

Article Enhanced Electrokinetic Remediation for the Removal of Heavy Metals from Contaminated Soils

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Abstract: The electrokinetic remediation of an agricultural soil contaminated with heavy metals was studied using organic acids as facilitating agents. The unenhanced electrokinetic treatment using deionized water as processing fluid did not show any significant mobilization and removal of heavy metals due to the low solubilization of metals and precipitation at high pH conditions close to the cathode. EDTA and citric acid 0.1 M were used as facilitating agents to favor the dissolution and transportation of metals. The organic acids were added to the catholyte and penetrated into the soil specimen by electromigration. EDTA formed negatively charged complexes. Citric acid formed neutral metal complexes in the soil pH conditions (pH = 2–4). Citric acid was much more effective in the dissolution and transportation out of the soil specimen of complexed metals. In order to enhance the removal of metals, the concentration of citric acid was increased up to 0.5 M, resulting in the removal of 78.7% of Cd, 78.6% of Co, 72.5% of Cu, 73.3% of Zn, 11.8% of Cr and 9.8% of Pb.

Keywords: contaminated soil; metal; citric acid; EDTA; electrokinetic remediation



Citation: Cameselle, C.; Gouveia, S.; Cabo, A. Enhanced Electrokinetic Remediation for the Removal of Heavy Metals from Contaminated Soils. *Appl. Sci.* 2021, *11*, 1799. https://doi.org/10.3390/app11041799

Academic Editor: Fulvia Chiampo Received: 3 February 2021 Accepted: 16 February 2021 Published: 18 February 2021

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1. Introduction

Soil is affected by various anthropogenic activities, including mining, waste dump, deforestation, urbanization, intensive agriculture practices and change in land use [1]. As a result, soils have been contaminated with a variety of organic and inorganic contaminants [2]. The metal-contamination in the soil is of special concern because metals show special toxicity for living organisms affecting the development of microorganisms and plants, enter the food change and extend the toxicity to animals and humans [3]. Contaminating metals cannot be degraded, and their removal from the soil is usually difficult, time-consuming and costly [4]. Many studies published in literature dealt with the removal of heavy metals from soil. However, the efforts in developing and testing various innovative technologies did not still result in a reliable and feasible technology to be generally applied in the remediation of metal-contaminated soils [5,6]. Recently, research has focused on the development of high-sensitivity sensors, usually based on electrochemical technology [7,8]. These sensors can be used for the detection of heavy metal ions in various media, allowing a new way to monitoring metal-contamination in hard-to-reach locations and remote environments.

Electrokinetic remediation has been proposed as an effective technology for the remediation of metal-contaminated soils [9]. Electrokinetic technology uses a low-intensity DC electric field to mobilize and transport the metals out of the soil. The benefits of electrokinetics rely on its capacity to be applied in situ with minimum disturbing of the surface, the possibility of treating low permeability soils and the low-cost in energy. However, electrokinetics is affected by the geochemical soil conditions that may limit the solubilization of metals. In order to increase the solubility of the metal in the soil interstitial fluid, various methods have been proposed [10]. The acidification of soil with the acid front electrogenerated in the anode is the most common option [11]. This option is usually combined with the depolarization of the electro-reduction of water on the cathode to



suppress the alkaline front [12]. The controlled addition of mineral acid in the cathode allows for the neutralization of the basic front and favors the acidification of the soil with the subsequent solubilization of metals (for example, Co^{2+} , Ni^{2+} , Cd^{2+} , ...). Alternatively, alkaline metals (for example, chromate) can be extracted from the soil matrix favoring the development of the basic front on the cathode and suppressing the acid front on the anode by the addition of alkali (e.g., NaOH). The modification of the soil pH with the acid or alkali front from cathode or anode is an effective method for the solubilization of metals in many cases, but it is important to consider the geochemistry of soils and contaminating metals. As an example, Ottosen et al. [13] used the controlled addition of ammonia to solubilize copper and arsenic. Ammonia forms a stable complex with copper $[Cu(NH_3)_4]^2$ in alkaline conditions that can be transported towards the cathode by electromigration. Conversely, various authors [12,14] used sulfuric acid to neutralize the basic environment of the cathode to mobilize the metals due to the acidification of the acid front from the anode. This method was very effective for metals, such as Cd^{2+} , Co^{2+} and Zn^{2+} , but Pb was not removed because it forms an insoluble salt with sulfate [14]. These results proved that the chemistry of facilitating agents with the metal-soil system is of crucial importance for a successful remediation. Furthermore, the acidification or alkalinization of soil may induce unacceptable changes in soil properties. The soil will require additional treatment to restore the natural properties of soil at the end of the remediation process [9].

The use of organic acids as facilitating agents in electrokinetics shows various benefits for the remediation of metal-contaminated soils. Organic acids are recognized as effective complexing and chelating agents that can keep metals in solution in a wide range of pH, even in an alkaline environment [15]. Moreover, the mild conditions of organic acids do not induce dramatic changes in the soil properties. Organic acids are usually biodegradable and can be removed by natural biodegradation at the end of the remediation process. Furthermore, the residual organic acids in the soil may help to enhance the activity of the natural soil microflora.

This paper studies the remediation of six metals (Cd, Cr, Co, Cu, Pb, and Zn) from agricultural soil with aged contamination. The different chemical nature of the metal species and the presence of these metals in high concentrations make the remediation of soil more difficult. The removal of metals was studied using organic acids (EDTA and citric acid) as facilitating agents with the objective to develop a feasible technology to be applied at a large scale. The aim of the study is to identify the facilitating agent and the experimental conditions to achieve the mobilization and removal of the six metallic species from the soil.

2. Materials and Methods

2.1. Soil Characteristics and Contamination Procedure

The characteristics of soil used in this study are listed in Table 1. The soil was sampled on a farm close to the campus of the University of Vigo in the NW of Spain. The soil was sampled from the upper layer of soil (0–20 cm depth) after removing the vegetative cover. The soil was extended in a thin layer (2–5 cm) in the lab to let it dry for 72 h to a moisture content of 5% (wet basis). Then, it was sieved through a 2 cm mesh to remove small stones, sticks, roots, and other non-soil components. The soil specimen was thoroughly mixed to obtain a uniform sample that was contaminated with 6 heavy metals: Cd, Cr, Co, Cu, Pb and Zn, using the necessary amounts of the corresponding salts to achieve the spiking concentration in Table 2. After the spiking process, the soil was stored in a plastic box in the darkness for 2 years to ensure the aging of the contaminants. The objective of this process was to ensure the behavior of the contaminated soil similar to the behavior of real contaminated soil.

Parameter	Value	Testing Method	
рН	4.4	ASTM D1293 [16]	
Electrical conductivity (mS/cm)	3.15	ASTM D1293 [16]	
Specific gravity (dry basis, g/cm ³)	2.7	ASTM D 854 [17]	
Water holding capacity	48.5%	ASTM D 2980 [18]	
Moisture content (wet basis)	22.4%	ASTM D2216 [19]	
Soil organic content (dry basis)	4.5%	ASTM D 2974 [20]	
Particle size analysis		ASTM D 422 [21]	
Clay (<0.002 mm)	44.3%		
Silt (0.002–0.05 mm)	43.2%		
Sand (0.05–2 mm)	12.5%		

Table 1. Characteristics of soil used in the experiments.

Table 2. Metal concentration in the contaminated soil.

Metal Species	Metal Salt	Spiking Concentration (mg/kg)
Cd ²⁺	Cd(NO ₃) ₂ 4H ₂ O	141
Cr(VI)	$K_2Cr_2O_7$	1000
Co ²⁺	CoCl ₂ 6H ₂ O	185
Cu ²⁺	CuSO ₄ 5H ₂ O	1023
Pb ²⁺	PbCl ₂	1000
Zn^{2+}	ZnSO ₄ 7H ₂ O	1001

2.2. Extraction Tests

The capacity of 9 extracting agents and water to dissolve the metals from soil was tested. The extraction tests used 2 g of soil (dry) and 100 mL of the extracting solution. Four mineral acids (hydrochloric, nitric, phosphoric and sulfuric acid), five organic acids (acetic, citric, EDTA, oxalic and tartaric acid) and deionized water were used as extracting solutions. The concentration of all the acid solutions was 0.1 M. The mixtures were shaken for 24 h at 180 rpm and 20 °C (± 0.5 °C) in an orbital shaker. The metals were determined by ICP-OES (Inductively coupled plasma–optical emission spectrometry) in the supernatant solution.

2.3. Electrokinetic Setup and Testing

Figure 1 shows the electrokinetic cell used in this study. The cell was composed of a central tube (20 cm long and 4 cm diameter) that holds the soil specimen. 320 g of contaminated soil was used in each test. The soil specimen was introduced manually in the central tube, and it was compacted with a plastic piston. The central tube was connected to two electrode chambers filled with the processing fluid selected in each test (deionized water, citric acid, EDTA or NaOH), as shown in Table 3. The volume of the electrode chambers was 300 mL, and the total volume of the processing fluid, including the electrode chamber and the expansion vessel, was 500 mL. The soil specimen was separated into the processing fluid by a porous stone and filter paper. The electrodes were installed in the electrode chambers immersed in the processing fluid and connected to a DC power supply. All the tests were conducted at constant DC electric potential (20 V) for 30 days, except test 4 with citric acid 0.5 M in anolyte and catholyte that was run for 65 days. The anode was made of titanium, and the cathode was made of stainless steel.

At the end of the tests, the electrode chambers were emptied, and the processing fluid was collected in plastic bottles and stored in the fridge at 4 °C until analysis. The soil was extracted from the central tube and divided into 6 equal sections. Solid and liquid samples were digested with nitric acid and hydrochloric acid as per the USEPA method 3010A (acid digestion of aqueous samples and extracts for total metals for analysis by FLAA or ICP spectroscopy) [22] or method 3050B (acid digestion of sediments, sludges, and soils) [23]. Metal concentrations were determined by ICP-OES in the supernatant solution of the acid digestions. Soil pH was determined by the ASTM D1293 [16] method using 1 g of soil and



2.5 mL of 1 M KCl solution. The mixture was shaken for 1 h, and the pH was measured in the supernatant fluid.

Figure 1. Experimental setup. (1) Soil specimen, soil sections are represented as S1–S6, (2) filter paper and porous stone, (3) electrodes (anode and cathode), (4) electrode chambers, (5) processing fluid vessel (anolyte and catholyte), (6) gas release valves, (7) recirculating pumps, (8) DC power supply.

Table 3. Experimental conditions of the electrokinetic tests.

Test	Anolyte	Soil	Catholyte	Potential Drop	Time
Test 1	Deionized water	320 g	DI water	20 V	30 days
Test 2	Deionized water	320 g	0.1 M citric acid	20 V	30 days
Test 3	0.1 M NaOH	320 g	0.1 M EDTA	20 V	30 days
Test 4	0.5 M Citric acid	320 g	0.5 M citric acid	20 V	65 days

3. Results

3.1. Extraction of Metals from the Soil

Figure 2 shows the metal extraction fraction when 2 g of soil was in contact for 24 h with 100 mL of 0.1 M solution of the corresponding extracting agent. In general, Cd, Co, Cu and Zn were easier dissolved than Pb and Cr, with both mineral acid and organic acids. The mineral acid solutions tended to show slightly better extraction ratios than organic acids. This is due to the lower pH solution of the mineral acids that extracted the metals from the surface of the soil particles by the direct attack of the H⁺ ions, stabilizing the metal in solution at pH below 1. Conversely, the organic acids showed a solubilization ratio based on their capacity to form soluble complexes and chelates in solution [24]. A closer analysis of the extraction results in Figure 2 revealed that the metal solubilization ratio depended on the chemistry of each pair of metal-acid. Hydrochloric acid and nitric acid showed 70-80% extraction for all the metals, but Cr, because this metal was present in the soil as Cr(VI) and the acidification was not able to desorb the anionic Cr species. Phosphoric and sulfuric acid also showed a high extraction ratio for Cd, Co, Cu and Zn, but very low extraction for lead because of the formation of insoluble salts between Pb and sulfate $(PbSO_4, Ksp = 1.6 \times 10^{-8})$ or phosphate $(Pb_3(PO_4)_2, Ksp = 9.9 \times 10^{-55})$. The organic acids showed a 60-70% extraction ratio for Cd, Co, Cu and Zn. The lead was extracted with EDTA, oxalic acid and tartaric acid, whereas acetic and citric acids showed negligible removal due to the tendency of lead to adsorb to the soil particles and organic matter [25]. Cr was extracted with oxalic acid due to the low acidity of the solution (pH = 1.40) and the reducing capacity of oxalic that transformed Cr(VI) into Cr(III) and formed stable complexes in solution [26].



Figure 2. Fraction of extracted metals from the soil with mineral acids, organic acids and water (All the compounds were tested at 0.1 M).

The information in Figure 2 can be used for the selection of facilitating agents for the electrokinetic remediation of the contaminated soil. Mineral acids were very effective in the mobilization of the metals, but their activity was always associated with a very acidic pH, below 1. In the remediation of soils, such low pH will affect the physicochemical and biological properties of soil to an unacceptable level, and further treatment would be necessary to restore the natural properties of soil. The organic acids seem to be more appropriate for soil remediation projects because they were able to extract the contaminated metals in less harsh conditions than mineral acids. Moreover, the organic acids tested in Figure 2 are biodegradable and can be removed from the soil for natural biotic degradation while enhancing the microbial activity of the soil [27]. Considering the results in Figure 2 and the available information in the literature, EDTA and citric acid were selected as appropriate facilitating agents for the electrokinetic remediation of soil [14,28]. EDTA is a complexing agent for all the contaminating metals in the soil specimen [24]. EDTA can be degraded by the soil microflora at the end of the electrokinetic treatment [29]. Citric acid is recognized as a non-toxic compound since it is present in all the eukaryotic cells in the Krebs cycle (the cycle of the tricarboxylic acids). Moreover, citric acid showed a special activity in the electrokinetic remediation of soils contaminated with metals [14].

3.2. Electrokinetic Treatment

The removal of heavy metals from the soil specimen was analyzed in a set of electrokinetic tests using EDTA and citric acid as facilitating agents to enhance the solubilization of the metals and their removal in the processing fluid in the electrode chambers. The results of the tests with EDTA and citric acid were compared with an unenhanced electrokinetic test using deionized water as processing fluid in anode and cathode (test 1). Test 2 used 0.1 M citric acid as catholyte and deionized water as anolyte. Test 3 used 0.1 M EDTA as catholyte and 0.1 M NaOH as anolyte. Finally, an additional electrokinetic test (test 4) was run with 0.5 M citric acid as processing fluid in anode and cathode with the objective to enhance the solubilization and removal of metals from soil (Table 3).

Figure 3 shows the pH in the electrode chambers and the pH profile in the soil for tests 1, 2, 3 and 4. The unenhanced electrokinetic test with deionized water as processing fluid (test 1) showed the typical pH profile induced by the electrolysis of water upon the electrodes [9]. The pH decreases in the anode to pH 2 and increases in the cathode to pH higher than 12. The pH of the soil in test 1 (the blue line in Figure 3) decreases in the fraction of soil close to the anode and increases in the fraction of soil close to the cathode. The profile of soil pH has an enormous influence on the speciation and mobilization of the contaminating metals in soil (Figure 4). Cd, Cu and Zn were mobilized in sections 1–3,

where the soil pH was lower than pH = 4 (the initial pH of soil). These metals were accumulated in sections 4-6, where the pH conditions induced the precipitation of metals in the soil forming the corresponding metallic hydroxide, especially in sections 5 and 6. Cobalt was mobilized in section 1–4 and mainly accumulated in section 6 because the immobilization of cobalt as $Co(OH)_2$ takes place at pH > 7. Chromium and lead were not mobilized or removed in the unenhanced electrokinetic test. Chromium is an anionic metal, and it was not expected to be mobilized in very acid conditions. In fact, a slight mobilization of Cr was observed in section 6, where the pH was alkaline. Lead is a metal that can be retained in the soil attached to the organic matter, and it is difficult to mobilize [25]. The alkaline environment in section 6 may have favored the dissolution of organic matter and a slight mobilization of Pb (Figure 4). Overall, the unenhanced electrokinetic test was not effective in the removal of metals from soil. Four metal species were redistributed in the soil (Cd, Co, Cu and Zn), and two species (Cr and Pb) showed no significant mobilization. No significant metal removal was observed, as presented in Table 4. Test 2 and 3 were designed to evaluate the efficiency of citric acid and EDTA to mobilize and remove the metals from soil.



Figure 3. pH in soil and processing fluid in the electrode chambers for the electrokinetic tests with deionized water (test 1), 0.1 M citric acid (test 2), 0.1 M EDTA (test 3) and 0.5 M citric acid (test 4).



Figure 4. Unenhanced electrokinetic test of soil contaminated with metals using deionized water as processing fluid in anode and cathode chambers. C is the metal concentration in soil at the end of the test, and Co is the initial metal concentration in soil.

Test—Catholyte	Fractions	Cd	Cr	Со	Cu	Pb	Zn
Test 1—Deionized water	Soil (%)	98.1%	97.4%	99.9%	97.4%	96.8%	98.5%
	Anode (%)	0.0%	0.5%	0.1%	0.0%	0.0%	0.0%
	Cathode (%)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Error (%)	1.9%	2.1%	0.1%	2.6%	3.2%	1.5%
T (2 01)()))	Soil (%)	96.1%	95.4%	92.7%	93.5%	97.8%	86.7%
	Anode (%)	0.1%	0.1%	0.1%	0.0%	0.0%	0.1%
lest 2—0.1 M citric acid	Cathode (%)	0.2%	0.0%	4.5%	2.1%	0.0%	9.3%
	Error (%)	3.7%	4.5%	2.7%	4.3%	2.1%	3.9%
Test 3—0.1 M EDTA	Soil (%)	99.7%	99.8%	98.3%	94.1%	99.4%	99.2%
	Anode (%)	0.0%	0.0%	0.1%	0.0%	0.0%	0.1%
	Cathode (%)	0.6%	0.1%	0.9%	0.2%	0.3%	0.9%
	Error (%)	-0.3%	0.1%	0.7%	5.6%	0.3%	-0.1%
Test 4—0.5 M citric acid	Soil (%)	21.3%	88.2%	21.4%	27.5%	90.2%	26.7%
	Anode (%)	1.2%	2.3%	0.3%	0.0%	0.0%	0.1%
	Cathode (%)	78.3%	6.3%	76.9%	71.4%	8.2%	73.9%
	Error (%)	-0.8%	3.2%	1.4%	1.1%	1.6%	-0.7%

Table 4. Mass balance of the metals in the soil at the end of the electrokinetic tests.

Test 2 used citric acid as a facilitating agent in the cathode. The citrate ion penetrated the soil specimen by electromigration, mobilizing the metals that could be stabilized in solution forming complexes or chelates with citrate. The presence of citric acid in the cathode avoided the formation of an alkaline environment. The pH in the cathode at the end of the test was pH = 5 that was the result of the partial neutralization of the 0.1 M citric acid solution (the natural pH of the citric acid solution was 2) with the electrochemical consumption of H⁺ on the cathode. The anolyte was deionized water. The electrolysis of water in the anode produced H⁺ ions that formed an acid front that acidified the soil specimen. As a result, the soil pH decreased in sections 1-4 and remained at the initial soil pH in sections 5 and 6 (Figure 3). The pH profile in the soil with the combination of the citrate as a complexing agent in the interstitial fluid showed a decisive influence in the speciation of metals and their transport along the soil specimen. As presented in Figure 5, Zn was mobilized in sections 1–3 and accumulated in sections 4 and 5. The concentration of Zn in the last section 6 remained unchanged. This behavior can be explained with a closer analysis of the pH in the soil and the chemical speciation of the system Zn²⁺-citrate (Figure 6). Zn^{2+} is the predominant species in the solution at a very acid pH < 1.5. In the presence of citrate, Zn²⁺ forms six different complexes (negative, neutral and positive complexes). The relative predominance of the complexes depends on the medium pH. At pH = 2–3 the dominant species is the positive complex $[ZnH_2L]^+$. L represents the ligand citrate. At pH = 3-4.5 the dominant species is the neutral complex [ZnHL]. At pH > 5, the dominant species is the negative complex [ZnL]⁻. The pH in the soil sections 1–4 was below pH = 4, so Zn was mobilized by the combined effect of the H⁺ attack and the stabilization in the solution of Zn²⁺ with citrate forming positive or neutral complexes. These complexes were transported towards the cathode by electromigration and/or electroosmosis. In soil sections 5 and 6, the pH is about 5, and the predominant species was the negative complex [ZnL]⁻. The negative complex will be transported towards the anode by electromigration. This explains why Zn is accumulated in section 5 of the soil specimen. Similar behavior was found for Cd, Cu, Co. These three metals form various neutral, positive and negative complexes with citrate [24], similar to the case explained for Zn. As a result, Cd was mobilized in sections 1–3 and 6 and accumulated in sections 4 and 5. Cu was removed from both ends of the soil specimen due to the formation of positive complexes on the anode side and negative complexes on the cathode side. Cu was accumulated in the center of the soil specimen (sections 3 and 4). In a similar way, cobalt was accumulated in sections 5 and 6. It is noteworthy the small but significant mobilization of Pb in the anode and cathode side and a slight accumulation in the center of the soil specimen. These results

confirm that Pb can be dissolved with citric acid, whereas it was not mobilized in test 1 with deionized water. Finally, chromium was mobilized on the cathode side by the combined effect of the pH and the presence of citrate. Cr was accumulated in soil sections 2–4. As a conclusion, citrate appeared to be an active compound for the mobilization of all the metals, including Cr and Pb, that showed major resistance to the mobilization in the unenhanced electrokinetic test 1. However, there was minor net removal of metals from soil in the electrode solutions. Only 9% of Zn, 4.5% of Co and 2% of Cu were found in the cathode chamber (Table 4). These results suggested that the treatment time and test conditions (pH, concentration of citric acid, etc.) were not enough for the effective removal of metals from contaminated soil.



Figure 5. Electrokinetic test of soil contaminated with metals using 0.1 M citric acid as catholyte and deionized water as anolyte. C is the metal concentration in soil at the end of the test, and Co is the initial metal concentration in soil.



Figure 6. Speciation of zinc and zinc complexes formation in an aqueous system with 0.1 M citrate and 0.1 M Zn^{2+} . (L represents the ligand citrate).

Test 3 was run with EDTA 0.1 M as catholyte. The electrokinetic phenomena would transport EDTA into the soil specimen by electromigration. EDTA forms complexes and chelates with all the metals [24] in the soil specimen. The analysis of the Zn²⁺ speciation with EDTA in an aqueous system is shown in Figure 7. EDTA formed three different complexes with EDTA formed three complexes with EDTA: [ZnL]²⁻, [ZnHL]⁻, [ZnOHL]³⁻. The relative abundance of each complex depends on the pH. EDTA is very effective in complexing Zn in the studied pH range. The relative abundance of the cationic species

 Zn^{2+} was always below 0.1% (<10⁻³ in Figure 7) at any pH. That is the reason the cationic Zn²⁺ does not appear in Figure 7. The speciation analysis informs that EDTA formed a very stable negative complex $[ZnL]^{2-}$ with zinc in all the pH intervals (pH = 3.5–10). The study did not include pH below 3.5 because EDTA is not stable in solution in acidic pH. In conclusion, the use of EDTA requires neutral or slightly alkaline pH to favor the solubility of EDTA and the stability of the metal complexes. Hence, in test 3, the analyte solution was 0.1 M NaOH to neutralize the acid environment generated by the electrolysis of water in the anode. Figure 3 shows the pH of test 3. The electrode solutions were alkaline as expected due to the electrolysis of water in the cathode and the use of NaOH in the anode. The penetration in the soil of the alkaline front from the cathode slightly increased the soil pH to 5. In these conditions, EDTA may form stable negative complexes with all the metals that would be transported towards the anode by electromigration. Figure 8 shows the residual metal in the soil at the end of test 3. EDTA was very effective in mobilizing Cd, Co, Cu, Pb and Zn, forming stable negative complexes that electromigrated towards the anode. However, in the time span of test 3, only the metal concentration decreased in section 6. The mobilized metals migrated towards the anode, confirming the formation of negative complexes, and accumulated in section 5. No significant changes in metal concentration were detected in sections 1–4. Cr did not show any mobilization because the anionic nature of this metal did not undergo any mobilization with EDTA at pH = 5. There was no net metal removal from the soil, as is shown in Table 4.



Figure 7. Speciation of zinc complexes in an aqueous system with 0.1 M EDTA and 0.1 M Zn^{2+} . (L represents the ligand EDTA).

Citric acid showed better mobilization of the metals than test 1 (with deionized water) and test 3 (with EDTA). Test 2 with citric acid showed a good mobilization of Cd, Co, Cu and Zn, but the metals were redistributed in the soil specimen with minor removal or accumulation in the electrode chambers (Table 4). It was hypothesized that the electrokinetic treatment with higher citric acid concentration and/or longer treatment time would increase the removal of metals from soil. Test 4 was designed to evaluate the capacity of citric acid to achieve an effective removal of the metals for the contaminated soil. Test 4 was operated with citric acid 0.5 M on both electrode chambers. Citric acid can be introduced into the soil specimen by electromigration from the cathode and by electroosmosis from the anode. It was expected that the most effective transportation of citric acid on the anode would assure the presence of citrate in the fraction of soil close to the anode, favoring the solubilization of metals. This test was operated on for 65 days. Figure 9 shows the residual metal concentration in the soil after the electrokinetic test. The metal concentration profile for Cd, Co, Cu and Zn shows transportation towards the cathode.

The soil pH at the end of the test was below 3.5 (Figure 3). The pH conditions assure the mobilization of the metals by the combined effect of citrate and H⁺ ions, and the subsequent stabilization in solution was forming neutral or positive complexes (Figure 6). The metal complexes were transported towards the cathode by electromigration and electroosmosis. The global removal ratio at the end of the test was 78.7% of Cd, 78.6% of Co, 72.5% of Cu, and 73.3% of Zn. The lead was difficult to mobilize due to the strong adsorption of this metal to the organic matter and soil particles [25]. Only a small fraction of Pb (9.8%) was removed at the end of test 4. However, the profile of the residual Pb concentrations in soil suggests a mobilization of lead in sections 1–3 and its transportation towards the cathode. Chromium was removed by 11.8%. The profile of the residual concentrations in soil suggests that Cr was mobilized and transported towards the cathode. Considering that the contaminant Cr species was chromate, the transportation towards the cathode suggests a reduction of Chromate in the acid environment of the soil during the test by reaction with citrate or organic matter in the soil. Cr(III) was the resultant product of the chemical reduction of chromate. Cr(III) was complexed with citrate forming neutral or positive complexes that were transported towards the cathode [30]. The global mass balances for the six metals in this study (Table 4) confirmed the removal and transportation of the metals towards the cathode due to the complexing activity of citrate.



Figure 8. Electrokinetic test of soil contaminated with metals using 0.1 M EDTA as catholyte and 0.1 M NaOH as anolyte. C is the metal concentration in soil at the end of the test, and Co is the initial metal concentration in soil.



Figure 9. Electrokinetic test of soil contaminated with metals using 0.5 M citric acid as catholyte and anolyte. C is the metal concentration in soil at the end of the test, and Co is the initial metal concentration in soil.

4. Conclusions

Metal-contaminated soil is a serious problem, and electrokinetic remediation is a practical technology that can be used for their remediation. The success of electrokinetic remediation in removing metals depends on the experimental conditions and the selection of facilitating agents. This study proved that:

- Organic acids are a good alternative as facilitating agents because of the mild operating conditions and their capacity to dissolve and stabilize the metals in solution, forming stable complexes and chelates;
- EDTA 0.1 M was effective in the dissolution and complexing of aged contamination of Cd, Co, Cu, Pb and Zn. However, the removal rate was too slow to be considered for a large-scale application;
- Cr was not mobilized or removed in the electrokinetic treatment with EDTA;
- The use of citric acid 0.1 M as processing fluid in electrokinetics is proposed due to its capacity to mobilize Cd, Co, Cu and Zn. Low mobilization was observed for Cr and Pb;
- The increase of the treatment time and the concentration of citric acid up to 0.5 M resulted in the effective removal of Cd, Co, Cu and Zn from aged contaminated soil. The removal ratios of Cd, Co, Cu and Zn were over 70–80%. It is expected to achieve complete remediation of these metals, increasing the treatment time;
- The remediation of soil contaminated with Cr and Pb requires further research to identify the appropriate experimental conditions that lead to significant mobilization and removal;
- The metal soil extraction tests suggest that oxalic acid could be an effective extractant for Cr and acetic acid for Pb. These two organic acids could be tested in combination with citrate for the simultaneous removal of the six metals. Alternatively, sequential electrokinetic treatment with citric acid, oxalic acid and acetic acid may result in the removal of the six metals.

Author Contributions: Conceptualization, C.C.; methodology, C.C.; validation, C.C., S.G. and A.C.; formal analysis, C.C., S.G. and A.C.; investigation, C.C., S.G. and A.C.; resources, C.C. and S.G.; data curation, C.C., S.G. and A.C.; writing—original draft preparation, C.C.; writing—review and editing, C.C., S.G. and A.C.; visualization, C.C., S.G., and A.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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