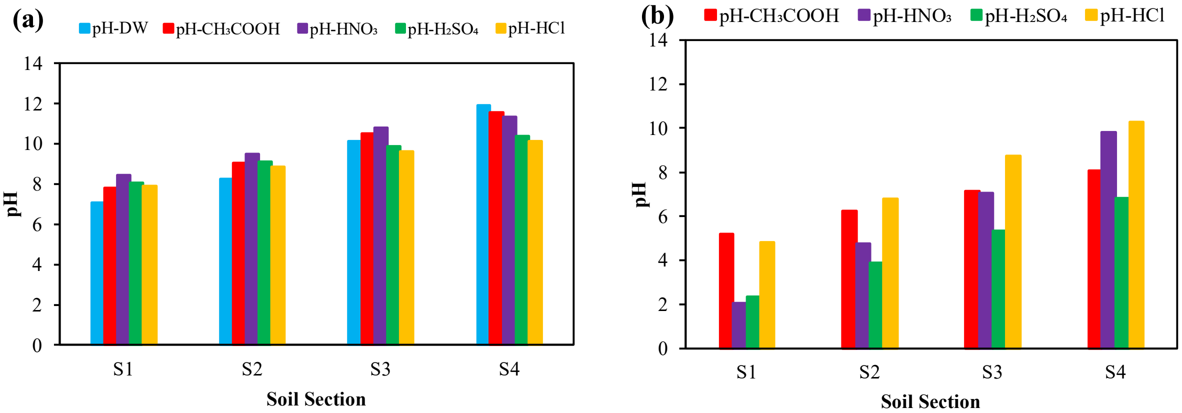

Figure 11. Soil pH variation in the (a) first series of experiments and (b) second series of experiments during electrokinetic treatment.

3.2. Current density and EC variations

Our experiments kept the voltage constant at 1.5 volts per centimeter of soil length. Figures 12(a) and 12(b) show the changes in current density from the first and second series of experiments, respectively. The current was continuously dropped in all experiments. It can be concluded that the soil current flow is determined by the EC of the soil, is determined by the concentration of particles in the pore fluid passing through the soil particles. During electrokinetic modification, as shown in Figures 11(a) and 11(b), the water electrolysis process generates a large amount of hydrogen ions, which move towards the cathode and raise the soil pH from the anode to the cathode. Soil acidification causes ion disabsorption, raising the ions' concentration in the electrolyte solution. The electric current's density increases as the ions' concentration in the electrolyte solution increases. Furthermore, the current density decreases over time due to the outflow of exchangeable species during the first hours of the experiment and metal deposition near the cathode, which increases the electrical resistance of the soil. As a result of the deposition of heavy metals near the cathode, the increased electrical resistance causes a decrease in electrical current. As shown in Figures 12(a) and 12(b) it reaches its maximum value quickly and gradually decreases until the experiment is completed. In general, if PTEs are present in the stationary phases, an inverse relationship between current intensity and removal efficiency will be established, such that an increase in current intensity under these conditions indicates a decrease in remediation efficiency [34]. The Electrical conductivity shows the amount of ionic particles in the solution and depends on the ionic strength of the pore solution in soils. According to Figure13, in the first series of experiments, distilled water was used in the anode tank and distilled water, acetic acid, nitric acid, sulfuric acid, and hydrochloric acid were used in the cathode, with the continuation of the test process and the entry of ions from the soil into the anode and cathode chambers, the electrical conductivity of these two tanks increases gradually. Increasing the electrical conductivity in the electrode solution can be assigned to the migration of various anionic and cationic particles due to the ion migration phenomenon. In addition, the electrical conductivity of the cathode shows a greater increase, the reason is that the ion of the target pollutant, lead and zinc, has a positive charge and has moved towards the negative pole under the electric field and accumulated in the cathode tank. As a result, the increased EC can be interpreted as an indicator of ion movement in the soil.

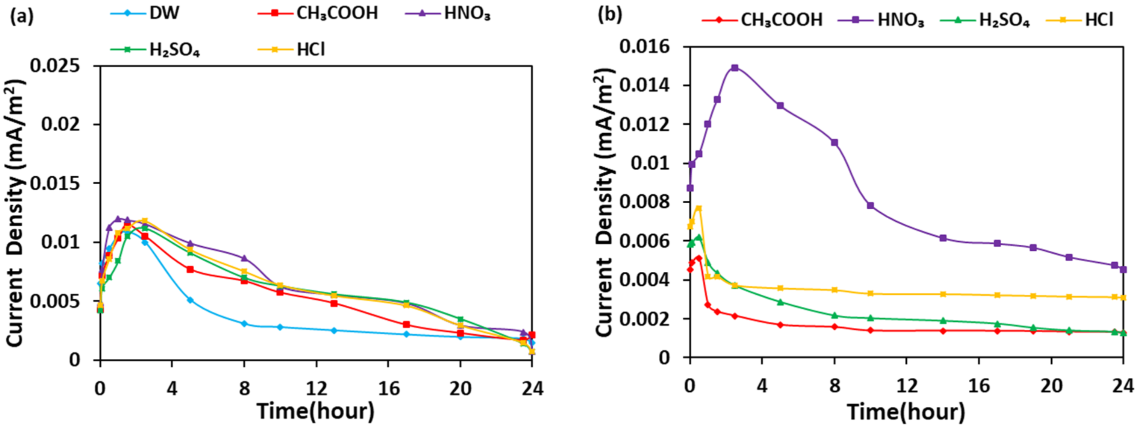

Figure 12. Current density variation observed during (a) the first series of experiments and (b) the second series of experiments.

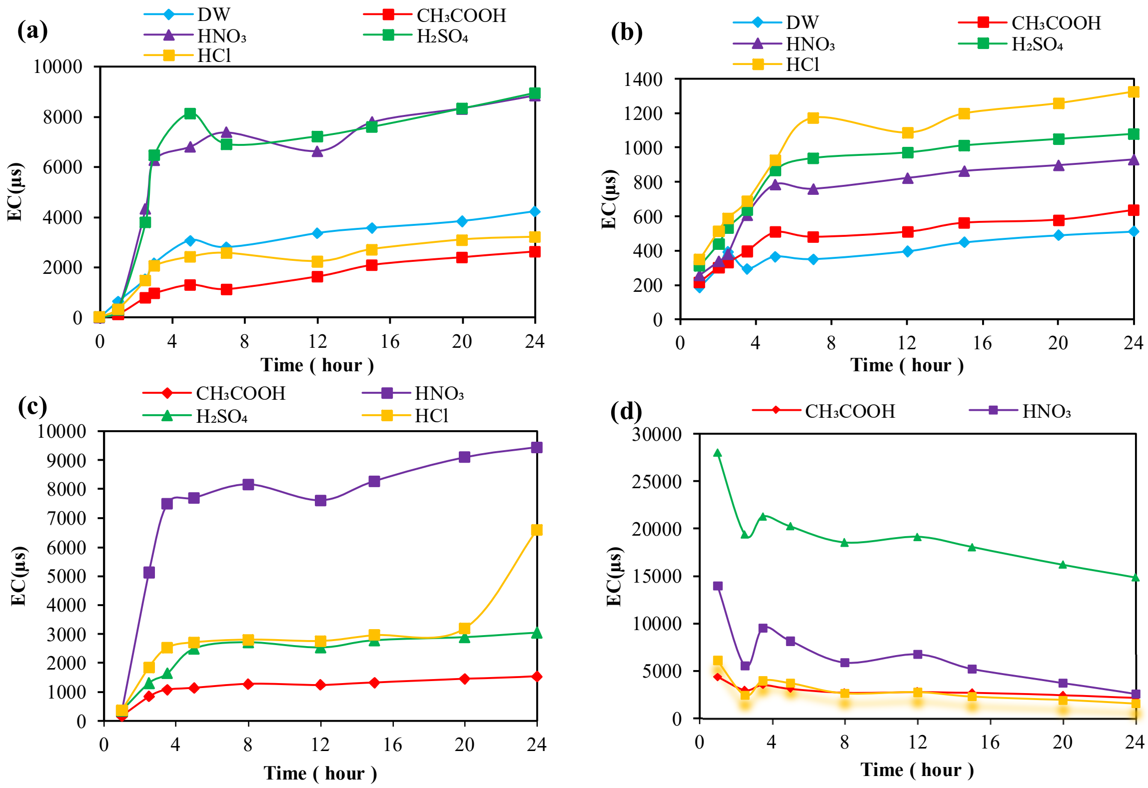

Figure 13. Electrical conductivity (EC) variation at (a) the anode and (b) the cathode in the first series of experiments, and at (c) the anode and (d) the cathode in the second series of experiments.

4. Conclusions

In this study, we conducted two experiments on contaminated soil from mine tailings to evaluate the removal of zinc and lead using different acid solutions. In the first series of experiments, we used acetic, hydrochloric, nitric, and sulfuric acids as catalyst solutions, all with a constant concentration of 0.1 M. In the second series of experiments, we applied the same acids as washing solutions through the soil samples.

Our findings indicated that in the first series of tests, hydrochloric acid achieved the highest removal rates for both zinc (25.5%) and lead (17.8%). Similarly, in the second series of tests, hydrochloric acid was found to be the most effective, with zinc and lead removal rates of 64% and 45%, respectively. The results suggested that the cleaning rate of zinc was approximately 30% higher than that of lead, on average.

This difference in behavior was attributed to the distinct absorption processes of these two heavy metals in the soil, as well as the formation of their deposits due to changes in pH. The soil's ability to retain lead particles was found to be much higher than that for zinc, necessitating more energy for lead removal via the electrokinetic method. This observation aligned with the C/C_0 results. Additionally, lead was determined to be more sensitive to pH changes in the pore fluid; as the pH increased, the concentration of dissolved lead decreased, reducing the amount of metal extraction. These findings were consistent with results from previous study [34, 35].

Moreover, our study demonstrated that soil pH and Cation Exchange Capacity (CEC) were critical factors in the removal of zinc from contaminated soil. The amount of zinc removed was proportional to the volume of electroosmotic flow; the greater the volume of flow, the higher the percentage of zinc removal. It was also noted that pH values below 4 should be avoided when using different acids as soil washing solutions, as this could harm the environment by destroying soil nutrients and microorganisms.

This comprehensive evaluation of the electrokinetic and washing methods for metal removal provided insights that can guide future remediation efforts in similar contaminated environments.

The nonlinear response observed in the cathodic region during electrokinetic remediation can be attributed to several factors. The accumulation of hydroxide ions (OH^-) near the cathode leads to significant pH gradients, which influence metal ion mobility and cause precipitation of metal hydroxides, reducing their availability for removal. Additionally, the altered electroosmotic flow due to pH-induced changes in soil surface charge further contributes to the nonlinearity observed.

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کاربرد همزمان روش الکتروکینتیک و حلال های شست و شو برای پاکسازی روی (Zn) و سرب (Pb) از پسماندهای معدنی سرب و روی انگوران

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چکیده:

فعالیت‌های معدنی موجب انباشت مقادیر زیادی از پسماندهای معدنی حاوی فلزات بالقوه خطرناک در محیط می شود که خاک‌های اطراف را آلوده می‌کنند. این مطالعه به بررسی اثربخشی روش پاک‌سازی الکتروکینتیک در ترکیب با حلال‌های شست‌وشو برای زدایش روی (Zn) و سرب (Pb) از پسماندهای معدنی پرداخته است. نمونه‌ها از مناطق مختلف معدن انگوران در استان زنجان، ایران، جمع‌آوری و غلظت کلی فلزات در آن‌ها با استفاده از روش استاندارد ICP مورد تحلیل قرار گرفت. آزمایش‌های الکتروکینتیک با استفاده از محلول‌های شست‌وشوی مختلف شامل اسید هیدروکلریک،اسید نیتریک، اسید استیک و اسید سولفوریک، هرکدام با غلظت ۰/۱ مولار و با نسبت محلول به جامد ۱:۲، انجام شد. در طول آزمایش‌ها، ولتاژ ۱/۵ ولت بر سانتی‌متر اعمال شد. برای کاهش رسوب فلزات سنگین در نزدیکی کاتد، از همان محلول‌های شیمیایی در محفظه کاتد استفاده شد. نتایج نشان داد که آب مقطر کمترین کارایی را در زدایش روی (۱۶٪) و سرب (۱۱/۵٪) داشت، در حالی که اسید هیدروکلریک بیشترین کارایی را با ۶۴٪ برای روی و ۴۵٪ برای سرب به همراه داشت. این یافته‌ها نشان داد که روش پاک‌سازی الکتروکینتیک، به‌ویژه با استفاده از اسید هیدروکلریک به‌عنوان عامل کمپلکس‌ساز، روشی مؤثر برای حذف مقادیر قابل توجهی از روی و سرب از خاک‌های آلوده است.

کلمات کلیدی: باطله معدن انگوران، اصلاح الکتروکینتیک، روی، سرب، الکترواسمز.
