

# Electrokinetic treatment for clayed and sandy soils

E. G. Sumbarda-Ramos · O. X. Guerrero-Gutierrez ·  
B. Murillo-Rivera · I. González ·  
M. T. Oropeza-Guzman

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**Abstract** Electrokinetic treatment has proven to be an attractive alternative to clean polluted soils. This friendly environmental procedure can be approached by a physicochemical model dealing with the oriented displacement of pollutants by means of the fluid and/or charge flow through a porous media induced by an electric field. Concerning the porous media, soil texture is the main issue to consider, since it is related with physicochemical properties that may define the electrokinetic phenomena. In this paper, two different soil textures were tested under the same experimental conditions. Physicochemical characterization of clayed and sandy unpolluted soils, later mixed with  $\text{PbCO}_3$ , were done. Zeta potential measurements were performed to approach the soil particles interphase with three aqueous solutions. Clayed and sandy soil, mixed with cerusite, were treated by electrokinetics during 24 h. Results for sandy soil contaminated with Pb, using ammonium acetate and acetic acid as anolyte and catholyte respectively, reported Pb mobility due to a fluid flow from anode to cathode; in accordance with zeta potential indi-

cating more negative values for ammonium acetate solution, compared with EDTA and acetic acid. For the clayed soil, lead mobility was detected, even if no electroosmotic flow appeared. Finally, the same experimental conditions were applied to a real soil containing mining wastes, in this case lead mobility was due to electroosmotic and electromigration flow.

**Keywords** Electrokinetic · Electromigration · Electroosmosis · Clayed soil · Sandy soil · Lead mobility

## 1 Introduction

Electrokinetic treatment is a friendly environmental option for sites containing mixed or adsorbed pollutants. The main principle of electrokinetic is the application of an electric field that promotes the displacement of pollutants agents through the soil solution. Three transport phenomena named: electroosmosis (water movement), electromigration (ion movement) and electrophoresis (colloidal movement) are occurring in an electrokinetic treatment [1]. On the other hand, there are several factors determining the extractability of pollutants when electrokinetic treatment is applied, these are: pollutants type and concentration, soil type, soil solution pH, soil buffer capacity, soil zeta potential, electroosmotic flow, operation parameters (electrodes, cell voltage and current) and addition of surfactants agents increasing removal efficiency [2]. Then, to follow-up the pollutant removal from different soil textures by electrokinetic treatment, in this paper authors propose to use model soils: clayed and sandy particles (clean and mixed with  $\text{PbCO}_3$ ). It is important to remark that soil samples packed inside an electrokinetic cell are similar to the experimental device used to measure the streaming potential (also named

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E. G. Sumbarda-Ramos · M. T. Oropeza-Guzman (✉)  
Instituto Tecnológico de Tijuana, Centro de Graduados, Blvd.  
Industrial s/n, Col. Otay 22500, Tijuana B.C., México  
e-mail: oropezal@yahoo.com

O. X. Guerrero-Gutierrez  
Universidad Autónoma de Baja California–Tijuana,  
Calzada Universidad No. 14418, Mesa de Otay 22390,  
Tijuana B.C., México

B. Murillo-Rivera · I. González  
Departamento de Química, Universidad Autónoma  
Metropolitana Unidad Iztapalapa, Av. San Rafael Atlixco,  
No. 186, Col. Vicentina 09340, México D.F., México

zeta potential), and has been used by several authors to determine adsorbed species and chemical reactions developing on a solid particle surface [3]. As well as the electrokinetic phenomena, streaming or zeta potential depends on the aqueous solution pH and is related to electroosmotic flow (EOF) value [4, 5] for low permeability soils, even clayed or sandy.

To demonstrate the influence of soil texture on the electrokinetic treatment, in this paper authors propose three main experimental steps. First, the measurement of zeta potential for clayed and sandy soils in different electrolyte solutions to point out the proper one improving soil permeability and pollutant desorption and/or mobility. Considering that sandy and clayed soils in water has naturally negative zeta potentials (silicates and aluminates groups), the more negative reached zeta potential value will favor the fluid flow through the porous media. Moreover, if the fluid has the proper composition to desorbs or move pollutants, the more convenient for an electrokinetic treatment. The second step is to perform electrokinetic experiments with both clayed and sandy soils expecting that texture may show the predominance of one or another electrokinetic phenomenon. Finally, the same experimental conditions were used to evaluate a real lead contaminated soil coming from Zimapan, Hidalgo, Mexico containing a mixture of sand and clay.

## 2 Experimental

Two soil samples of different texture were used for the electrokinetic experiments, they were labelled as: SS (sand) and CS (sandy clayed loam). The SS soil was used in its original conditions (commercial sand), the CS soil was sieved to select only the soil passing sieve 200 (74  $\mu\text{m}$ ). Another sample from a real site (Zimapan, Hidalgo, Mexico) polluted with mining wastes, was used to evaluate the electrokinetic extraction of lead under the same experimental conditions as those used for CS and SS.

### 2.1 Characterization of the soil samples

Each soil sample was submitted to a physicochemical characterization: pH [6], conductivity [7], buffer capacity [8], moisture [7], texture [7], cation exchange capacity C.E.C. [9] and zeta potential. The Zimapan's sample was characterized by another research group (UAM-I, UASLP and UAEH), reporting 98.5% sand, 1.5% of clayed and 500 mg Pb/kg soil. It is important to remark that this lead concentration is higher to the established by the Mexican authorities at NOM-147-SEMARNAT/SSA1-2004. Two lead species were detected:  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $\text{PbCO}_3$ , mixed with other metals as copper and arsenic.

### 2.2 Electrolyte selection for the electrokinetic experiments

To select the conditioning and anodic electrolyte for electrokinetic experiments, zeta potential measurements were performed. Nanosizer Malvern Instrument was used with the well known Smolouchouski model (electrophoretic mobility). Soil dispersions were prepared with 25 mg in 25 mL of 1 mM solution of  $\text{NH}_4\text{CH}_3\text{COO}$ ,  $\text{HCH}_3\text{COO}$  and  $\text{Na}_2\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$  ( $\text{EDTANa}_2$ ) and  $\text{H}_2\text{O}$  [10]. These solutions were tested due to their well known chemical equilibriums. For example, ammonium solution improved Cu and Pb extraction during CEC measurements. Concerning  $\text{HCH}_3\text{COO}$  and  $\text{EDTANa}_2$ , they have been reported as good complexing and chelating agents that will form lead complexes and may increase its mobility in a fluid media.

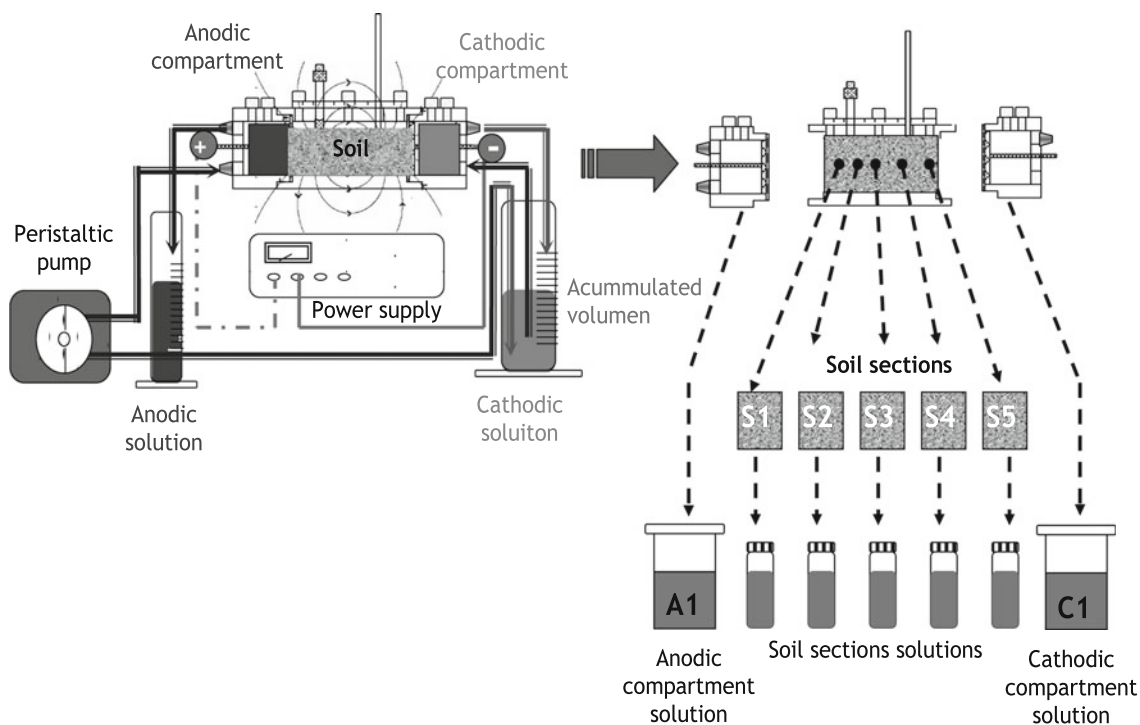
### 2.3 Electrokinetic treatment applied to soil samples

The cell used for the electrokinetic experiments was the OSMIC-I [11]. Figure 1 described the experimental system and the reported cell sections. This cell was fully constructed in the workshop of the University. Constant current of 1 mA was applied (potentiostat/galvanostat PAR173) for each experiment. Prior experiments, not reported in this paper, changing the current intensity applied to sandy soil served to decide that 1 mA was the more suitable value, since fluid flow was registered with in the first 6 h and continue until 24 h. Experiments without electric field but with electrolyte recirculation in each compartment confirmed that the fluid flow was related with the electric current intensity [12].

During the electrokinetic experiment, potential distribution was registered across the soil sections, each hour. Electric potential gradient was measured using one electrode of the same material as those of the cell (Ti/RuO<sub>2</sub>). The EOF during the electrokinetic process was calculated through the water volume accumulated at the cathodic compartment (assuming its direction from anode to cathode). To register how the acid and alkaline fronts (product of water electrolysis) advanced, pH measurements were also taken each hour.

Electrokinetic treatments were performed for different soil textures under the same experimental conditions: pollutant (type and concentration), anodic solution ( $\text{NH}_4\text{CH}_3\text{COO}$  1 mM), cathodic solution ( $\text{CH}_3\text{COOH}$  1 mM), applied current (1 mA) and experimental time (24 h).

Electrokinetic treatment was evaluated by data measured during the experiment, as well as the pollutant mobility across the soil section in the cell (see Fig. 1). Each soil section in the cell was submitted to a microwave



**Fig. 1** Electrokinetic cell named OSMIC-I showing the main components as well as the soil sections cuts after the each experiment

digestion to prepare the samples for atomic absorption analysis [13].

### 2.3.1 Soil sample preparation

The samples CS and SS are naturally clean soils. To obtain a lead concentration of 500 mgPb/kg soil, pure reagent  $\text{PbCO}_3$  was used. The contaminated soil was prepared as follows: 300 g of soil were mixed with an equivalent quantity of  $\text{PbCO}_3$  to complete 500 mg Pb/kg soil. The soil was manually spread on a plastic sheet bending it 100 times to mix solid components until homogeneity. Finally the mixture was moisturized at its field capacity. SS sample was moisturized at 26% and CS sample at 16.8%, both with 1 mM  $\text{NH}_4\text{CH}_3\text{OO}$ , 24 h before the electrokinetic experiments. After this time the soil sample was packed in the cell. Cerusite,  $\text{PbCO}_3$ , was selected since the Zimapan's soil has this pollutant as the principal lead specie.

## 3 Results

### 3.1 Soil sample characterization

The physicochemical characterization gives useful information for understanding the experimental results during and after the electrokinetic treatment. Bouyoucos tests performed to each soil sample are shown in Table 1. As

observed SS is mainly sand, while CS has a high clayed percentage, but also considerable sand content.

### 3.2 Electrolyte selection

In another paper of the EREM 2009 Symposium, authors discuss about the electrolyte influence into the electrokinetic experiments. To attend those conclusions, different electrolyte solutions were tested by the zeta potential measurements:  $\text{CH}_3\text{COOH}$  1 mM that is a weak acidic electrolyte used to overcome the generation of  $\text{OH}^-$  at the cathodic compartment,  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM used in the CEC measurements to promote metals desorption and in this case to improve lead removal from soil, and  $\text{EDTANa}_2$  1 mM for its complexing properties. Zeta potential measurements of the clean and polluted soil samples were also registered in the same solutions. Figures 2 and 3 revealed the results for SS and CS samples. In  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM solution, zeta potential values are above  $-30$  mV, suggesting a stable soil suspension. In addition, the negative zeta potential value indicate a good electroosmotic permeability expecting a fluid flow from anode to cathode [7], as well as the transport of soluble Pb by electromigration. To confirm this prediction predominance zone diagram for Pb species was constructed using MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) (not shown). It exhibits  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM as the best option for moisturizing solution to promote  $\text{Pb}^{2+}$  mobility. This

**Table 1** Characterization of the soil samples SS y CS

Sample	EC ( $\mu\text{S}$ )	pH	Field capacity %	Zeta Potential, $\zeta$ (mV)/ $\text{H}_2\text{O}$	Buffer capacity ( $\text{mMpH}^{-1}$ )	C.E.C. ( $\text{mmol/kg}$ )
SS	44	5.12	26.00	-11.1	1.202	10
CS	212	5.89	16.80	-31.5	1.479	71

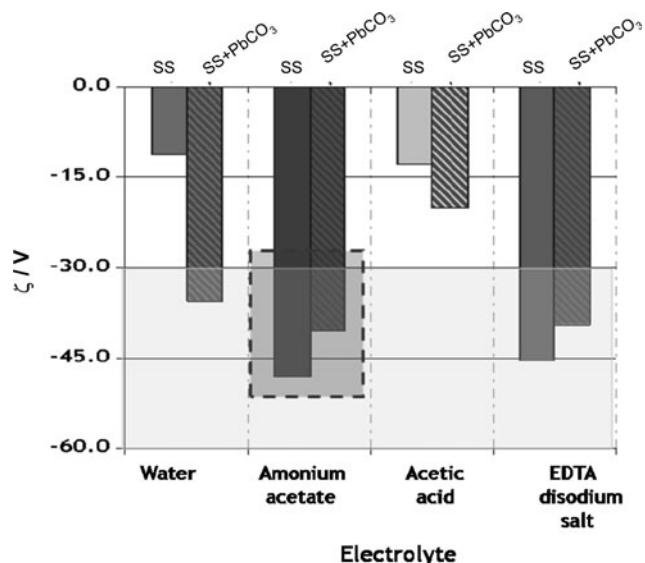
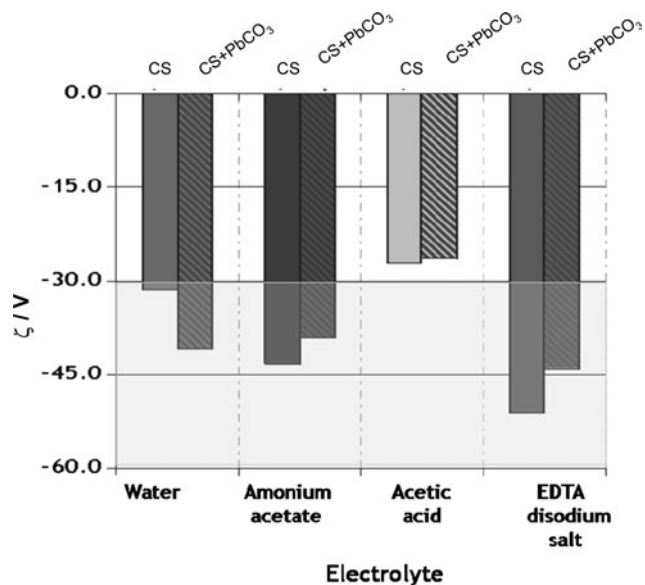
**Fig. 2** Graphic representation of the zeta potential variation under the effect of the electrolyte solution in which SS (sandy soil) was dispersed**Fig. 3** Graphic representation of the zeta potential variation under the effect of the electrolyte solution in which CS (clayed soil) was dispersed

diagram also reveals the solution pH and concentration to ensure Pb's soluble species, avoiding the crystal or the hydroxide solids.  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM was also used in the

anodic compartment to analyze lead mobility in the real site sample. Another interesting observation is the increase of soils zeta potential when  $\text{PbCO}_3$  is added, except when  $\text{NH}_4\text{CH}_3\text{COO}$  and  $\text{EDTA Na}_2$  is added. This effect is probably due to the chemical reactions occurring on the soil particles surface, since  $\text{NH}_4\text{CH}_3\text{COO}$  and  $\text{EDTA Na}_2$  provide several complexing possibilities for metallic cation contained in the soil phase.

### 3.3 Electrokinetic treatment

This section resume the results obtained during electrokinetic treatment, and the analysis of the soil sections in the cell to compare the initial and final conditions. Also CS and SS results were compared with Zimapan's soil.

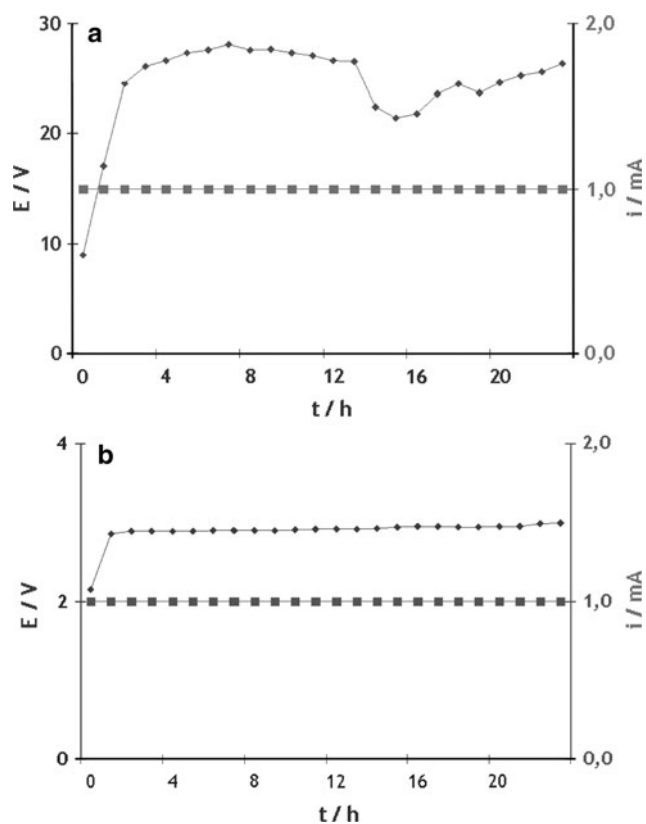
#### 3.3.1 Measurement during electrokinetic treatment

During electrokinetic experiment the sample SS shows higher cell potential compared with that of the sample CS. For both samples the higher potential was reached at the first hour, sample SS (sand) presents a second potential jump after the first hour. For the next hours the potential variation is minor (see Fig. 4a). The sample CS does not show any significant potential variation after the first hour, (see Fig. 4b).

Figure 5 shows the comparison of cell potential, accumulated water volume and EOF for SS. On the contrary CS does not show at all any accumulated volume during the electrokinetic treatment. To prove that water flow through the SS was due to the electric field, blank experiments were performed without electric perturbation but only with electrolyte recirculation. No water flow was registered for SS nor for CS.

Regarding the pH profile, Fig. 6 shows that the buffer capacity of clayed soil allows more stable values, in contrast with sandy soil that does not showed any tendency.

The pollutant mobility across the cell is showed in Fig. 7, different mobility patterns are observed for each case. In SS, Pb was accumulated between sections S2 and S3. During this experiment a white deposit over the cathode was observed and at the end of the experiment, the white deposit was analyzed for lead presence using an Energy dispersive X-ray probe for elemental analysis (Fig. 8). For the sample CS lead mobility was toward the cathodic compartment (see Fig. 7) with higher



**Fig. 4** Electric potential variations during 24 h of electrokinetic treatment applied to **a** SS and **b** CS, polluted with  $\text{PbCO}_3$ , premoisturized with  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM at 1 mA, recirculation of  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM at the anodic compartment and  $\text{HCH}_3\text{COO}$  1 mM at the cathodic compartment was maintained during the electrokinetic experiment

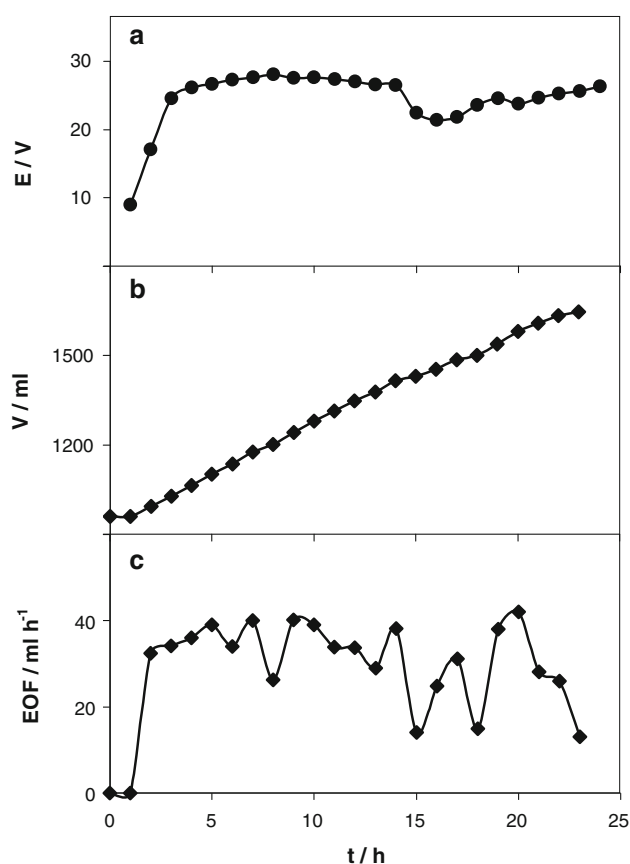
concentration at the S5 section. Further calculations are in progress to obtain the mobility coefficient for lead species during electrokinetic treatments for both soil textures.

For the Zimapan sample, the electric potential showed lower values than SS and CS, and similar potential distribution to CS. This behaviour is probably due to the high electric conductivity. After 11 h, water volume was accumulated in the cathodic compartment (see Fig. 9). However lead mobility is lower than that registered for SS and CS (see Fig. 7).

#### 4 Conclusions

In this paper the main contributions are related with the polluted soil texture. Depending on the soil texture the exhibited electrokinetic phenomena change since it is linked to the buffer capacity and cation exchange capacity of the soil.

For the sandy soil the driving force was the fluid flow through the porous media induced by the electric field. This



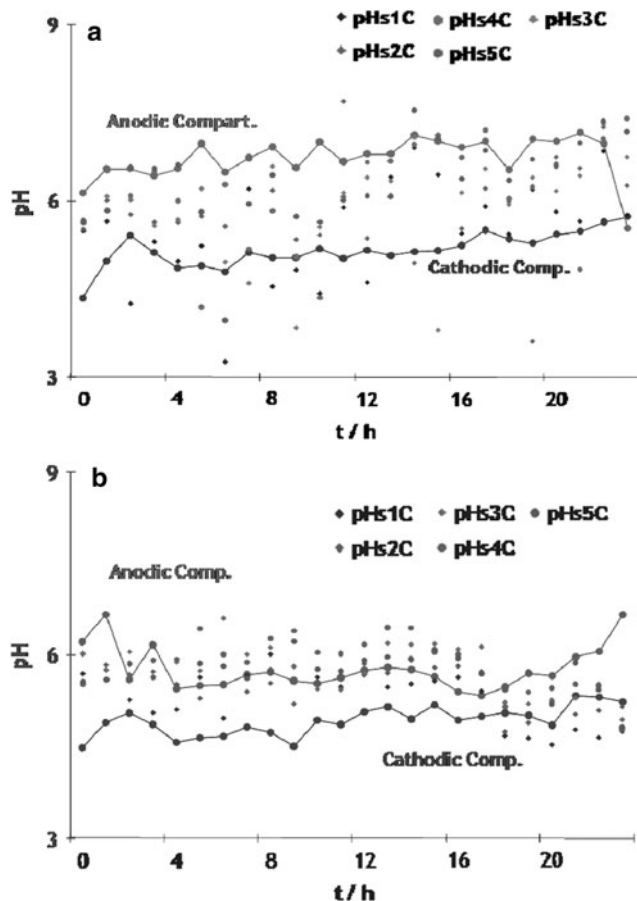
**Fig. 5** **a** Cell potential, **b** Accumulated water volume and **c** EOF during 24 h of electrokinetic treatment applied to SS soil polluted with  $\text{PbCO}_3$ , premoisturized with  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM at 1 mA constant current, recirculation of  $\text{NH}_4\text{CH}_3\text{COO}$  1 mM at the anodic compartment and  $\text{HCH}_3\text{COO}$  1 mM at the cathodic compartment was maintained during the electrokinetic experiment

effect was evaluated comparing two experiments, one at  $i = 1$  mA and the other without current (no electric field and no fluid collected on the cathode compartment after 24 h). For the clayed soil no fluid flow was registered after 24 h for experiments with and without electric field. However the analysis of Pb content revealed the contaminant mobility. In both cases, it can be stated that soil texture determine the electrokinetic remediation efficiency, thus the contaminant desorption mechanism.

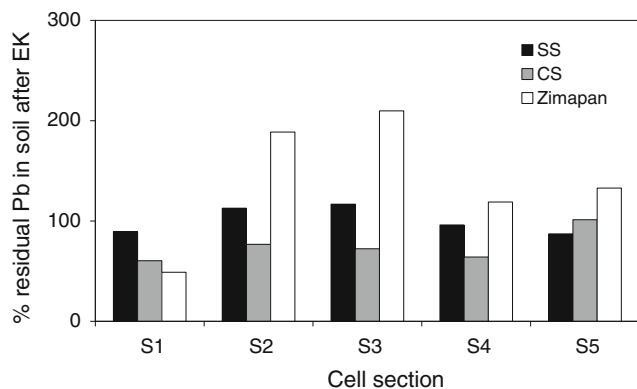
It must be recognized that sandy soils are not usually reported for electrokinetic treatment, since it is considered that electrokinetic phenomena are exclusively for clayed soils. However, in this paper the experimental data allowed to identify a fluid flow phenomenon coupled to the electric current through the sandy soil.

Concerning the electrolytic solutions reported in this paper (acetic acid in the cathodic side and ammonium acetate in the anodic side), it is remarkable the effect achieved for pH and Zeta potential, but also the chemical species distribution in the soil matrix and in the fluid phase.



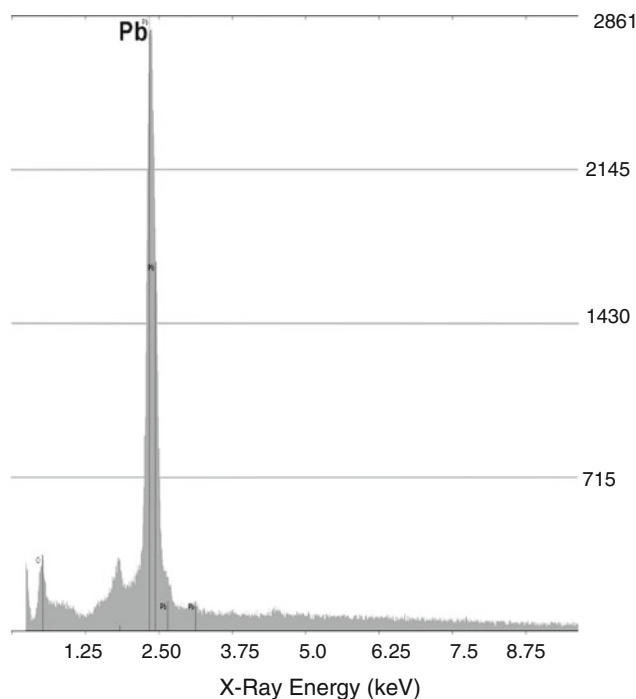


**Fig. 6** pH variation at the anodic and cathodic compartments and at each cell section during 24 h of electrokinetic treatment applied to **a** SS and **b** CS, polluted with  $PbCO_3$

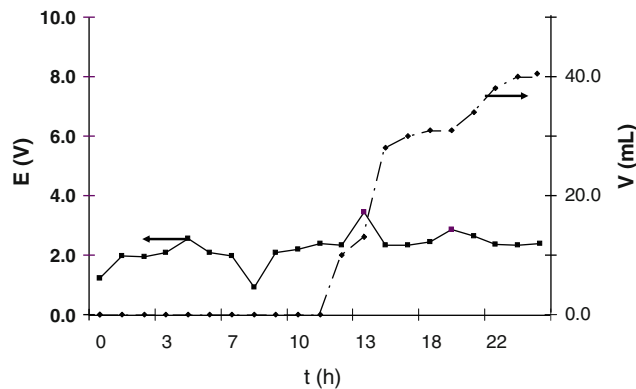


**Fig. 7** Residual Pb % at each cell section comparing SS (polluted with  $PbCO_3$  and moisturized to 26% with  $NH_4CH_3COO$  1 mM), CS (sandy clayed loam, polluted with  $PbCO_3$  and moisturized to 16.8% with  $NH_4CH_3COO$  1 mM) and Zimapan’s soil under the same experimental conditions

Variation of zeta potential under different pH simulate the experimental conditions for the soil-pollutant-soil solution interaction, since the pH at the interface changes



**Fig. 8** EDAX spectrum of the cathode surface after the electrokinetic treatment applied to the SS sample



**Fig. 9** Comparison of electrokinetic treatment applied to SS, CS and Zimapan’s site using the same experimental conditions

the zeta potential value and this one can induce the conditions for pollutant desorption.

The pH variation at the interface also depends on the buffer capacity of the soil sample as observed for the sandy and clayed soil in this paper. If the buffer capacity is high, the soil will keep the same interfacial conditions regardless the fluid pH.

Pb mobility was detected for  $pH \leq 5$  for sandy soil and  $pH \leq 6$  for clayed soil. The distribution species diagram revealed that cationic species as  $PbCH_3COO^+$  and  $Pb^{2+}$  are suitable to be formed; however the greater percentage of Pb is  $PbCO_3$  crystal. Under this consideration it should be assumed that lower pH values will promote cationic Pb

species and improve Pb mobility toward the cathode. However, the zeta potential values showed that, at lower pH, the electric potential surrounding the soil particles decrease ( $pZ \rightarrow 0$ ). For this reason it is important to find-out the best pH value to favor the electroosmotic flow and/or the ionic Pb(II) mobility, depending on the soil texture.

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