J Appl Electrochem (2010) 40:1145–1152
DOI 10.1007/s10800-010-0085-y

ORIGINAL PAPER

Evaluation of lead removal from sandy soils using different electrolytes in electrokinetic experiments: prospective for remediation of a real site contaminated with mining wastes

**B. Murillo-Rivera · I. González ·
M. T. Oropeza-Guzman · V. Escobar-Guerrero ·
E. G. Sumbarda-Ramos · M. M. M. Teutli-León**

Received: 11 September 2009 / Accepted: 11 January 2010

Abstract The mixture of mining wastes with native soil has similarities with a low permeable porous structure in respect of electrical conductivity and adsorption capacity; therefore, electrokinetics appears as a suitable remediation treatment for sites containing potential toxic elements as Pb, Cd and As. In particular, this paper focuses on the evaluation of the main electrokinetic phenomena that removes Pb(II) from the model sandy soil (98.5% sand and 1.5% clay). For this purpose a study of five different electrolytes, used as moisturizing solution, as well as electrolytes, was done. Results from zeta potential measurements and electrokinetic experiments indicate that ammonium acetate and acetic acid were the best electrolytic solution that ensures the greater Pb removal from sandy soil contaminated with $PbCO_3$.

Keywords Electrokinetics · Pb removal · Zeta potential · Electroosmotic flow · Electromigration

B. Murillo-Rivera · I. González · V. Escobar-Guerrero
Departamento de Química, Universidad Autónoma
Metropolitana Iztapalapa, San Rafael Atlixco 186,
Col. Vicentina, 09340 Mexico, D.F., Mexico

M. T. Oropeza-Guzman (✉) · E. G. Sumbarda-Ramos
Instituto Tecnológico de Tijuana, Centro de Graduados, Blvd.
Industrial sn, Col. Otay, 22500 Tijuana, B.C., Mexico
e-mail: oropeza1@yahoo.com

M. M. M. Teutli-León
Facultad de Ingeniería, Benemerita Universidad Autonoma
de Puebla, Edificio 123, Ciudad Universitaria,
72570 Puebla, Pue, Mexico

1 Introduction

In this century, all industries related with explotation and processing of minerals are facing serious environmental problems. Only in Mexico, mining wastes production is estimated to be 123 million tons each year; however, the real status of wastes from mineral processing and their potential impact into the environment are still unclear [1].

As example of a critical case is the one at the mining district of Zimapan in the State of Hidalgo, Mexico, where many tons of mining wastes have been disposed under open sky. This fact has produced a severe contamination of soils and groundwater, which is mainly attributed to the dispersion of weathered accumulated wastes [2]. Reliable studies in the zone have shown that Zimapan's site presents a high content of potentially toxic elements (PTE) as: arsenic (As), cadmium (Cd), lead (Pb) and zinc (Zn) [2–4]. But, the real danger of these elements depends on their mobility (soluble fraction) and the physico-chemical and mineralogical properties of soil, where PTE could be adsorbed, encapsulated or precipitated with some components in soil matrix [5].

Under these considerations, application of one or several remediation techniques, it is limited by a critical step of the overall decontamination process. Remediation approaches have considered phytoremediation, mechanical removal as well as addition of carbonates, lime and zeolites to immobilize PTE [6, 7]. Nevertheless, successful of all these procedures has been limited because of the high concentration of PTE and expenses involved in large volume transportation and final confinement.

At this point, electrokinetic process is an alternative technology that has proven to be able to remove efficiently heavy metals from low permeability soils like sediments, limes and clays [8]. The electrokinetic process has the versatility to be applied in situ, allowing for contaminants removal without excavating the site, so the process is less expensive. Under this regard, estimated costs of remediation are in the range of 26–260 USD/m^3, which makes it highly competitive in respect to other technologies [7]. Also, an electrolysis control of solution during electrokinetic processes favors to set up acidic conditions through soil and allow heavy metal release into the solution phase [8].

From the physicochemical point of view, electrokinetics involves application of a low intensity electrical field through a porous matrix, which is usually saturated with water or with an electrolyte. Among the expected effects, there are three simultaneous transport phenomena: electromigration, electroosmosis and/or electrophoresis [9]. In some cases metal removal is mainly due to electromigration while in other cases, for soluble metals the total flux is obtained from the addition of electroosmotic and the electromigration flows [10]. For this reason, metal mobility is always related with electromigration as well as with electroosmosis, and only few cases of metal removal are related with electrophoretic flow. Considering that the mixture of mining wastes with native soil resulted in a low permeable porous structure, it is possible to assume that an electrokinetics remediation can be used for lessen the impact of pollution exerted by mining waste.

Recent laboratory experiments have showed the suitable removal of PTE from mining waste by means of electrokinetic phenomena [6, 11–13]; however, a complete understanding of contaminants transport in soils containing mine tailings is necessary in order to establish the appropriate operational conditions for the technique to be applied *on-site*.

An approach based on the double layer model expression, it is known as zeta potential and it can be helpful to understand how the driving forces act for metal removal from contaminated soils. Other authors have already characterized different kind of soil structures surrounded by electrolytic solutions [14].

This paper presents an approach to determine the main phenomena associated to the electrokinetic Pb removal, by using a contaminated sandy soil prepared with different electrolytes for both moisturizing the soil as well as a replenishment solution in the electrode compartments of electro-kinetic cell.

The removal percentage is used as the merit figure to establish the more convenient electrolyte, as well as the best current density which ensures maximum metal removal from contaminated sandy soil.

2 Experimental

2.1 Selection of soil model

Taking into account previous studies of Zimapan's site, which were performed by the Institute of Environmental Geochemistry and Geomicrobiology, of the UASLP Metallurgy Institute [3, 4], authors sampled a real soil around the mining site. The mineralogical analysis allowed classifying it as sandy soil according to the Unified Classification System procedure (based on STMD-2487), also it was found cerusite crystals ($PbCO_3$) as the main lead species. From this analysis, and to be in accordance with the textural class of the real soil, a mixture of 98.5% sand and 1.5% clay, was used as model soil named A100. The physicochemical properties of Zimapan and A100 soils are reported in Table 1.

2.2 Contamination of sandy soil and initial analysis

Sandy soil was synthetically contaminated with an initial concentration of Pb (500 mg Pb/kg soil), using $PbCO_3$ (Reasol, A. R.). Both solid phases were mechanically mixed and three representative samples were taken for analysis of Pb initial concentration. Soil pH and electrical conductivity was measured in water suspension at 1:2.5 soil-solutions with pH meter Orion PC-45. The soil moisture at field capacity (θ_{fc}) for the model and real soil was evaluated by weight differences between soil moisture determined 2–3 days after irrigation and soil moisture of a sample dried at ambient temperature [15].

The soil was humidified at field capacity (θ_{fc}) with five different aqueous solutions: deionised H_2O and 1 mM solutions of CH_3COONH_4, CH_3COOH, $C_6H_8O_7$, HNO_3. All soil preconditioning solutions and electrolytes were prepared with J. T. Baker analytic reagents. A suitable quantity (about 200 g) of humidified soil was packed in a constructed cell made at the workshop of the University, which was named OSMIC-I.

Table 1 Physicochemical characterization of the soil samples A100

Sample	Sand %	Clay %	EC μS cm^{-1}	pH	θ_{fc} %	ζ mV/H_2O	Buffer capacity (mM pH^{-1})	C.E.C. mmol/kg
Zimapán (P-39)	89	10	535	8.1	45.2	−0.01	–	–
A100	98.5	1.5	48	5.1	26.0	−24.9	1.20	2

2.3 Electrokinetic experiments

2.3.1 Experimental set-up

All experiments were performed in the OSMIC-I cylindrical cell of radius = 1.8 cm and length = 20 cm, which is divided in three compartments: anodic chamber, soil sample and cathodic chamber. A flow diagram of the experimental device is shown in Fig. 1. This cell is easy assembling and handling, it has several sampling ports for introducing pH electrodes, as well as for circulation of fresh electrolyte solution in both electrode chambers [16].

The flow rate in the anodic compartment was fixed to 20 mL/min (speed which ensures no pressure drop through the cell). Five different dissolutions were tested in both compartments: H_2O, CH_3COONH_4, CH_3COOH, $C_6H_8O_7$, HNO_3; and with each solution five different experiments were performed at constant current densities of: 0.003, 0.008, 0.016, 0.024, 0.031 mA cm^{-2} for 24 h. A summary of conditions, for the named Experimental series A, it is shown in Table 2. Another set of experiments, named Experimental series B, was performed in the same conditions but without electric field, this set was used as reference for evaluating electrokinetic effect in Pb removal in a sandy soil.

2.3.2 Hardware set up

Potentiostat–Galvanostat from Princenton Applied Reserch model EG &G, PARC 173 was used as electronic power supply, and Ti/RuO_2 electrodes were prepared using a well-known method [17] and used as cathode and anode. Both of them have an estimated area of 31.836 cm^2.

2.4 Analysis of soil samples after electrokinetic treatment

At the end of each electrokinetic experiment, the soil specimen contained in the cell was partitioned in five sections named d_1, d_2, d_3, d_4 and d_5; each fraction was dried at room temperature and hand-mixed again. After doing that, a fraction of the soil was separated and mixed with deionised water (1:2.5 w/w) in order to prepare an analytical sample for pH and electrical conductivity detection. These parameters were measured with a portable Hanna Instruments immersion electrode for solids, HI 2031.

Two representative samples were taken, (from each section d) for analysis of final Pb concentration. The samples were processed by acid digestion following a standard digestion procedure (Method USEPA 3050B) and Pb concentration was measured by Atomic Absorption Spectroscopy (AAS) in a Varian SpectrAA 220FS.

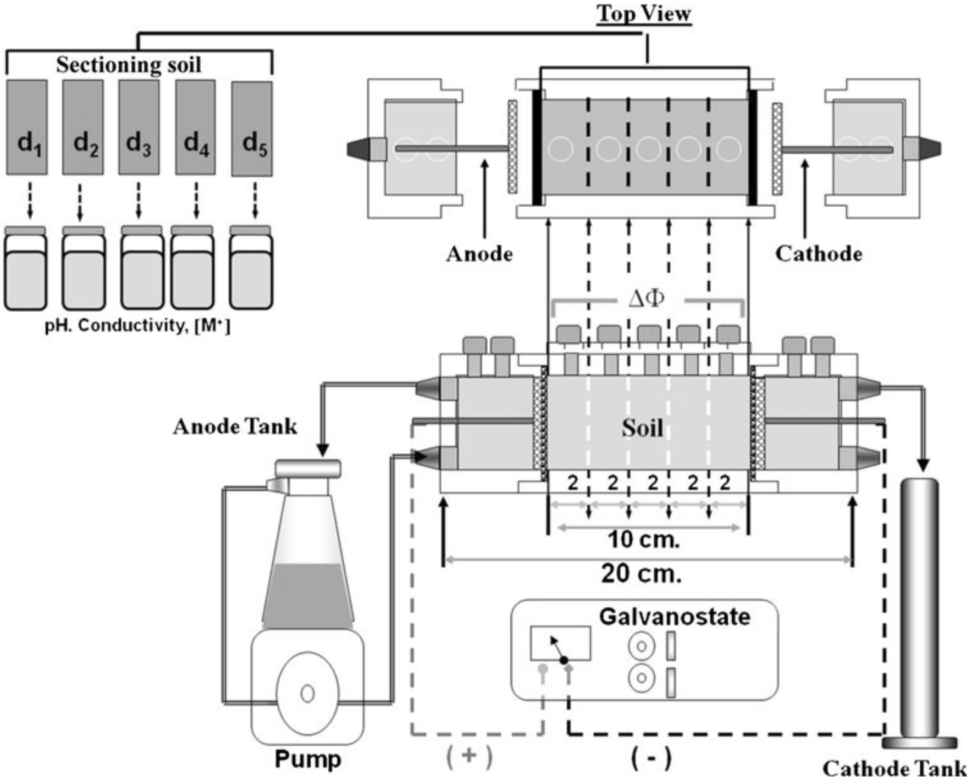

Fig. 1 Flow diagram of the experimental device used for the electrokinetic experiments. All the elements are indicated in the figure. The flow rate in the anodic compartment was fixed to 20 mL/min (speed which ensures no pressure drop through the cell). At the end of each electrokinetic experiment, the soil specimen contained in the cell was partitioned in five sections named d_1, d_2, d_3, d_4 and d_5

Table 2 Experimental design of electrokinetic treatments

Exp. ID	Electrolytes			Applied current density J = mA cm^{-2}	Treatment time (h)
	Soil humectation	Cathode chamber	Anode chamber		
EA-1	Deionized H_2O	Deionized H_2O	Deionized H_2O	0.003, 0.008, 0.016, 0.024, 0.031	24
EA-2	1 mM CH_3COONH_4	1 mM CH_3COONH_4	1 mM CH_3COONH_4	0.003, 0.008, 0.016, 0.024, 0.031	24
EA-3	1 mM CH_3COOH	1 mM CH_3COOH	1 mM CH_3COOH	0.003, 0.008, 0.016, 0.024, 0.031	24
EA-4	1 mM $C_6H_8O_7$	1 mM $C_6H_8O_7$	1 mM $C_6H_8O_7$	0.003, 0.008, 0.016, 0.024, 0.031	24
EA-5	1 mM HNO_3	1 mM HNO_3	1 mM HNO_3	0.003, 0.008, 0.016, 0.024, 0.031	24

Experimental Series B (EB) same conditions but without electric field

2.5 The zeta potential (ζ) measurements

The zeta potential (ζ) was determined at the Nanosizer Malvern Instrument using Smolouchouski model (electrophoretic mobility). Soil dispersions were prepared with 25 mg in 25 mL of 1 mM solution of CH_3COONH_4, CH_3COOH, $C_6H_8O_7$, HNO_3 and H_2O.

2.6 Analysis of deposits on electrodes after electrokinetic treatment

During experiments it was observed the occurrence of a white film on the cathode electrode, this film was analyzed employing Scanning Electron Microscope (SEM) JSM-5900 microscope to obtain topographical views of the surface.

3 Results and discussion

The mineralogical characterization of the real soil suggests that Pb(II) species was not adsorbed, but mixed as salt and potentially exposed to dissolution in an aqueous media. Under this fact, the model sandy soil (98.5% sand and 1.5% clay) was prepared with the equivalent quantity of $PbCO_3$ to obtain 500 mg Pb/kg soil an approximated value for the Zimapan's soil condition (Table 1).

In the experimental series B, not shown here, the electrokinetic cell was assembled with sandy soil and using the same hydrodynamic and chemical conditions of series A (Table 2) but without electric field. No water permeation was observed even when the water was recirculated in both compartments. The first experimental series gather the electrokinetic experiments with water (as moisturizing agent and fluid in anodic and cathodic compartments) and five different current densities: 0.003, 0.008, 0.016, 0.024 0.031 mA/cm^2. The results showed that the water volume collected in the cathodic compartment increases with time, as well as with the current density. This behaviour is typical of an electroosmotic flow in low permeable soils when they are subjected to electroremediation. The standard knowledge on electrokinetics assumes that this phenomenon predominates in clayed soils; however, in this case, the increasing fluid volume in the cathodic compartment with greater current densities suggests a direct relation of the fluid flow with electric changes in the soil/fluid interface. Then, even if the soil has a sandy texture, the fluid flow can be considered as an electroosmotic phenomena. However, when the electrokinetic experiments were performed with a sandy soil humected with either, acetic, citric or nitric acid aqueous solutions (1 mM), the electroosmotic flow stopped, indicating that electromigration was the main process on the electrokinetic phenomena. To confirm this hypothesis, a follow up of the pH and conductivity profiles during the electrokinetic experiments, have shown that an acid and alkaline limits are reached at the anode and cathode compartments, respectively.

pH measurements in the cathodic and anodic compartments were considered as the merit figure to evaluate the influence of the electrolyte composition used to moisturize the soil sample, prior to run the electrokinetic experiment, as well as those used as electrolyte in both compartments. Figure 2 shows the variation of pH at the anode and cathode compartments (Fig. 2 anod and cat, respectively), during the time of electrokinetic experiments performed at a current density of 0.016 mA cm^{-2}, on a sandy soil polluted with Pb and using different electrolytic solutions. Similar behaviour was observed for the other current densities considered in this study. The pH changes should be generated by oxidation (acidic) and reduction (alkaline) of water during the electrokinetic experiments. For the three acid solutions the pH evolution exhibit the same trend in the cathodic compartment (Fig. 2c, d, e, cat), while the anodic one remains in the initial value (Fig. 2c, d, e and) since the anolyte was recirculated during the experiment. Concerning the use of water or CH_3COONH_4, (Fig. 2 a, b), it was observed that the pH values changed in both compartments, the most important variation was observed in water (Fig. 2a). For ammonium acetate (Fig. 2b), the pH trend indicates a buffer action during the first eight hours, and after that the pH began to change in each compartment.

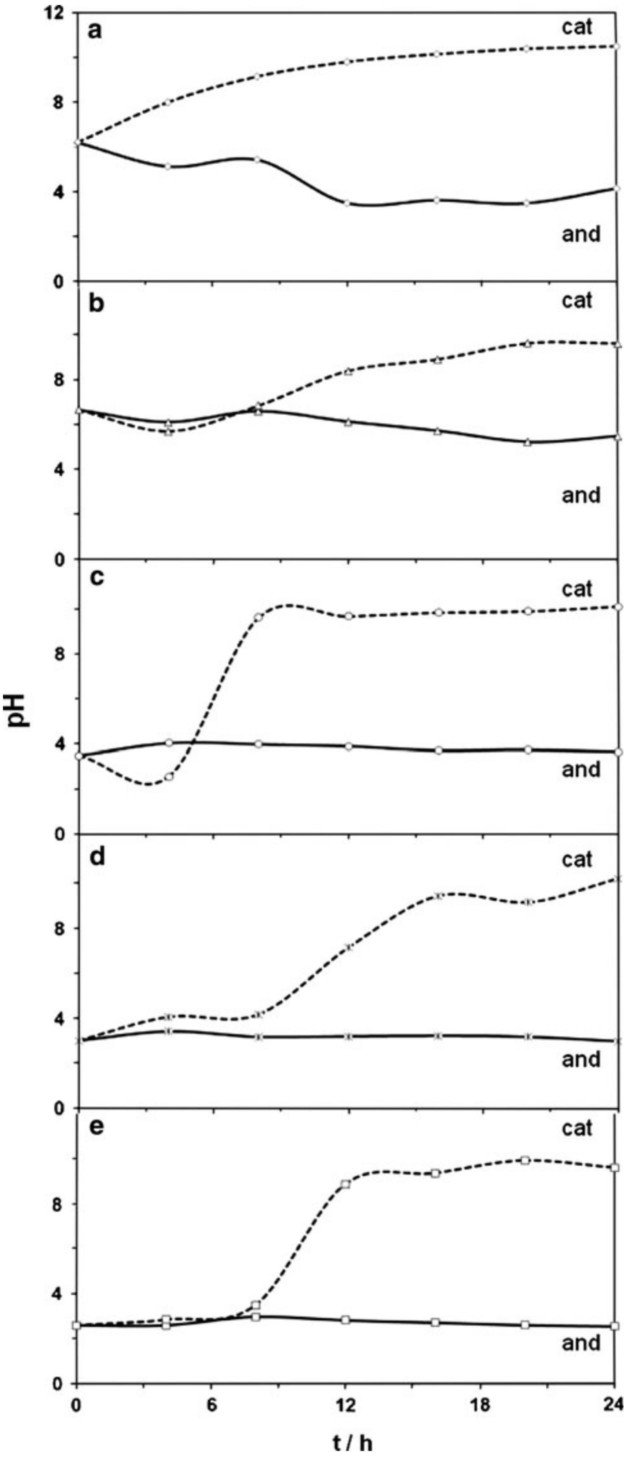

Fig. 2 Variation of pH at the anode (and, *solid line*) and cathode (cat, *dashed line*) compartment, during the time of electrokinetic experiments performed at a current density of 0.016 mA cm^{-2}, on a model sandy soil (98.5% sand and 1.5% clay) containing 500 mg Pb(II)/kg soil, using different solutions: **a** H_2O, **b** 1 mM CH_3COONH_4, **c** 1 mM CH_3COOH, **d** 1 mM $C_6H_8O_7$ and **e** 1 mM HNO_3

Figure 3 shows the variation of pH in anodic and cathodic chambers during the electrokinetic experiments performed with the sandy soil mixed with $PbCO_3$ at five different current densities using CH_3COONH_4 as electrolyte. This electrolyte posses a buffer capacity for the hydroxyl ions formed at the cathodic compartment, capacity which diminishes when the applied current density is increased, this behaviour has a great influence on associated processes to the electrokinetic phenomena taking place in sandy soil and consequently on the Pb remotion (see below).

In this regard, Fig. 4 shows the results of lead removal during the electrokinetic experiments for the ammonium acetate at five different current densities. It is observed that by incrementing the applied current density, higher removed values are obtained in the zone nearest to the anode region (Fig. 4d1), this fact takes place since this region corresponds to a zone with high proton concentration generated by water oxidation. Also it is observed that removed lead, travelling through the cell, accumulates in the region nearest to the cathode, and this accumulation becomes higher as the applied current density is greater. It is important to mention that lead is being recovered on the cathodic compartment, in amounts that allows a visual detection of a white layer formed over the cathode. The SEM-EDAX analysis of this layer indicated the presence of lead hydroxide. At higher current densities applied during the electrokinetic experiments, water reduction is taking place at higher rate, and lead hydroxide precipitation conditions are reached. Otherwise, by increasing the current density, it is observed that the associated pH profiles produce a greater disturbance at the soil–solution interface; phenomena which are related to the electric field and according to the local pH, promotes a greater amount of dissolution, precipitation and complexation of Pb(II). An additional reference experiment was performed without electric field to prove that the Pb(II) mobility is due to the electric phenomena in the soil/electrolyte interface.

Considering the experiment performed at the smaller current density (0.003 mA cm^{-2}), it is observed that the removal percentage is approximately uniform throughout the soil sample (Fig. 4a), suggesting that electromigration phenomenon was not affected by electrolysis reactions, because of the buffering capacity of ammonium acetate.

Similar behaviour was found when the electrokinetic experiments were run using different electrolytes. Moreover, the influence of the current density on the pH profile with time is more sensitive to the electric perturbation (imposed current density) than chemical concentration.

Figure 5 shows the residual Pb profile, after applying a current density of 0.024 mA cm^{-2} for 24 h, on a sandy soil contaminated with 500 mg kg^{-1} Pb(II) and moistured at field capacity (θ_{fc}) with different electrolytes. The profile was partitioned in five sections (d_1, d_2, d_3, d_4 d_5) numbered in direction anode- cathode. The Fig. 5 shows that in all cases, the lead removal exist in all different soil

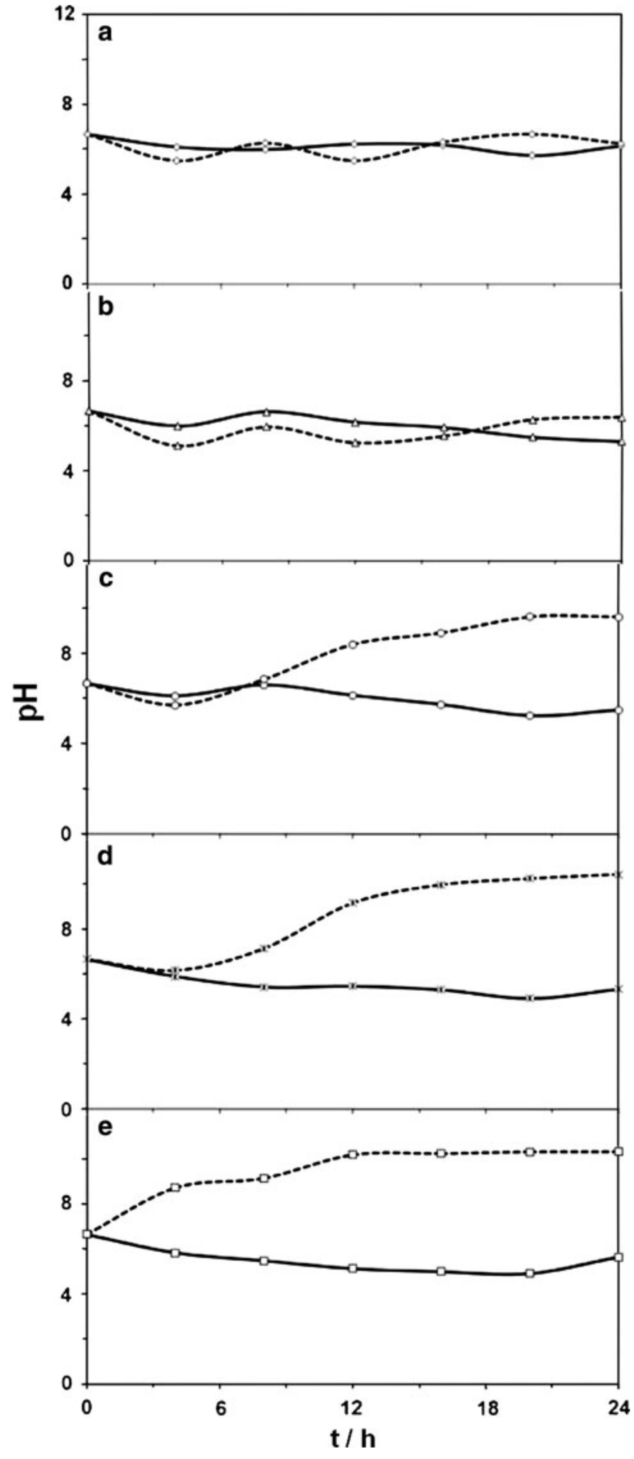

Fig. 3 Variation of pH at the anode (*solid line*) and cathode (*dashed line*) compartment, during the time of electrokinetic experiments performed on a model sandy soil (98.5% sand and 1.5% clay) containing 500 mg Pb(II)/kg soil, previously humidify with 1 mM CH_3COONH_4. The anodic and cathodic compartment contained 1 mM CH_3COONH_4. Different current densities were applied (mA/cm^2): **a** 0.0031, **b** 0.008, **c** 0.016, **d** 0.024 and 0.031

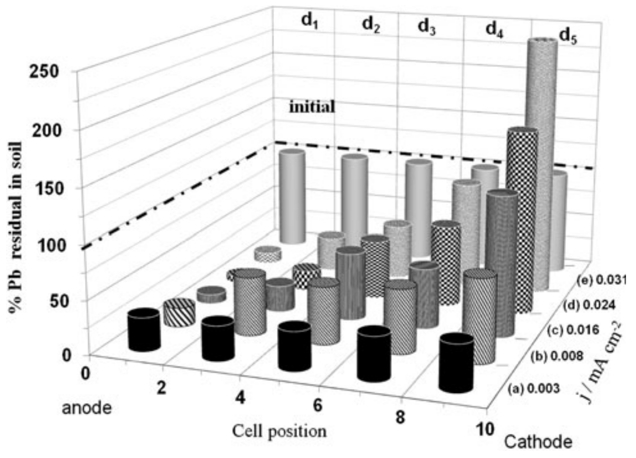

Fig. 4 Lead percent in different sections of the soil (see Fig. 1), after 24 h of the electrokinetic treatment on a model sandy soil (98.5% sand and 1.5% clay) containing 500 mg Pb(II)/kg soil, previously humidify with 1 mM CH_3COONH_4. The anodic and cathodic compartment contained 1 mM CH_3COONH_4. Different current densities were applied (mA/cm^2): (*a*) 0.0031, (*b*) 0.008, (*c*) 0.016, (*d*) 0.024 and (*e*) 0.031

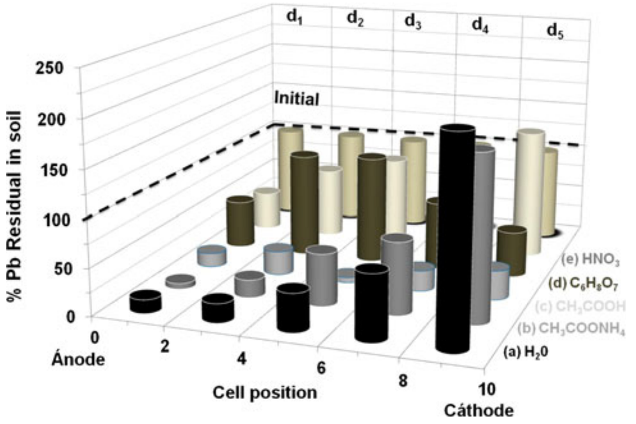

Fig. 5 Lead percent in different sections of the soil (see Fig. 1), after 24 h of the electrokinetic treatment (the applied current was: 0.024 mA cm^{-2}) on a model sandy soil (98.5% sand and 1.5% clay) containing 500 mg Pb(II)/kg soil. The soil was previously humidified with different electrolytes (also used on the electrode compartments): (*a*) H_2O, (*b*) 1 mM CH_3COONH_4, (*c*) 1 mM CH_3COOH, (*d*) 1 mM $C_6H_8O_7$ and (*e*) 1 mM HNO_3

fractions, but for water, acetic acid and ammonium acetate, there is a similar trend removal on anode–cathode direction (Fig. 5a, b, c) being higher for the acetic acid case (Fig. 5c). It is important to point that when water was used as a moisturizer solution (Fig. 5a), a considerable lead removal was obtained in d1, d2, d3, d4 fractions; also, an important accumulation takes place at the d5 fraction which is the nearest to the cathode. Although

$PbCO_3$ is non soluble in water, the observed behavior suggests that the H_3O^+ ions, released at the anode, get into the soil and dissolve selectively carbonates and release the Pb(II) ions, which are transported by the electric field up to reaching the cathodic region high in OH^-, in which Pb precipitation takes place.

Moreover, when a strong complexing agent like the citric acid was used, a greater pollutant removal would be expected, but it is interesting to note that it occurs the opposite phenomena: lead removal decrease considerably, and it gets accumulated at the middle section (see Fig. 5, section d2, d3 and d4); the last phenomena can be associated to a low mobility of the lead-citrate complex, and a lower carbonate dissolution due to the lead-citrate complex sorption on soil surface. Also, in a classic nitric acid soil washing a high lead removal should be expected, but experimental results show that this alternative produced the lowest removal (Fig. 5e).

From the above discussion, it can be proposed that electrokinetic lead removal taking place in samples prepared with the different electrolytes, it is not only function of lead carbonate solubility, but also of some other phenomena in which the soil particle interaction with its surroundings, and the interfacial electric field, should be playing a decisive role on the observed response.

The Zeta potential (ζ) is a useful tool to diagnose the interfacial region for a soil particle surrounded by an aqueous dissolution. When the soil particle has more negative ζ potential, the soil particles tends to be separated and the fluid flow may pass through the soil sample, indicating better electroosmotic permeability [12]. So far, ζ of sandy soil samples was measured with the five different electrolytes, results are reported in Fig. 6. The soil particles in presence of the acetic acid show the more negative ζ potential (Fig. 5c), furthermore the ζ potential, from more to less negative potentials follows the sequence: ammonium acetate, water, citric acid and nitric acid (Fig. 6). This sequence is similar to the removal efficiency reported in Fig. 4 (where the higher removal was for acetic acid, and the lowest for the nitric acid). These results suggest that an increase in soil permeability, acts increasing the amount of solution in contact with lead carbonate particles (smaller than sand), and so far enhances its dissolution, therefore Pb(II) ions can be removed by the electric field effect (electromigration),

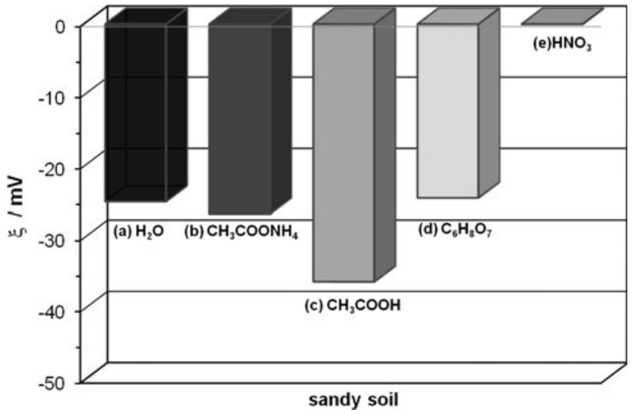

Fig. 6 Zeta potential (ζ) measurements for sandy soil in five different electrolytic solutions: (*a*) H_2O, (*b*) 1 mM CH_3COONH_4, (*c*) 1 mM CH_3COOH, (*d*) 1 mM $C_6H_8O_7$ and (*e*) 1 mM HNO_3

4 Conclusions

This paper is oriented to find the convenient electrokinetic treatment for removing Pb from a real contaminated site. The first approach was to simulate the real contaminated soil taking as a reference the textural composition of a typical waste mining site named Zimapan in Hidalgo, Mexico containing $PbCO_3$ as the main contaminant species. The simulated contaminated soil was a sandy soil (98.5% sand and 1.5% clay) sprinkled with $PbCO_3$ (identified as the main source of lead in the real site).

Based on the theoretical principles of the electrokinetic phenomena in a porous media and the experimental findings in this paper, authors state that a water flow through the soil, as well as the contaminant removal can be controlled using a specific electric current density (depending on soil conductivity and texture), and the convenient electrolytes (type and concentration), since both variables define physical and chemical driving forces through-out the soil.

Attending to the definition of electroosmotic flow, authors propose an equivalent phenomenon for sandy soil, containing $PbCO_3$, due to its low intrinsic permeability. Experiments performed with water, as preconditioning and anodic and cathodic fluid, showed water permeation increase as a function of the applied electric current.

Performing the ζ potential measurements in different aqueous solutions, prior to an electrokinetic experiment, is useful to select the electrolytic solutions (preconditioning as well as anodic and cathodic). In addition, the electrolyte selection could be done considering the chemical compatibility between the contaminant metal and its speciation in the soil–solution interface.

ζ potential measurements and electrokinetic experiments in this paper indicated that ammonium acetate and acetic acid were the best electrolytic solutions that ensure the greater lead removal from sandy soil contaminated with $PbCO_3$. However, if there are other metals in the soil, the soil–solution interface may change and citric acid could compete in effectiveness with ammonium acetate.

References

1. Díaz-Barriga F (1996) Salud Pública Mex 38:280
2. Ongley LK, Armienta A, Mango H (2003) J Phys 107:983
3. Moreno TR, Tellez HJ, Monroy FM (2003) Characterization of sulphide mining wastes helping the identification of geoenvironmental models in Hidalgo, Mexico (in Spanish) Memoria XXV Convención internacional de Minería de la AIMMGM. Acapulco, México
4. Jiménez-Arévalo I (2003) Dispersion and movility of potential toxic elements (arsenic, lead and cadmium) in Zimapan, Hidalgo, M.Sc. Thesis, Facultad de Ingeniería, UASLP, San Luis Potosí, SLP
5. Ongley LK, Sherman L, Armienta A, Concilio A, Ferguson Salinas C, Garcia-Escobar A (2007) Environ Pollut 145:793
6. Hansen HK, Rojo A (2007) Electrochim Acta 52:3399
7. Martin TA, Ruby MV (2004) Remediat J 14:35
8. Virkutytea J, Sillanpaa M, Latostenmaa P (2002) Sci Total Environ 289:97
9. Reddy KR, Shirani AB (1997) Geotech Geol Eng 15:3
10. Alshawabkeh AN, Yeung AT, Bricka RM (1999) J Environ Eng 125:27
11. Hansen HK, Ribeiro AB, Mateus EP, Ottosen LM (2007) Electrochim Acta 52:3406
12. Hansen HK, Rojo A, Ottosen LM (2005) J Hazard Mat 117:179
13. Garcia-Gutierrez MD, Gomez-Lahoz C, Rodriguez-Maroto JM, Vereda-Alonso C, Garcia-Herruzo F (2007) Electrochim Acta 52:3372
14. Alkan M, Demirbas O, Dogan M (2005) Micropor Mesopor Mater 83:51
15. Reyes JI (1996) Fundamentos teóricos prácticos de temas selectos de la ciencia del suelo, 1^{a} Edición Universidad Autónoma Metropolitana, México DF, pp 113–117
16. Murillo-Rivera B, Labastida I, Barrón J, Oropeza-Guzman MT, González I, Teutli-León MMM (2008) Electrochim Acta 9:54
17. Freitas RG, Marchesi LF, Oliveira RTS, Mattos-Costa FI, Pereira EC, Bulhoes LOS, Santos MC (2007) J Power Sources 373:171