



Enhancement of electrokinetic remediation of lead and copper contaminated soil by combination of multiple modified electrolyte conditioning techniques

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ABSTRACT

Electrokinetic soil remediation is often impeded by the aggregation of small particles, within soil, during the procedure. The soil porous network is subsequently clogged which results in immediate process termination. In order to overcome this limitation, the feasibility of electrokinetic remediation coupled simultaneously with two enhancing techniques was investigated: modified periodic polarity reversal and catholyte pH control. The objective is to keep the soil pores unclogged in order to remove Pb and Cu from soil. Citric acid was used as anolyte, and 1 DCV.cm⁻¹ was applied through the processing cell. This strategy showed 9.0 times better remediation results than that of unenhanced electroremediation. It was mainly owed to: (i) The pH adjustment that kept the catholyte ideally acid, thus avoiding the formation of metal hydroxide precipitates that could clog the soil pores. (ii) An increase of electro osmotic flow due to the modified polarity reversal technique. Approximately 96% of Pb and Cu were removed from soil. Duplicate results were obtained on soil with 10-fold the initial heavy metals concentration. This combined configuration ensured an unclogged path within soil and enhanced electrokinetic mechanisms efficiency against pollutants remediation.

Keywords: Catholyte pH control, Copper, Electroremediation, Lead, Polarity reversal, Soil pores

1. Introduction

In the present time, environmental pollution is a worldwide crisis of varying intensity and significance. Soil bears the greatest burden of environmental pollution. It is getting contaminated in different ways, commonly of industrial origin and waste mismanagement [1]. One of the major chemicals involved in causing soil pollution are heavy metals. They are toxic, carcinogenic and strongly adsorbed onto the soil [2], which poses a risk to human, animal, and plant health. As a result, development of a clean-up strategy, which is based on a sustainable and economical solution, has widespread appeal.

Soil electrokinetic remediation (EKR) is one of the promising *in situ* soil cleaning techniques that is continuously being developed [3-6]. EKR process is suitable for low permeability soil where pollutants are trapped in grain pores, and thus difficult to remove. Recently, a considerable literature has grown up around the successful removal of heavy metals by soil EKR, such as: cadmium [7],

arsenic [8], chromium [9], copper and lead [10]. However, the performance of this design is limited by some factors including: (i) the sorption and persistent behavior of heavy metals into the soil [3]. Their mobilization inside a porous media was found to be strongly dependent on the metal speciation [11]. That is why conventional EKR, which uses only deionized water as electrolytes, can only remove ionic form of metals that are available in the soil pores fluid [12]. (ii) Also, the pH gradient that is formed by water electrolysis in electrolyte chambers, and transported into the soil [13]: Hydrons (H⁺) favor the dissolution and extraction of heavy metals from the soil. Whereas, hydroxides (OH⁻) act as a bridging ligand to metals of concern, thus form hydroxides complexes that precipitate in soil [6]. (iii) Moreover, the effects of soil composition that may strengthen the retention of contaminants onto soil [14, 15]. These interferences clog the network of soil pores, and obstruct the proper functioning of EKR main mechanisms; electromigration and electroosmotic flow (EOF), that are



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responsible for the contaminants removal [3]. In order to optimize the soil EKR method, it is fundamental to exploit the advances that were made in this field to this day. In this context, researchers had explored different enhancing techniques [16-19]. One of which is acid enhanced EKR [20], using different organic, inorganic weak or strong acid [21, 22] as electrolytes; heavy metals are dissolved as a result of low pH environment created in soil. Citric acid is commonly used, at weak concentration, as anolyte to be transported into the soil by EOF. The benefits of this facilitating agent have been reported in many articles [12, 20]. Furthermore, one of main used EKR optimization is pH regulation. It is a key factor in preventing the formation of alkaline pH in soil which favors the sorption of heavy metals onto the soil [23]. Although, several practical solutions have been proposed to condition the soil pH, catholyte pH control (Cpc) and polarity reversal are the most popular EKR enhancer. Cpc is coupled to EKR to prevent the high pH zone generated at the cathode chamber by adding diluted acid [24] directly into the catholyte. In the process, heavy metals are kept in soil under acid condition, and soil electrical conductivity is improved, thus facilitating the exit of pollutants outside the soil. In polarity reversal (or exchange polarity), the EKR polarity is switched for repetitive short intervals of time. The anode compartment is transformed into the cathode compartment, and vice versa. It is performed during enough time to allow water electrolysis to generate the necessary amount of H^+ in the anolyte (former catholyte), to neutralize the OH^- ions. Thus, preventing the complexation of metals in soil and favoring their dissolution [25].

To summarize, the path of remediation needs to remain clear or without impeding obstruction that may clog the soil, and therefore limit the EKR process. The main objective of this work is to ensure a decontamination path within the soil pores, during the EKR time, for maximum heavy metals removal. The study was achieved through the combination of three EKR enhancing techniques: (i) Catholyte pH control with acetic acid; (ii) Periodic polarity reversal technique. Also, (iii) the feasibility of increasing the electric voltage, during

a reduced polarity reversal time, was explored. The effectiveness of this boosting EKR approach was demonstrated through the application of each enhancing techniques individually and simultaneously together on soil electroremediation. The experiments were conducted under constant voltage gradient of 1 DCV.cm^{-1} on Cu and Pb spiked sand. Citric acid and sodium nitrate were used as purging solution in the EKR treatment. The performances of this work was evaluated through the aspect of Pb and Cu removal efficiency, heavy metals concentration, electroosmotic flow, influence of soil pH, soil moisture and energy consumption of the process.

2. Materials and Methods

2.1. Choice of Soil and Metal Concentration

Sahara Desert constitutes 84% of Algeria's land surface area. The underground of this barren area comprises a massive water underground reserve (it is estimated to 6.8 billion m^3) [26]. In this country the majority of military shooting ranges are situated in the desert. Pb and Cu molecules in shooting range are most likely to be transported by rainwater to the underground and contaminate this precious water reserve. In this study a sandy soil was chosen to simulate the contamination of Pb and Cu from a shooting range. The soil used in this work was collected from the dunes of Adrar's desert situated in Algeria. The choice of contaminants concentration in this research was based on the amount of copper and lead usually present in shooting range. [27].

2.2. Soil Preparation

The soil was previously characterized by Boulakradeche and Cameselle [28], the main results are showed in Table 1. The sample was sieved through a $< 2 \text{ mm}$ stainless steel mech. It was subsequently spiked with copper nitrate and lead nitrate in order

Table 1. Physicochemical Properties of Soil Used in the Experiments

Properties	Value	Method
Soil particle distribution %		
> 50 and $< 2,000 \mu\text{m}$	96	
> 20 and $< 50 \mu\text{m}$	< 3	Sieving
$< 20 \mu\text{m}$	< 1	
Soil moisture %	4	Thermogravimetric
pH	5.2	USEPA SW-846 Method 9045D
Electrical conductivity (mS/cm)	0.34	ISO 11265
Point of zero charge pH (PZCpH)	3.1	PZCpH with Long equilibrium time method
Total organic carbon % (TOC)	1.3	ISO 10694
The major minerals (weight %)		
Si	22.96	
B	10.92	Characterized by SEM/EDX
Al	1.72	
Mg	1.50	
Heavy metals (mg.kg^{-1})		
Cu	3	EPA Method 3050
Pb	< 1	

to obtain approximately $1,000 \text{ mg}\cdot\text{kg}^{-1}$ of each metal. Another simulation sample was prepared with the same pollutants at $10,000 \text{ mg}\cdot\text{kg}^{-1}$ concentration of each metal. The samples were homogenized, air dried and aged under a fume hood in room temperature for 8 months. The purpose of this step was to strengthen the metals sorption into the soil, thus simulating a real contaminated soil. The equilibrium concentration of Cu and Pb, after the aging period, were respectively: 933 ± 26.21 and $920 \pm 27.14 \text{ mg}\cdot\text{kg}^{-1}$ for the first soil sample; $9,720 \pm 245.91$ and $9,821 \pm 228.82 \text{ mg}\cdot\text{kg}^{-1}$ for the second soil sample.

2.3. Experimental Set Up

The electrokinetic cell used in this work comprises three glass compartments: the main compartment and two electrode compartments. The soil is introduced in the central compartment, which is a cylindrical tube of 140 mm length and a capacity volume of 453 cm^3 . The electrode compartments have a working volume of 300 cm^3 . They contain the electrolyte solutions and the carbon graphite electrodes. The effective surface contact of the latter is 40 cm^2 . Gas vent valves, located at the top of both electrode chambers, allow a controlled release of the gas generated by electrolysis of water. The flushing solutions are continuously homogenized with a magnetic stirrer. The three compartments are held together by two socket threaded cups, as shown in Fig. 1. The contaminated soil is separated from the electrolytes by a fritted glass membrane and a glass microfiber filters (Whatman GF/C). A power supply is directly connected to the electrodes. The cumulative

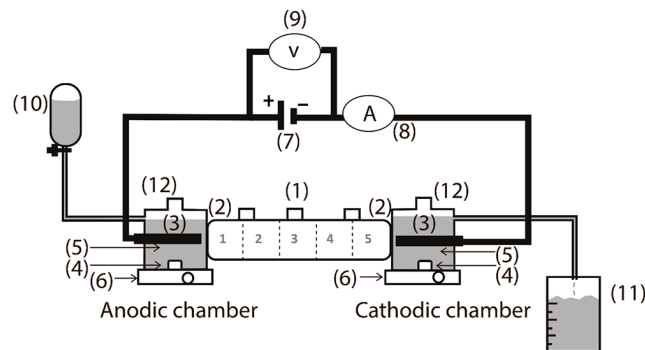


Fig. 1. Experimental setup: (1) Soil specimen, (2) Glass microfiber filter and porous stone, (3) Electrode, (4) Magnet, (5) Electrolyte, (6) Magnetic stirrer, (7) DC power supply, (8) Ampere meter, (9) Voltmeter, (10) Feeding bottle, (11) Expansion vessel, (12) Gas vent valve.

electroosmotic flow is collected in a glass beaker placed near the cathode. On the other cell's end, an anolyte feeding reservoir (1 L) is attached in order to compensate the liquid drained by the electroosmotic flow. The two electrode chambers were levelled evenly in order to eliminate hydraulic gradient across the specimen.

2.4. Electrokinetic Procedures

In this work, EKR was performed on two level of soil contamination:

- Soil 1: The soil was mixed with $1,000 \text{ mg/kg}$ of Pb and $1,000 \text{ mg/kg}$ of Cu.
- Soil 2: The soil was contaminated with $10,000 \text{ mg/kg}$ of Pb and $10,000 \text{ mg/kg}$ of Cu.

Each experiment was performed with 280 g of dry contaminated soil. The sample was thoroughly mixed with 110 mL of deionized (DI) water in all experiments. The soil moisture aimed in each mixture (liquid, soil) was 40%. The sample was carefully placed and compacted in the central compartment. Then, 300 mL of appropriate electrolytes were poured in each electrode compartments. Table 2 summarizes the experimental conditions of each test. All experiments were performed under a constant DC voltage gradient of 14 V ($1 \text{ V}\cdot\text{cm}^{-1}$) during 19 to 29 d. The daily measures were the cumulated EOF, current intensity, electrolytes pH and specific electrical conductivity.

2.5. Polarity reversal and Catholyte pH Control

Polarity reversal (PR) was applied during three hours by alternating the polarity of the electric generator and keeping the same voltage (14 DCV). The daily application frequency was three times a day (3.0 d^{-1}) spaced out by two hours of normal electrokinetic treatment (without PR), as depicted in Fig. S1(a). Catholyte pH control (Cpc) was carried out by connecting the cathode chamber to a pH controller, and injecting acetic acid of 1 M solution to adjust the catholyte pH to a specific value of $\text{pH} = 4$.

The simultaneous use of PR and Cpc was carried out at the same rate of application as mentioned above. When PR and Cpc were combined with higher voltage, the polarity reversal application frequency was kept the same (3.0 d^{-1}) but the duration time was reduced to 30 min, and the electric voltage was risen up to 42 V , only during the PR half hour application. Afterward, the voltage was set back to its original value (14 V), as depicted in Fig. S1(b).

2.6. Analytical Methods

2.6.1. Soil characterization

The chemicals used in this study are of analytical grade, all solutions

Table 2. Experimental Configuration of All EKR Tests

Test	Anolyte	Main compartment	Catholyte	Controlled parameters	Time (d)
T1	NaNO_3 (0.1 M)	Soil 1	NaNO_3 (0.1 M)	--	19
T2	Citric acid (0.1 M)	Soil 1	NaNO_3 (0.1 M)	--	19
T3	Citric acid (0.1 M)	Soil 1	NaNO_3 (0.1 M)	PR	19
T4	Citric acid (0.1 M)	Soil 1	NaNO_3 (0.1 M)	Cpc	19
T5	Citric acid (0.1 M)	Soil 1	NaNO_3 (0.1 M)	PR + Cpc	19
T6	Citric acid (0.1 M)	Soil 1	NaNO_3 (0.1 M)	High voltage PR + Cpc	19
D7	Citric acid (0.1 M)	Soil 2	NaNO_3 (0.1 M)	High voltage PR + Cpc	29

were prepared using DI water. The soil was analyzed with scanning electron microscopy (SEM) from FEI model Quanta 400, coupled to a microanalyzer X type from EDAX, model Ametex [28]. The soil pH and electrical conductivity were determined by Thermo scientific orion 5 star plus meter respectively, with a ratio of 1:2.5 soil to water [29]. Total organic carbon was analyzed with Multi N/C 3100 from Analytik Jena AG (Germany) by dry combustion technique [30]. Pb and Cu content in soil sample were determined by acid digestion followed by flame atomic absorption spectroscopy analysis (Thermo Scientific, model ICE 3500) [31].

2.6.2. Electrokinetic assessment

Upon completion of each procedure, the electrode chambers were emptied. The electrolytes along with EOF liquid were stored in individual glass bottle at 4°C for metal analysis. Soil specimen was carefully extruded from the central tube of the electrokinetic cell and was sliced in five equal pieces numbered between 1 and 5 from anode to cathode, as shown in Fig. 1. Five grams of soil was sampled, from each soil slice, to determine the soil moisture content (in dry basis) [32]. Subsequently, the rest of the treated segments were dried and mixed separately into powder form in order to make the Cu and Pb concentration homogeneous within each sample. Finally, the electrolyte solutions along with the five soil samples were analyzed for pH, electric conductivity (EC) and Pb, Cu content.

All Cu and Pb chemical extraction and analysis procedures were performed in accordance with EPA Method 3010 and Method 3050 [31, 33]. The metals concentration was determined by Flame atomic absorption spectroscopy and analyzed in triplicate. The results were within the Standard deviation range of $\pm 4\%$. In each experiment, a mass balance analysis was calculated. Removal efficiency of each test was obtained by Eq. (1) as follow:

$$R \% = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

Where C_i is the initial metal (Pb or Cu) concentration in soil and C_f is the metal (Pb or Cu) concentration remained in soil after EKR treatment.

In this study, power consumption (P_c) is expressed as the electric energy (kWh) required to process 1 ton of contaminated dry soil (Eq. (2)).

$$P_c = \frac{1}{m} \int_0^t I \phi . dt \quad (2)$$

Where: ϕ (Volt) is the electrical DC voltage, a constant in these experiments, I (A) is the current intensity of the EKR cell at time t (s), and m (ton) is the processed mass of dry contaminated soil.

3. Results and Discussion

The results obtained in the physicochemical characterization of

soil, as shown in Fig. S2 and detailed in Table 1, indicates that the soil is fine sand, basically composed of silicon and boron as major elements along with aluminum and magnesium as minor elements.

3.1. Current intensity and Soil Moisture

The current intensity (I) versus elapsed EKR time is represented in Fig. 2(a). The (I) of test T1 and T2 could not be sustained at the high starting level for more than 4 d. It was mainly due to a high depletion of ionic species in the medium. Fig. 2(c) and 2(d) shows the initial and final soil moisture (SM) of the 7 tests carried out in this study. The soil sections 2, 3 and 4 of tests T1 and T2 showed poor (SM) values, ranging from 28.5 to 21%, as they were all below the initial (SM). Therefore, indicating a considerable dewatering of soil pores. Since ions and pore water are the *sine qua non* of electric current in soil, the (I) was expected to stope in the prevailing conditions. The cause of soil dewatering could be due to the clogging of soil pores by precipitates of complexed metals in basic soil pH.

In the tests, T3 and T4 (I) started initially at approximately 40 mA, then decreased and fluctuated until the 12th day of EKR treatment, and subsequently stabilized below 10 mA. The soil moisture of these tests was enhanced above the initial (SM). In PR technique, the reversal of polarity in EKR cell will reverse the cathode and anode (as explained in the introduction), H^+ ions are now being generated into the new anode (former cathode) which will re-dissolve Pb and Cu precipitates in soil. Consequently, the movement of pore fluid was enhanced by unclogging the soil pores from metal precipitates, and enriched the medium with ions, therefore an appropriate level of (SM) was maintained and the current intensity was enhanced [34]. Cpc favored the movement of H^+ , supplemented CH_3COO^- onto the soil and increased the EOF which enhanced the (SM). The application of both techniques in test T5, T6 and D7 resulted in the best (I), as shown in Fig. 2(b), values which were sustained at a high level. This phenomenon could be attributed to a better flow of water in the soil, and suggests the absence of soil pore clogging phenomenon by any precipitating molecules or small soil particles.

3.2. Soil pH

In this work, soil electrokinetic remediation was highly dependent on soil pH. Especially with citric acid which efficiency was strongly related to its predominant forms, $CitH_3$, $CitH_2^-$, $CitH^-$ and Cit^{3-} with respective acid dissociation constant (pKa) values of 3.10, 4.80 and 6.39 [35]. However, electrokinetic soil remediation has a tendency to form basic front in the cathode and acid front in the anode due to the electrolysis of water.

In Tests T1 and T2, H^+ were produced by oxidation of water at the anode, and OH^- were formed by reduction of water at the anode [9]. These ions electromigrated toward the soil and caused pH changes in different parts of the soil: acid in sections 1, 2 and basic in sections 3, 4, 5, as shown in Fig. 3(a).

The negative effect of electrolysis in the following experiments (T3-D7), as presented in Fig. 3(a), and 3(b) was reduced because the OH^- generated at the cathode were neutralized by the pH control

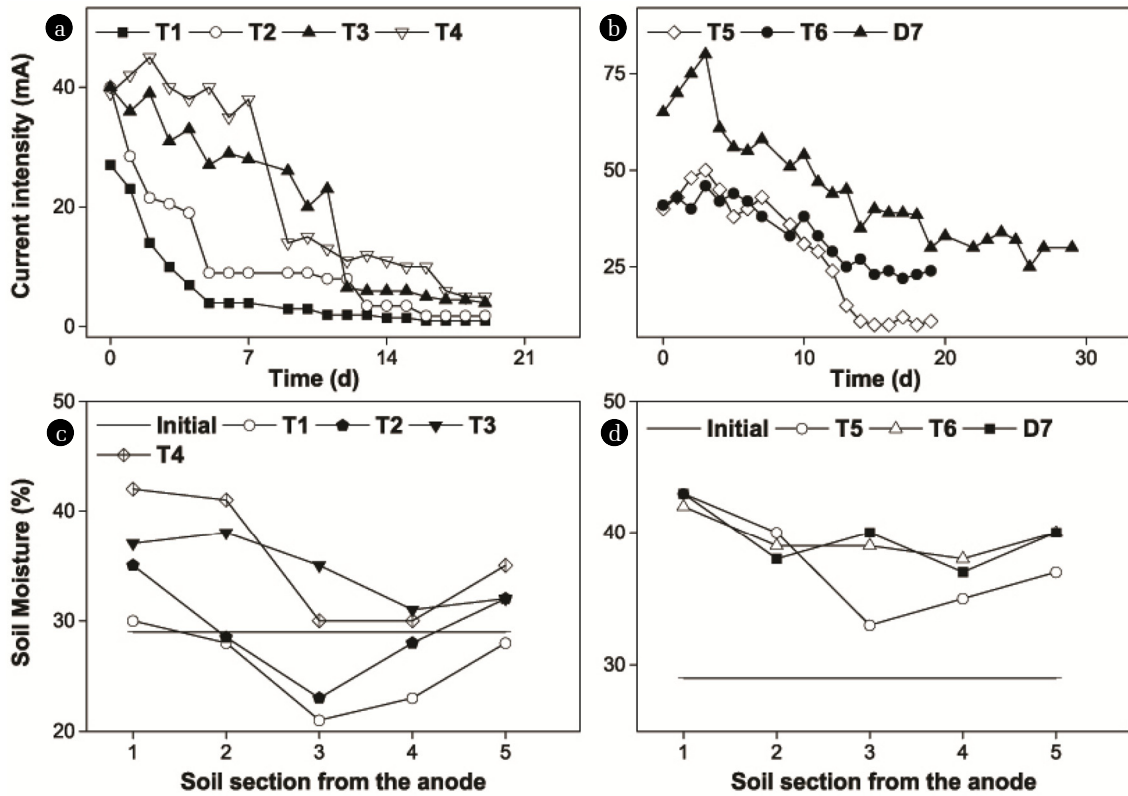


Fig. 2. Current intensity profile (a), (b) in electrokinetic tests, and soil moisture variation (d), (c) of before - after treatment in all experiments.

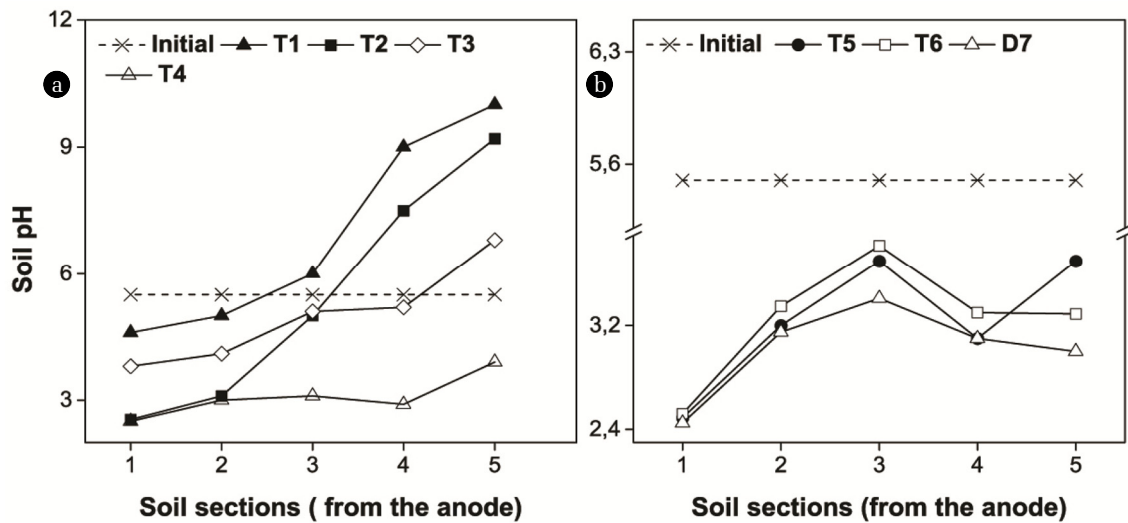


Fig. 3. Soil pH at the end of electrokinetic tests.

techniques. In test T3, the pH was 3.8 in section 1 and 6.8 in section 5, owing to the polarity reversal technique. During PR time the poles of water electrolysis were inverted which retarded the formation of basic medium near the cathode. In test T4 to D7 the soil remained acid with pH values below 3.9. Acetic acid was directly injected, in these experiments, into the catholyte in order to counter the alkaline environment yielded in the

cathode. The amount of H^+ consumed to control the catholyte pH can be estimated as follow: 1 mole of e^- produces 1 mole of OH^- , and therefore needs 1 mole of H^+ to neutralize it [23]. The consumed amount of H^+ increased from test T4 to D7, respectively 1.38 and 3.04 mol.kg⁻¹, as presented in Table 3. This was owed to the difference of current intensity which produced higher amount of OH^- .

Table 3. The Main Soil Electrokinetic Remediation Results of All Tests

Test	Controlled parameter	R% (Cu)	R% (Pb)	Average S.M (%)	EOF (mL)	consumed H+ (mol.kg ⁻¹)	Energy consumption (kWh.t ⁻¹)
T1 ^a	--	11.18	11.65	26.00	44.00	--	121.80
T2 ^a	--	32.85	30.53	32.00	138.00	--	235.56
T3 ^a	PR	62.19	58.82	35.00	126.50	--	455.40
T4 ^a	Cpc	74.56	65.47	36.00	230.50	1.38	519.60
T5 ^a	PR + Cpc	92.73	87.32	38.00	251.00	1.79	672.00
T6 ^a	Modified PR + Cpc	99.11	97.13	41.00	492.00	2.04	768.00
D7 ^b	Modified PR + Cpc	97.22	92.67	45.00	732.00	3.04	1,556.00

^aTreatment time was 19 d and initial soil [Cu] and [Pb] are respectfully 933 ± 26.21 and 920 ± 27.14 mg.kg⁻¹

^bTreatment time was 29 d and initial soil [Cu] and [Pb] are respectfully 9,720 ± 245.91 and 9,821 ± 228.82 mg.kg⁻¹

3.3. Electroosmotic Flow

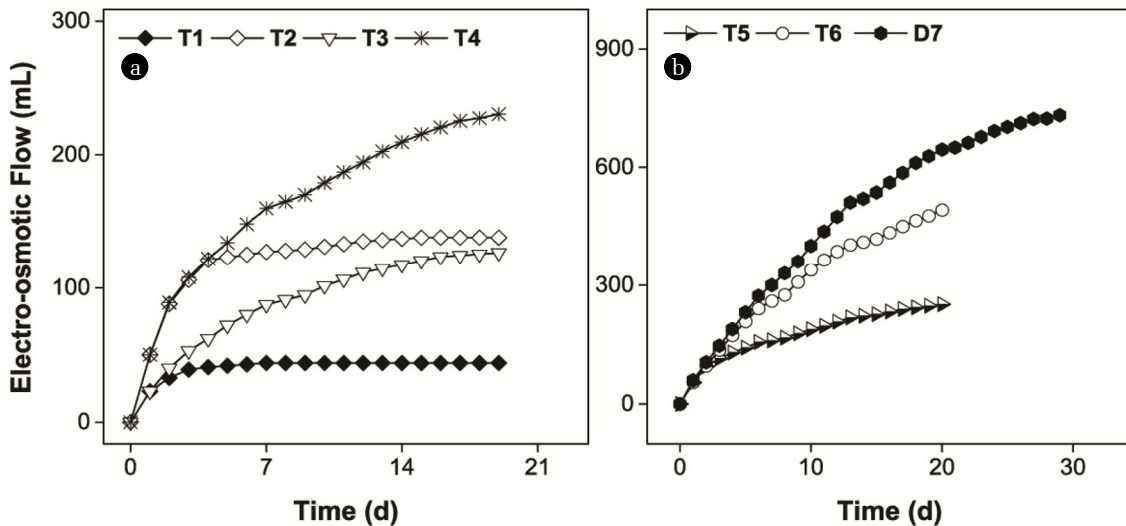
The direction of the EOF in all experiments was potentially from the anode to the cathode compartment during the EKR process. The electroosmotic flow was relatively low when compared with other experiment in the literature [8, 36]. According to Helmholtz–Smoluchowski theory, electroosmotic flow is strongly related to the soil zeta potential (ζ), the dielectric constant of the fluid (D), the fluid viscosity (η), and the electric potential (E_z), as shown in Eq. (3): [6, 37]:

$$q_{eo} = nAE_z \frac{D\zeta}{\eta} \quad (3)$$

Where q_{eo} is the volumetric flow rate, A is the cross sectional area of the soil and n is the porosity. There is no significant difference regarding the porosity of soil, the voltage gradient applied through the same EKR cell, or the viscosity of each diluted fluid used in this study. The conditions were approximately the same apart from the important ionic strength of test D7 due to the quantity of heavy metals present in soil. Consequently, EOF was influenced by soil zeta potential variation, where negative ζ favors the electro-

osmotic flow in the direction of the cathode, and positive ζ stops and could reverse the direction of EOF. Zeta potential is dependent on the interactions between the pore fluid and the soil particles, these interactions are strongly affected by pore fluid pH and ionic strength of the soil [38, 39]. Thus, the EOF difference between all experiments, as presented in Table 3, can be attributed to the variation of interstitial fluid pH. Typically, soil zeta potential is neutral at the point of charge zero pH (PZC_{pH}), and acquires positive value when soil pH is reduced beyond PZC_{pH} , and negative value when soil pH is higher than PZC_{pH} [40].

As presented in Fig. 4(a), cumulative EOF of tests T1 and T2 were relatively low due to the precipitation of metals in basic soil pH near the cathode which in turn clogged the soil pores. In Tests T3, T5 and T6 the soil was in acid environment which lead to a final average soil pH between 3.2 and 4.18. These soil pH values are higher than the soil PZC_{pH} (3.1) which implies that the soil zeta potential was potentially negative, therefore the EOF direction was from anode to cathode. Test T3 shows 8.3% less cumulative EOF than that of T2. This trend was expected since EOF cannot be generated during the PR intervals. Also, the PR time was too short to properly generate a negative EOF, i.e., from


Fig. 4. Cumulative electro-osmotic flow at the end of electrokinetic tests.

cathode to anode, hence the poor gap between cumulative EOF values of tests T2 and T3. Several studies reported that although PR technique provides an appropriate pH for heavy metals extraction, it is often impaired by poor EOF level [25, 41].

Test T4 shows an average final soil pH of 3.0, the low pH implies that zeta potential should be either neutral or slightly positive. Despite the low soil pH, EOF of test T4 was still cumulating in the cathode to reach 230 mL, and no negative EOF was detected. These observations indicate that zeta potential was potentially negative during the EKR process. Yang and Baek [36] reported similar EOF behavior in EKR process. In test T5, when the Cpc and PR were coupled, Cumulative EOF, as shown in Fig. 4(b), hardly varied in regard to test T4. This confirms the insignificance of negative EOF that may be produced in this limited PR time.

In test T6, polarity reversal time was reduced to 30 min and its voltage gradient was tripled. The use of PR was not meant to regulate the pH because 30 min was too short of a time to create a window of suitable pH in the cathode. However, the strategy aimed to shake the soil charged particles and possibly minerals that potentially were blocking the incoming water flow. Cumulative EOF of test T6 (492 mL) was enhanced to nearly double that of T5 (251 mL). The authors hypothesize that this maneuver may have created very small gaps within the soil, which allowed a better flow of the interstitial fluid in soil.

Cumulative EOF, in test D7, was higher (732 mL) than that of T6. This was probably due to the presence of higher amount of ionic species in soil as a result of: (1) the longer contact of soil with H^+ ions on account of catholyte pH control [18]; and/or (2) the amount of heavy metals present in D7 soil. Most of these metals, during EKR process, were in ionic form (divalent ions or complexed ions). The overall ionic species transferred momentum to the surrounding water fluid, and thus enhanced the EOF [6]. Although the current intensity was kept relatively high, the cumulative EOF curve slope drastically decreased. Consequently, an effective rate of EOF did not sustain for more than 13 d of EKR treatment. As time passed on, more ionic species were introduced into the interstitial fluid due to solubilization and electrokinetic extraction on soil. The increase of ionic species would lower the thickness of the diffused double layer of the pore fluid [42]. This would impair the dielectric properties of the pore fluid and, according to Eq. (3), slow down the cumulative EOF.

3.4. Heavy Metals Removal

Mass balance of the EKR experiments, as shown in Table S1, revealed that Pb and Cu accumulated at the cathode. This indicates direction and mechanisms of the removal process: from anode to cathode by electromigration and electroosmotic flow.

3.4.1. Tests without EKR controlled parameters

The first experiment was carried out with sodium nitrate as purging solution, and resulted in poor Pb and Cu removal efficiency of 11%, as shown in Table 3. Sodium nitrate is a strong electrolyte that can supplement soil medium with ions (Na^+ , NO_3^-). It improves the electrical conductivity of the soil, and thus the overall EKR process. However, the capability of $NaNO_3$ as flushing solution is limited as it is unable to neither form complexes nor dissolve heavy metal from soil [43].

The remediation of heavy metals in test T1 was also restrained by the formation of basic pH near the cathode compartment. Which favored the formation of complexes such as $Pb(OH)_2$ and $Cu(OH)_2$. These complexes subsequently clogged the soil pores and blocked the decontamination process.

In test T2, citric acid was used as anolyte to be transported by EOF toward the cathode. The removal efficiency was greatly enhanced to reach approximately 32% and 30% of Cu and Pb. The efficiency of this flushing agent in electroremediation of heavy metals contaminated soil, has been demonstrated and confirmed by many anterior studies [12, 20]. In addition of providing a low pH medium, citric acid is a viscous fluid that can decrease the diffuse layer of soil particle, allowing the removal and solubilization of metals ions from the porous media. Also, the ionic species, generated or extracted by citric acid, has potential for improving the electrical conductivity of soil, and thus enhancing the EKR process [44]. Despite the advantages of this washing agent, the decontamination process of T2 did not show any further enhancement. This could be due to the negative effect of OH^- on heavy metals, and also to the formation of anionic citrate complexes, as presented in Table S2 [45], in basic soil pH near the cathode compartment. The latter complexes could hardly electromigrate toward the anode because of the EOF encountered in the opposite direction.

In all citric acid enhanced experiments (T2-D7), as shown in Fig. 5(a)~(d), the removal of Cu from soil was favored in regard of Pb. This could be explained by the Cu constant of stability that is always higher than that of Pb with respect to the same citrate ligand, as shown in Table S2. This implies that citrate ligand has a tendency to form more stable complexes with Cu than Pb.

3.4.2. Tests with EKR controlled parameters

Tests T3-D7 focuses on the optimization of soil EKR conditions for maximum Pb and Cu removal. The objective is to work in acid medium to enhance the overall process.

Polarity reversal during soil EKR (PR, EKR) has been tested in Test T3. PR was carried out for a total 9h daily. The frequency was selected to avoid the generation and impact of negative EOF, that could be yielded during PR time, on heavy metals decontamination path which was toward the cathode. When compared to test T2, the removal efficiency of the PR test doubled to reach 62.19 and 58.82%, respectively of Cu and Pb. It is assumed that PR provided a suitable soil conditions for the EKR treatment, as it prevented pH gradient jump, and no additional buffer electrolyte was required. Moreover, this technique enhanced the remediation process through a better penetration of citric acid into soil which eventually facilitated the extraction, and transportation of Pb and Cu. Pazos et al. [25], Cai et al. [41] and Lu et al. [34] have tested the polarity reversal technique on heavy metals contaminated soil. They all concluded that PR is efficient against the formation of acid and basic front during the soil EKR process. The results of experiment T3, as presented in Fig. 5(a), and 5(c), lead to the same conclusion. Nonetheless complete removal was not attained. In test T3, the pH of soil sections 3 to 5 ranged from 5.1 to 6.8. According to the pKa of citric acid, these pH values probably promoted the formation of neutral complexes, such as PbH_2Cit and CuH_2Cit . The mobility of these nonionic species by advection,

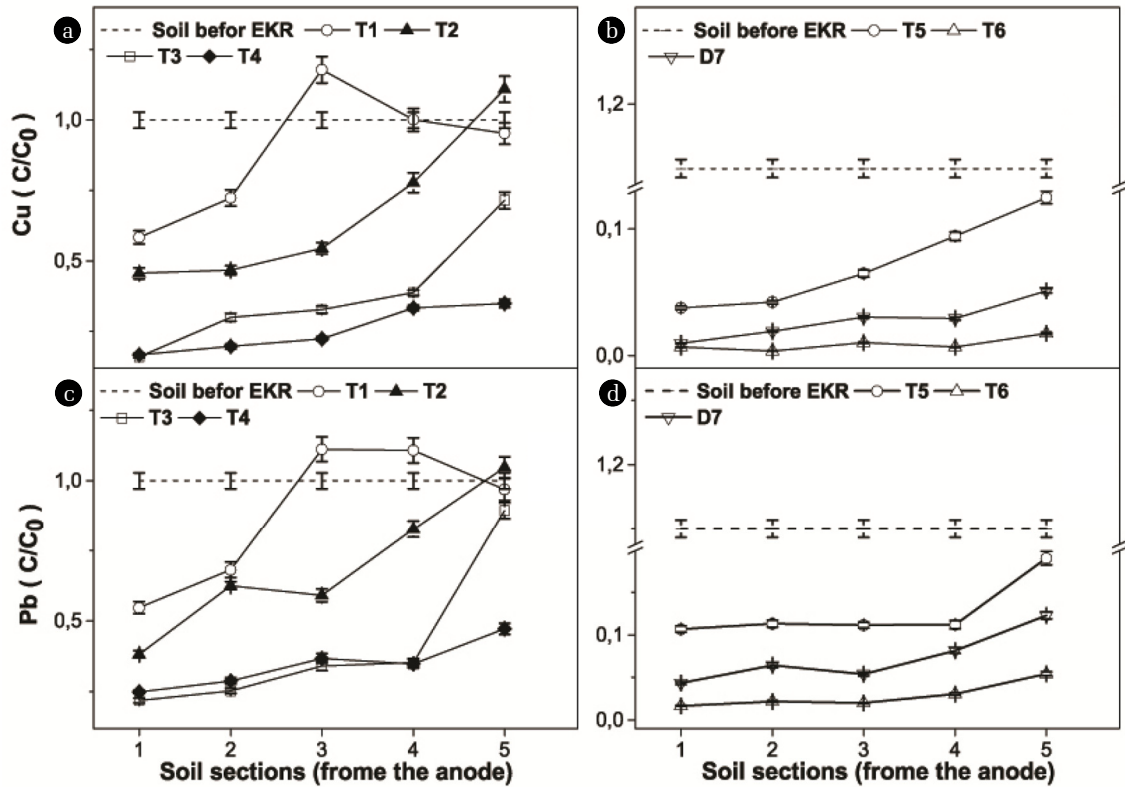


Fig. 5. Normalized concentrations of lead and copper after electrokinetic treatment.

in the interstitial fluid, is very low. Hence the difficulty of their removal by the EKR process [46]. Cumulative EOF of test T3 was low and practically stopped. Since the remediation of precipitates relied only on EOF, the decontamination process ended, thus the rest of heavy metals remained in soil.

The R% results of Test T4 showed approximately 10% improvement of both metals with respect to test T3. It could be due to the acidic soil environment induced by the addition of acetic acid directly into the catholyte. In acid medium, Pb and Cu are desorbed from soil surface, by citric acid enhanced EKR, into the interstitial fluid in two possible forms: divalent ions (Cu^{2+} or Pb^{2+}) and/or soluble cationic citrate complexes [47]. In test T4, soil pH ranged from 3 to 2 which means that citric acid was in H_2Cit^- ligands form, conforming with its pKa value. The ligands formed cationic citrate complexes, such as $\text{Pb}(\text{H}_2\text{Cit})^+$ and CuH_2Cit^+ . These species electromigrated toward the cathode in the same direction as normal EOF which favored the decontamination process. Furthermore, these positively charged molecules, are very stable water soluble complexes due to their relatively high values of the stability constants, as shown in Table S2. This indicates the high potential of citric acid to enhance the EKR process. Similar results are obtainable by chelating metals with EDTA. Song et al. [48] used EDTA as flushing solution and applied a Cpc (at pH 2) in EKR of Pb and Cd contaminated red soil, the EOF generated toward the anode due to very low soil pH. They confirmed that the main EKR mechanisms for metal- EDTA (EDTA-Me^{2-}) transport in soil are both EOF and electromigration (toward the anode).

However, the soil remediation, once again, was not complete. The cause for process limitation could be due to a clogging happening in the soil pores by the aggregation of soil colloid particles. More specifically, partial soil particles were transported with EOF, which increased the percentage of aggregation of soil colloid particles [49]. This remolded the flocculated soil fabric into aggregated fabric [50] and subsequently, the soil had little to no void fraction. Correspondingly, the EKR mechanisms were forced to shut down.

The purpose of test T5, T6 and D7 is to overcome the clogging of soil pore particles emphasized in test T4. In test T5, PR and Cpc are used simultaneously on soil EKR. The R% increased up to 92.73% and 87.32% of respectively Pb and Cu. The combination of Both EKR enhancers highly and effectively reduced the influence of pH variation on soil caused by water electrolysis. Consequently, avoiding any metal precipitates that could clog the soil pore, thus, favoring the EKR decontamination mechanisms (EOF and electromigration) on Pb and Cu from soil. Moreover, the enhancement observed in test T5 could also be attributed to a low rate of the aggregate colloid particles, in soil sections near the cathode. The authors of this paper hypothesize that the clogging of soil particles was probably reduced by the application of PR intervals. During which, charged particles in soil could have electromigrated back and forth, for a very small and restricted distance considering that PR time was limited (see Fig. S1), by the repetitive change of medium polarity. These movements would have transferred enough momentum to move the surrounding small aggregate soil particles, thereby creating or unclogging potential paths within

the pores soil network for heavy metals transportation.

Test T6 resulted in the best removal efficiency with more than 97% of total decontamination. This could be principally owed to a better flow of the interstitial fluid across the EKR cell. Unlike test T5, experiment T6 produced more cumulative EOF which allowed a better current conductivity. This generation of higher volumes of EOF was favored considering that the normal EKR treatment time was increased by reducing the PR time, as shown in Fig. S1(b). One could argue, with a short PR application, how could the pore particles, near the cathode, be kept free of colloid particles aggregation. The answer could be in the application of 3.0 times the initial voltage gradient, i.e. 3 DCV/cm, during the 30 min of polarity reversal. The stress of these multiple electric shocks, per day in soil, may have created small cracks in the clogged area of soil. During this stress, ionic species strongly electromigrated, in the opposite direction, by the high DC voltage. The transport of these ionic species may have induced the movement of nano particles, thus clearing small paths for the pore water fluid. Consequently, the interstitial fluid spread through the small gaps, created by the electric shocks, and enhanced the overall process through a better function of the EKR main mechanisms. Since the heat of soil increases the sorption of heavy metals into soil, the PR was also limited to 30 min to avoid the joule effect [51].

As expected, the removal efficiency of test D7 was close to that of test T6. This behavior can be explained by the same controlled parameter in both experiments, and can be confirmed by the similarity of R% trend in all soil sections, as shown in Fig. 5(b), and 5(d). In test D7, Soil 2 contained 10,000 mg/kg of each contaminant (Pb and Cu). The treatment time was extended to 29 d, as the heavy metals removal was not finished. EOF still cumulated and the current intensity leveled off at high values due to the presence of higher amount of ions, in the porous media, and to the low soil pH. These conditions favored, proportionately, an efficient soil decontamination of 97.22% and 92.67% of respectively Cu and Pb.

Additional data, figures and captions of this work are provided as supplementary materials: Pb and Cu content in soil before and after EKR treatment is presented, respectively, in Table S3 and Table S4. Pictures of the EKR main compartment in test T6 at different time laps are presented in Fig. S3, Fig. S4, Fig. S5 and Fig. S6. Also, pictures of the soil chamber in Test D7 at different time laps is provided in Fig. S7, Fig. S8 and Fig. S9.

3.5. Power Consumption

The results of power consumption per unit weight of soil (kWh.t^{-1}) were estimated and reported in Table 3. The EKR pH control techniques required more energy consumption than that of the conventional EKR. The catholyte controlled pH in test T4 increased the Pc due to the addition of H^+ and CH_3COO^- in the system which favored a better electric conductivity. The application of both PR and Cpc resulted in higher Pc, it is probably due to a better transport of the pore water fluid by EOF, thus favoring a better current intensity. The energy consumption increased relatively with the soil moisture content and efficiency removal. Soil moisture enhanced the passage of electrical current through the soil. Therefore, enabling a better performance of the EKR mechanisms enhanced

the R%. The soil of test D7 required 10 more days of EKR process than that of test T6 because of the high Cu and Pb content. This time extension along with metals content resulted in a highest power consumption with $1,556 \text{ kWh.t}^{-1}$. In short, the current consumption of this study depended on soil moisture, metal content and EKR treatment time. Overall, the power consumption is relatively low when compared with other remediation techniques [6]. The results of the enhanced electrokinetic soil remediation, presented in this paper, suggest that this process could be an effective alternative for the decontamination of soil contaminated with heavy metals such as Pb and Cu. Nevertheless, the lab scale experiments of this work should be performed on pilot scale in order to extrapolate results and useful information for potential field scale application. The energy consumption should be inversely related to the experimental scale; i.e. bigger scale process requires less electric power [23].

4. Conclusions

This paper shows promising results for the application of electrokinetic soil remediation on aged heavy metal contaminated soil. The use of citric acid alone with EKR was not sufficient to remediate Pb and Cu from soil. The addition of periodic polarity reversal or catholyte pH control techniques separately increased the removal efficiency but did not achieve complete soil depollution. On one hand, these techniques could potentially yield better results if the EKR duration time was extended but will surely result in more power consumption. On the other hand, with the same 19 d of experiment, better results were obtained when the two enhancing techniques were combined together. Furthermore, this combination is hypothesized to have overcome the problem of soil clogging caused by the aggregation of colloid particles and heavy metals precipitates. Finally, coupling EKR with a combination of periodic Polarity reversal electric shock and Catholyte pH control yielded the best removal efficiency with 99.11% of Cu and 97.13% of Pb. These results are mainly owed to (i) the Cpc that provided an ideal soil pH for Pb and Cu removal. (ii) The short time of PR which increased the cumulative EOF, and therefore enhancing the R%. (iii) The stress caused by the repetitive PR electric shocks on charged particles within soil, which possibly have created small gaps within the clogged soil pores, and assured a path of transport for heavy metals. This method is proposed as a new approach for large scale applications.

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Author Contributions

All authors contributed to the study conception and design. O.M.B (Ph.D.) performed all experiments and analysis along with data

collection, discussion of the results, and wrote the manuscript. O.M. (Ph.D. student/engineer in physical and chemical analysis) worked on the chemical analysis and data plotting. D.E.A. (professor) revised and edited the manuscript.

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