

A dynamic model for the electrokinetic removal of copper from a polluted soil ¹

Alexandra B. Ribeiro ^{a,*}, João T. Mexia ^b

^a *Department of Environmental Sciences and Engineering, Faculty of Sciences and Technology, New University of Lisbon, Quinta da Torre, P-2825 Monte da Caparica, Portugal*

^b *Department of Mathematics, Faculty of Sciences and Technology, New University of Lisbon, Quinta da Torre, P-2825 Monte da Caparica, Portugal*

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Abstract

The electrokinetic process is a promising decontamination technique for removal of heavy metals from polluted sites. The authors have studied the removal of copper (Cu) from an industrially heavy-metal-contaminated soil, using the application of electric current. A sequential extraction procedure was used to monitor changes in the chemical associations of Cu during the electrokinetic treatment of the soil. A dynamic model is presented for the removal of Cu by electrokinetic decontamination. This model, based on a biregional design, enables a joint analysis of the experiments which were carried out in a laboratory cell. The removal of Cu was found to be a local phenomenon, dependent on the release of metal by different soil fractions, cumulative and controlled by time as well as pH. © 1997 Elsevier Science B.V.

Keywords: Electrokinetic decontamination; Copper; Sequential extraction; Biregional design

1. Introduction

Pollution of soil by heavy metals is of great concern because many added metal ions tend to be immobilized in the top layer of soils, except under extremely acid conditions [1]. Soils act as traps for heavy metals that are mobilized in the environment. In the case

* Corresponding author. Fax: +351 1 294 8554; e-mail address: abr@mail.fct.unl.pt.

¹ This article is dedicated to Jørgen Birger Jensen (1937–1995).

of copper (Cu), for example, Bowen [2] estimated a soil residence time of between 1000 and 3000 yr. As each soil has its own limited retention capacity, and assuming the maintenance of today's rate of release of metals, increasing numbers of cases of soil contamination are to be expected [3].

The electrokinetic process is a promising decontamination technique for removal of heavy metals from polluted sites [4–12]. Due to the electric field present when a direct current (dc) is passed between a pair of electrodes placed in contaminated soil, the pollutant species are driven towards one of the electrodes, from where they may be removed. Two main mechanisms are responsible for this movement: electromigration and electroosmosis. On inert electrodes (titanium, for example) the electrode reactions will produce H^+ ions at the anode and OH^- ions at the cathode, which means that if pH is not controlled, an acid front will be propagated into the soil pores from the anode, and a base front will move out from the cathode. This development can have a significant effect on the magnitude of electroosmosis, as well as on solubility, ionic state and charge, and level of adsorption of the contaminants [8].

A wide range of chemical extractants and sequential extraction procedures has been applied to the study of metals in soils, sediments and atmospheric particulates (Kersten and Förstner [13] summarize 25 schemes applied between 1973 and 1993). These procedures are designed to remove metals selectively from various fractions of the substrate with which they might be associated. Despite uncertainties as to the selectivity of the various extractants, metal re-adsorption, sample handling and procedure validation [14], sequential extraction provides qualitative evidence regarding the forms of association of the metals, and indirectly regarding their mobility and bioavailability. The use of sequential extraction techniques appears to be an efficient method for making comparative studies between natural and contaminated areas [15], providing a pragmatic approach for the description of heavy metals speciation in contaminated soils and sediments [16].

Artificial contamination by equilibrating a soil with contaminant solutions does not reproduce the contaminant geochemistry encountered for hazardous waste site soils [17]. Sequential extraction procedures applied to hazardous waste site soils indicated significant differences between the samples that had metals added in the laboratory and those which were from waste sites. Metals in the waste site samples were more difficult to remove [18]. Conclusions regarding treatment efficiency based on the removal of metal salts added in laboratory experiments must be evaluated with caution [6].

Although extremely relevant, until now the mathematical models formulated to simulate the transport and electrochemical metal removal process (whether or not incorporating complexation, adsorption and precipitation reactions) were developed only for heavy-metal-spiked specimens (e.g. Cd-, Pb-, Cr-spiked Georgia kaolinite specimens [19] and Georgia kaolin clay contaminated with zinc [20,21]).

The present study reports results from the application of a sequential extraction procedure to the study of the chemical associations of Cu in a Portuguese contaminated soil during electrokinetic treatment of the soil. The main goals are: establishment of a model for the removal of Cu by electrokinetic decontamination; assessment of the main soil fraction(s) responsible for metal release; and identification of other key parameters that might be relevant to the process.

2. Experimental section

2.1. Soil

Three different laboratory experiments of differing duration were carried out using a contaminated soil from a Portuguese wood preservation site, at Famalicão, in the north of the country. The soil was sampled from a storage area for freshly treated wood, which was the source of pollution by Cu in addition to arsenic and chromium. The 'total' Cu content of the soil (prepared as described below in connection with sequential extraction), extracted by $\text{HNO}_3\text{--HClO}_4\text{--HF}$ [22], as well as other soil characteristics are presented in Table 1.

By means of a six-step sequential chemical extraction procedure (adapted from [23–25]), the 'total' Cu content was sub-divided into six different fractions: a) 'soluble and exchangeable', b) attached to 'Mn-oxides', c) 'organic matter', d) attached to 'amorphous Fe-oxides', e) attached to 'crystalline Fe-oxides', and f) 'strongly bound' (Table 1). This procedure was applied to particles of size < 2 mm diameter (crushed to 200 mesh in an agate mill). The solid:solution ratio used was 0.5 g:20 ml extractant for steps a), b), c), d) and e), and 0.5 g:25 ml for step f). After extractions, the suspensions were centrifuged for 30 min at 3000 rpm and the supernatants collected for Cu determination. Between extractions, the samples were washed with 0.025M $\text{Ca}(\text{NO}_3)_2$ to remove occluded solutions, centrifuged and the supernatant solutions discarded.

All the reagents used were 'pro analysis'.

Table 1
Characteristics of the soil used in the experiments

Depth = 0–10 cm		
$\text{pH}_{(\text{H}_2\text{O})} = 7.15$, $\text{pH}_{(\text{KCl})} = 6.10$		
texture = loamy sand (coarse sand = 49.4%, fine sand = 24.4%, silt = 21.7%, clay = 4.5%)		
organic matter = 70.9 g/kg; cation exchange capacity = 12.75 $\text{cmol}_{(\text{c})}/\text{kg}$.		
		mg Cu/kg \pm sd (n = 9)
"total" Cu by $\text{HNO}_3\text{--HClO}_4\text{--HF}$ extraction		322 \pm 21
Cu distribution by the 6-step sequential extraction	operational condition	
E(a): 0.5M $\text{Ca}(\text{NO}_3)_2$	16 h contact	1.5 \pm 0.5
X(b): 0.1M $\text{NH}_2\text{OH.HCl}$ acidified T to pH 2 with 0.1M HNO_3	30 min continuous agitation	40 \pm 15
R(c): 0.1M $\text{K}_4\text{P}_2\text{O}_7$	24 h contact	91 \pm 7
A(d): 0.25M $\text{NH}_2\text{OH.HCl}$ + C + 0.25M HCl	40 min in a water-bath at 50°C	95 \pm 16
T(e): 0.25M $\text{NH}_2\text{OH.HCl}$ + A + 0.25M HCl	40 min in a water-bath at 90°C	58 \pm 8
N(f): 4M HNO_3 T	16 h in a water-bath at 80°C	29 \pm 4
Recovery ratio (quantitative mass balance) of the sequential extraction		97% Cu

The extractant sequence from a) to f) represents increasing vigour of extraction.

The soil used for electrokinetic decontamination was not crashed or graded, but large foreign objects were removed by hand and then well mixed. All soil weights given in the results are dry soil weights.

2.2. Laboratory cell

All experiments were carried out in a cell recently developed at the Technical University of Denmark [26]. The cell is divided into 3 compartments, consisting of two electrode compartments and a central one ($L = 15$ cm, internal diameter = 8 cm), in which the contaminated soil is placed (Fig. 1). The soil was saturated [27] with distilled water before it was put in the cell. The electrode compartments and the soil were separated by ion exchange membranes (cation exchange membrane [CAT]: IC1-61CZL386, anion exchange membrane [AN]: IA1-204SXZL386, both from Ionics, Massachusetts, USA). Each electrode compartment contained 1000 ml 10^{-2} M NaNO_3 , $\text{pH} = 3$ as electrolyte solution and was equipped with a circulation system. Power supplies were used to maintain a constant current and the voltage was monitored.

When a voltage was applied between the two titanium electrodes, the ions in the 3 compartments moved in the electric field, but the AN placed between anode and soil prevented cations from passing into the soil. In a similar way, the CAT placed between cathode and soil prevented anions from passing into the soil (Fig. 1). With this configuration of membranes, there is a decrease in the amount of salt in the soil.

The catholyte pH was maintained at 3, with HNO_3 , by neutralization of the hydroxyl ions as they were generated at the cathode.

The following experimental conditions were used: Current density = 0.2 mA/cm² and duration of treatment = 18 days, 35 days and 85 days for experiments 1, 2 and 3, respectively.

At the end of each experiment, the soil from the central compartment of the cell was cut vertically into 5 slices of thickness 3 cm each. Determinations of $\text{pH}_{(\text{H}_2\text{O})}$, 'total' Cu content and the sequential chemical extraction were made with each slice, in order to establish the concentration profile of Cu in the various fractions in relation to the distance from the AN. By comparing the amounts of metal in the soil before and after the passage of the current, the fractions where metal had been removed were identified. All the results are the mean of two or three replicates and Certified Reference Material

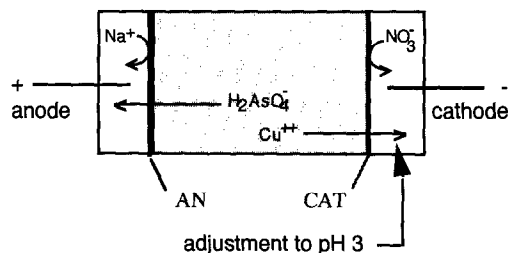


Fig. 1. Schematic representation of the cell used in experiments. AN - anion exchange membrane; CAT - cation exchange membrane.

Table 2

Soil pH_(H₂O) values and total Cu concentrations found in different cell sections at the end of experiments 1, 2 and 3 of durations 18 days, 35 days and 85 days, respectively

Anolyte (mg Cu/l)	AN ^a (mg Cu/l)	Distance from AN (cm)					CAT ^a (mg Cu/l)	Catholyte (mg Cu/l)	Cathode ^b (mg Cu/l)
		0–3	3–6	6–9	9–12	12–15			
1 = 0.07	1 = 3.54	Soil compartment					1 = 1.10	1 = 0.18	1 = 0.36
2 = 0.15	2 = 0.52						2 = 74.10	2 = 10.27	2 = 11.87
3 = 0.14	3 = 0.28						3 = 15.73	3 = 16.90	3 = 179.20
pH _(H₂O)	1	3.586	3.781	3.823	4.304	5.463			
	2	3.211	3.626	3.715	3.810	4.238			
	3	2.488	2.893	4.127	4.157	4.394			
mg Cu/kg	1	190.0	306.5	389.5	406.5	282.5			
	2	146.0	223.0	281.0	309.0	396.0			
	3	60.0	123.5	165.5	170.5	227.0			

AN = anion exchange membrane; CAT = cation exchange membrane.

^aMembranes immersed in 100 ml HCl 1M during 48 h, filtered (0.45 μm) and filtrate analyzed.

^bRecovery of the deposited Cu at the cathode by reversal of potential in 100 ml HCl 1M, which was filtered (0.45 μm) and filtrate analyzed.

(CRM) BCR 142 [28] was used. Cu was determined by Atomic Absorption Spectrophotometry (Perkin Elmer 5000-AAS).

2.3. Results

Table 2 presents the soil pH_(H₂O) values and 'total' Cu concentrations found in different cell sections at the end of experiments. Table 3 presents the total quantities of charge transferred between the electrodes, the charge removed by removal of Cu ions and the percentage of the total charge passed carried by Cu in the soil in experiments 1, 2 and 3.

Table 3

Quantities of charge carried by Cu in the soil in experiments 1, 2 and 3 of durations 18 days, 35 days and 85 days, respectively

Experiment	Q_{total} (mol)	Q_{Cu} (mol)	P_{Cu} (%)
1	0.159	0.0002	0.134
2	0.316	0.0017	0.539
3	0.759	0.0052	0.683

Q_{total} (mol) - total charge transferred between the electrodes; Q_{Cu} (mol) - charge corresponding to the net loss of Cu²⁺ from the total mass of soil in cell; P_{Cu} (%) - percentage of the total charge passed carried by Cu; where: $Q_{\text{total}} = I \times t_r / F$; I = current (A); t_r = duration of treatment (s); F = Faraday constant (96485 C/mol); $Q_{\text{Cu}} = (Z \times (c_i - \bar{c}_f) \times m_{\text{soil}}) / M_{\text{Cu}}$; Z = valence (2); M_{Cu} = molar weight (63.546 g/mol); c_i = initial concentration of Cu in the soil (g/kg); \bar{c}_f = mean final concentration of Cu in soil (g/kg); m_{soil} = soil weight (kg); $P_{\text{Cu}} = (Q_{\text{Cu}} / Q_{\text{total}}) \times 100\%$.

Experimental data has not been rounded off to indicate the expected precision, since most of the data is used for subsequent calculations.

A dynamic model for the electrokinetic removal of Cu is now presented.

3. A model for the electrokinetic removal of Cu

The dynamic model we propose is based on a biregessional design. In these designs the treatments are given by level combinations of quantitative factors. A first set of regressions is adjusted, one per treatment. We now have, as controlled (independent) variables, the levels of the factors for the treatment and, as dependent variables, the adjusted coefficients. A second set of regressions is then adjusted, in order to study the effects of the factor levels on the coefficients of the initial regressions. The assumptions behind the adjustment of the regressions in the second set are checked and the possibility of discarding one or more of the controlled variables is tested. Estimatable vectors and simultaneous confidence intervals are considered in connection with the regressions in the second set [29].

The starting points for the model are:

- a positive current goes from anode to cathode within the cell.
- Cu is mainly in the form of Cu^{2+} moving towards the cathode;
- the independent variables are: time (18 days, 35 days and 85 days) and distance (0–3 cm from the AN for slice 1; 3–6 cm for slice 2; ...; 12–15 cm for slice 5);
- the dependent variables are: current; soil pH; 'total' Cu; Cu contents from 6-step sequential extraction ((a), b), c), d), e) and f)); % of the total charge passed carried by $\text{Cu}^{2+} = P_{\text{Cu}}$.

The model proposed for the electrokinetic removal of Cu and a summary of the system used are illustrated in Figs. 2 and 3, respectively. In these figures, Z_j represents the removal of Cu from the soil and is directly estimated by the Σ Cu quantities obtained in sequential extraction steps b), c), d), e) and f), before and after passage of the current ($Z_j = \Sigma \text{Cu}_{\text{initial}} - \Sigma \text{Cu}_{\text{final in slice } j}$). ΔS_j represents the variation of Cu in 'solution' and is directly estimated by Cu obtained from step a) of the sequential extraction, before and after passage of the current ($\Delta S_j = \text{Cu}_{\text{final in slice } j} - \text{Cu}_{\text{initial}}$). W represents the flux: W_0 is directly estimated from the Σ Cu measured in the AN and the

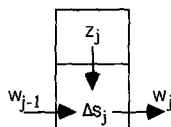


Fig. 2. Model for the electrokinetic removal of Cu. ΔS_j - variation of Cu in 'solution' (directly estimated from Cu obtained in step a) of the sequential extraction, before and after passage of the current), $\Delta S_j = \text{Cu}_{\text{final in slice } j} - \text{Cu}_{\text{initial}}$; Z_j - removal of Cu from the soil (directly estimated from Σ of the quantities of Cu obtained in sequential extraction steps b), c), d), e) and f), before and after passage of the current), $Z_j = \Sigma \text{Cu}_{\text{initial}} - \Sigma \text{Cu}_{\text{final in slice } j}$; W - flux, W_0 directly estimated from Σ Cu measured in anion exchange membrane and the anolyte, W_5 directly estimated from Σ Cu in the cation exchange membrane, the catholyte and the cathode and W_1, W_2, W_3, W_4 are calculated from the equation $\Delta S_j = W_{j-1} + Z_j - W_j$.

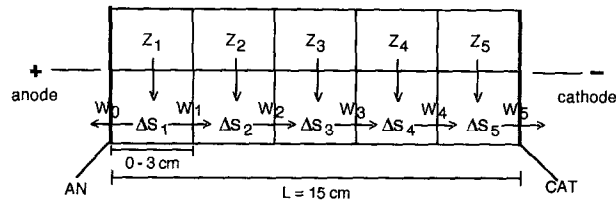


Fig. 3. Summary of the electrokinetic system used. AN - anion exchange membrane; CAT - cation exchange membrane.

anolyte; W_5 is directly estimated from the Σ Cu in the CAT, the catholyte and the cathode, and W_1, W_2, W_3, W_4 are calculated from the equation $\Delta S_j = W_{j-1} + Z_j - W_j$.

In Fig. 4 parts of the system are shown with pertinent Z data (mg Cu/kg) obtained from experiments 1, 2 and 3 of durations 18 days, 35 days and 85 days, respectively.

The data from Fig. 4 suggested a symmetry in relation to yy' axis, so that the use of quadratic expressions without linear terms (second degree parabolas)

$$Z_i = \alpha_i + \beta_i x^2 \quad (i = 1,2,3; x = \text{distance from anion exchange membrane, cm}) \quad (1)$$

for the three experiments. The results obtained are presented in Table 4, showing that only α differed significantly between experiments (the application of SCHEFFÉ's method [30] demonstrated that β did not differ significantly). Thus it was decided to carry out a second phase regression only for α , as it was thought worthwhile to express the effect of the duration of experiment on the coefficients of the adjusted regressions. The data in Table 4 suggested the use of a linear regression.

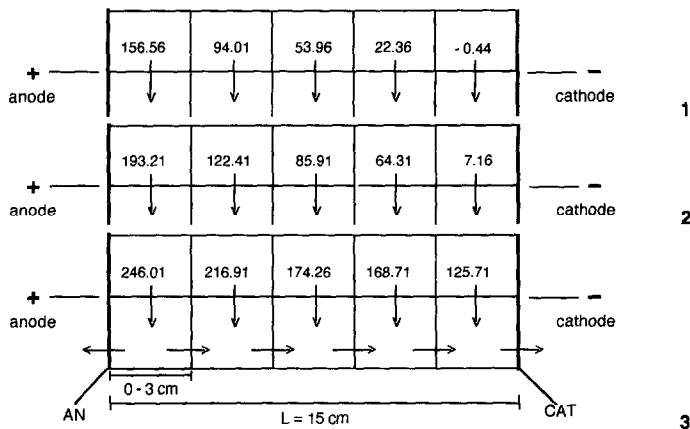


Fig. 4. Parts of the system with Z data (mg Cu/kg) obtained from experiments 1 (18 days), 2 (35 days) and 3 (85 days). AN - anion exchange membrane; CAT - cation exchange membrane.

Table 4

Results obtained with the adjustment of second degree parabolas with the Z data of experiments 1, 2 and 3

Experiment	Time (days)	α	β	r^2
1	18	130.760	-5.952	0.858
2	35	169.276	-6.789	0.901
3	85	237.011	-4.608	0.920

The linear regression between α (Cu removal from the soil) and time of experiment leads to the result:

$$\alpha = 108.477 + 1.533 t \quad (t = \text{time of experiment} \geq 18 \text{ days}), \text{ with } r^2 = 0.986 \quad (2)$$

We also tried to adjust second degree parabolas

$$\text{pH}_i = \alpha'_i + \beta'_i x^2 \quad (i = 1, 2, 3; x = \text{distance from the anion exchange membrane, cm}) \quad (3)$$

to the soil $\text{pH}_{(\text{H}_2\text{O})}$ data obtained after each of the experiments 1, 2 and 3 of durations 18 days, 35 days and 85 days, respectively (Table 2), and we obtained the results presented in Table 5.

Since soil pH is an important variable, it was decided to study its influence, as measured by α' , on the amount of Cu removed, as expressed by α . A preliminary study has shown that α (Cu removal from the soil) varied linearly with α' (pH), by the following relation:

$$\alpha = 657.446 - 151.851 \alpha' \quad \text{with } r^2 = 0.911 \quad (4)$$

Summing up: the electrokinetic removal of Cu from the soil (Σ Cu obtained with steps b), c), d), e) and f) of sequential extraction) to Cu in 'solution', ready to migrate towards the cathode (step a) of sequential extraction), is a local phenomenon (dependent on the distance from AN), cumulative and controlled by time as well as by pH.

In order to study the effects of these variables on the coefficients α of the initial regressions, a second set of regressions was adjusted. For that, the five Z values (Z_1 , Z_2 , Z_3 , Z_4 and Z_5 corresponding to the five soil slices of each experiment) were subdivided into the Σ Cu quantities of the sequential extraction steps b), c), d), e) and f), before and after passage of the current (Table 6), and second degree parabolas were adjusted. For each experiment we obtained five sets of values, as presented in Table 7. Then, five

Table 5

Results obtained with the adjustment of second degree parabolas with the pH data of experiments 1, 2 and 3

Experiment	Time (days)	α'	β'	r^2
1	18	3.367	0.075	0.913
2	35	3.324	0.036	0.890
3	85	2.761	0.077	0.757

Table 6
Sequential extraction results

1 (18)	Experiment (days)	
	2 (35)	3 (85)
(0–3 cm from AN) Z ₁ = 156.56 mg Cu/kg	193.21 mg Cu/kg	246.01 mg Cu/kg
b) <i>i</i> – b) <i>f</i> = 18.98	30.98	35.38
c) <i>i</i> – c) <i>f</i> = 62.16	66.36	84.16
d) <i>i</i> – d) <i>f</i> = 51.69	52.49	80.69
e) <i>i</i> – e) <i>f</i> = 26.96	36.36	39.76
f) <i>i</i> – f) <i>f</i> = –3.22 ^a	7.03	6.03
(3–6 cm from AN) Z ₂ = 94.01 mg Cu/kg	122.41 mg Cu/kg	216.91 mg Cu/kg
b) <i>i</i> – b) <i>f</i> = 3.58	23.98	30.98
c) <i>i</i> – c) <i>f</i> = 42.36	40.36	75.76
d) <i>i</i> – d) <i>f</i> = 22.69	25.49	72.89
e) <i>i</i> – e) <i>f</i> = 30.36	26.56	32.76
f) <i>i</i> – f) <i>f</i> = –4.97 ^a	6.03	4.53
(6–9 cm from AN) Z ₃ = 53.96 mg Cu/kg	85.91 mg Cu/kg	174.26 mg Cu/kg
b) <i>i</i> – b) <i>f</i> = –6.82	16.18	24.58
c) <i>i</i> – c) <i>f</i> = 28.36	27.36	64.16
d) <i>i</i> – d) <i>f</i> = 14.09	15.09	60.69
e) <i>i</i> – e) <i>f</i> = 20.56	20.76	23.56
f) <i>i</i> – f) <i>f</i> = –2.22 ^a	6.53	1.28
(9–12 cm from AN) Z ₄ = 22.36 mg Cu/kg	64.31 mg Cu/kg	168.71 mg Cu/kg
b) <i>i</i> – b) <i>f</i> = –16.62	9.78	21.98
c) <i>i</i> – c) <i>f</i> = 22.36	19.76	61.36
d) <i>i</i> – d) <i>f</i> = 10.49	9.49	58.09
e) <i>i</i> – e) <i>f</i> = 19.36	24.76	26.76
f) <i>i</i> – f) <i>f</i> = –13.22 ^a	0.53 ^a	0.53 ^a
(12–15 cm from AN) Z ₅ = –0.44 mg Cu/kg	7.16 mg Cu/kg	125.71 mg Cu/kg
b) <i>i</i> – b) <i>f</i> = –18.02	–12.22	12.58
c) <i>i</i> – c) <i>f</i> = 21.16	0.96	42.56
d) <i>i</i> – d) <i>f</i> = –7.11	–4.91	46.69
e) <i>i</i> – e) <i>f</i> = 6.76	19.56	22.36
f) <i>i</i> – f) <i>f</i> = –3.22 ^a	3.78	1.53

AN = anion exchange membrane; Z_{*j*} = removal of Cu from the soil and is directly estimated by the Σ of the quantities of Cu obtained in sequential extraction steps b), c), d), e) and f), before and after passage of the current ($Z_j = \Sigma Cu_{\text{initial}} - \Sigma Cu_{\text{final in slice } j}$); b), c), d), e) and f) = steps of the sequential extraction; *i* = initial amount of Cu in the contaminated soil; *f* = final amount of Cu obtained after treatment.

^aAnomalous results and therefore rejected.

linear regressions were made between α (Cu removal from each considered step of the sequential extraction) and duration of experiment (Table 8).

As there is no replication of the experiments we must assume that there is no interaction present. Thus, two two-way ANOVA without replication were performed: (i) over the α values, considering the factors time (days) and removal by a certain step of sequential extraction (Table 9); and (ii) over the pH values, considering the factors time (days) and distance from AN (Table 10).

For the F tests and the SCHEFFÉ's method [30] we used the sum of squares for the interaction as sum of squares for the errors.

Table 7

Results obtained with the adjustment of second degree parabolas to sequential extraction step data of experiments 1, 2 and 3

Experiment	Time (days)	Step of sequential extraction	α	β	r^2
1	18	b)	12.00	-1.43	0.811
		c)	51.95	-1.52	0.724
		d)	40.46	-2.01	0.811
		e)	30.56	-0.89	0.896
		f)	0.00	0.00	-
2	35	b)	32.33	-1.69	0.974
		c)	57.10	-2.38	0.887
		d)	41.73	-2.02	0.828
		e)	31.29	-0.52	0.564
		f)	7.94	-0.76	0.828
3	85	b)	34.92	-0.89	0.970
		c)	83.18	-1.60	0.956
		d)	78.35	-1.32	0.930
		e)	35.72	-0.61	0.662
		f)	6.54	-1.16	0.733

The results of F tests presented in Table 9 show that the differences among steps of sequential extraction are highly significant ($p = 0.001$), and that the differences among time of treatment are significant for a level of 0.05, but not for a level of 0.01 ($p = 0.026$).

This ANOVA was completed through the use of SCHEFFÉ's multiple comparison method [30] applying the critical 5% differences:

$$\Delta_{(I)} = \sqrt{2(I-1)F_{0.95; I-1; (I-1)(J-1)} \text{MSE}} = \sqrt{89.20 \text{MSE}} = 90.90$$

$$\Delta_{(J)} = \sqrt{2(J-1)F_{0.95; J-1; (I-1)(J-1)} \text{MSE}} = \sqrt{92.16 \text{MSE}} = 92.40$$

where $\Delta_{(I)}$ and $\Delta_{(J)}$ = minimum significant difference (derived from the SCHEFFÉ's method), where I and J = time and extraction step (i.e., removal) factors, respectively, and MSE = mean square error. Thus, from the obtained values $\Delta_{(I)}$, $\Delta_{(J)}$ and the results for Σ presented in Table 9 we find: Time 18 is significantly different from Time 85

Table 8

Linear regressions obtained between α (Cu removal from each step of the sequential extraction) and time of the experiments

Step of sequential extraction	Regression	r^2
b)	$\alpha_{\text{b}} = 13.71 + 0.28 t$	0.588
c)	$\alpha_{\text{c}} = 42.05 + 0.48 t$	0.992
d)	$\alpha_{\text{d}} = 25.76 + 0.63 t$	0.954
e)	$\alpha_{\text{e}} = 28.86 + 0.08 t$	0.987
f)	$\alpha_{\text{f}} = 1.65 + 0.07 t$	0.323

Table 9
Two-way ANOVA without replication over the α values

Factor J: Removal ($j = 5$)	Factor I: time (days) ($i = 3$)			Σ
	Time 18	Time 35	Time 85	
Step b)	12.00	32.33	34.92	79.25
Step c)	51.95	57.10	83.18	192.23
Step d)	40.46	41.73	78.35	160.54
Step e)	30.56	31.29	35.72	97.57
Step f)	0.00	7.94	6.54	14.48
Σ	134.97	170.39	238.71	544.07

ANOVA table

Source of variation	df	SS	MS	F	p	F crit
Time	2	1112.30	556.151	6.003	0.026	4.459
Removal (Step)	4	6510.78	1627.695	17.569	0.001	3.838
Error	8	741.17	92.646			
Total	14	8364.25				

(Time 18 \ll Time 85), as their variation, $\Delta (\Sigma \text{ Time 18 to } \Sigma \text{ Time 85}) = 103.74 > 90.9$; steps c) and d) of sequential extraction are the most important in the removal of Cu from the soil (they have higher Σ), although it is not possible to distinguish between them in terms of importance (the value of $\Delta = 31.69$ is less than 92.40). Step b) \ll step c) ($\Delta = 112.98$), step e) $<$ step c) ($\Delta = 94.66$), step f) \ll step c) ($\Delta = 177.75$), and step f) \ll step d) ($\Delta = 146.06$).

The results of F tests presented in Table 10 show that the differences among distances from AN in the cell are highly significant ($p = 0.008$), and that there are no differences among times of treatment ($p = 0.102$).

Table 10
Two-way ANOVA without replication over the soil $\text{pH}_{(\text{H}_2\text{O})}$ values

Factor K: Distance ($k = 5$)	Factor I: time (days) ($i = 3$)			Σ
	Time 18	Time 35	Time 85	
0–3 cm	3.586	3.211	2.488	9.285
3–6 cm	3.781	3.626	2.893	10.300
6–9 cm	3.823	3.715	4.127	11.665
9–12 cm	4.304	3.810	4.157	12.271
12–15 cm	5.463	4.238	4.394	14.095
Σ	20.957	18.600	18.059	57.616

ANOVA table

Source of variation	df	SS	MS	F	p	F crit
Time	2	0.950	0.475	3.083	0.102	4.459
Distance	4	4.566	1.142	7.411	0.008	3.838
Error	8	1.232	0.154			
Total	14	6.748				

Table 11
Simplified three-factor ANOVA table

Source of variation	df	MS	F
Time	2		71.77 ^a
Step	4		37.46 ^a
Distance	4		80.07 ^a
Time × Step	8		0.71 ^{ns}
Time × Distance	8		10.97 ^a
Step × Distance	16		3.22 ^b
Error		55.55	

^aVery highly significant $p < 0.001$.

^bsignificant $p < 0.05$.

^{ns}not significant.

This ANOVA was also completed through the use of SCHEFFÉ's multiple comparison method [30] (critical 5% differences) and we concluded:

- soil slice 1 (0–3 cm from AN) has a pH significantly different from slice 5 (12–15 cm from AN) and
- soil slice 2 (3–6 cm from AN) has a pH significantly different from slice 5 (12–15 cm from AN).

In order to test the possibility of discarding one or more of the controlled variables we advanced to a three-factor ANOVA (Table 11) involving: i - time, $I = 3$; j - step, $J = 5$; k - distance, $K = 5$.

This ANOVA was performed with the data presented in Table 6.

The results of F tests presented in Table 11 show that the differences among times of treatment, steps of sequential extraction and distances from AN in the cell are all very highly significant ($p < 0.001$). Also the interaction between time and distance in the cell is very highly significant, but not the interaction between time and step. The interaction between step and distance is barely significant.

As we have already concluded that the electrokinetic removal of Cu is a cumulative process, we complete this examination of the dynamic model by trying a linear regression between the percentage of the total charge passed carried by Cu (P_{Cu}), and the Z_{total} ($Z_1 + Z_2 + Z_3 + Z_4 + Z_5$) in each experiment. The result was:

$$P_{Cu} = 0.003 + 0.001 Z_{total} \text{ with } r^2 = 0.856 \quad (5)$$

4. Discussion

All the electrokinetic experiments show the development of an acid front that progressed towards the cathode (Table 2). pH influences the adsorption and desorption, precipitation and dissolution, and speciation reactions of the heavy metals. At low pH, metals tend to desorb from the soil and enter into solution as positively charged ions [19,20]. Not unexpectedly, pH changes seem to play an important role in all the experiments.

There is a general tendency for Cu to migrate towards the cathode, and if the experiments had been carried out longer, more Cu would have been removed from the soil into the cathode compartment as shown in Table 2 (for experiment 1, much Cu was found in the anion membrane, probably due to complexation).

The results obtained with the sequential extraction show that the passage of current induced a redistribution of Cu in the soil. The most important mobilization of Cu seems to have occurred from various associations with the soil to the fraction extracted with extractant a) 'soluble and exchangeable' forms (see Section 2.1); in other words, to the fraction weakly bound to soil particles, or non-specifically adsorbed. These results are in accordance with previous data obtained with a different soil [31]. Since for electromigration to occur the ions have to be in solution and in exchangeable forms, the results are important because they show that electrokinetics is very promising for the decontamination of soils.

The proposed model succeeded well in describing the system and enables us to obtain the following statistically significant conclusions: the electrokinetic removal of Cu from other soil fractions to Cu in 'solution', ready to migrate towards the cathode (Σ Cu steps b)–f) of sequential extraction to Cu in step a)), is a local phenomenon (dependent on the distance from the AN), cumulative and controlled by time as well as by pH (Eqs. (1)–(4), Tables 4 and 5).

In fact, α (Cu removal from the soil) in the first set of regressions (Eq. (1), Table 4) can be considered as a location parameter for the curves (Fig. 5). Thus when this parameter varies the parabola moves parallel to itself and in the same sense (Fig. 5). The second phase regression shows how this location parameter (α) varies with time (Eq. (2)). The good fit obtained points towards a cumulative process (Eq. (2)). For the moment, we are not able to extrapolate Eq. (2) for time of experiment < 18 days, since this equation can lead to absurd results for Cu removal. Further work with shorter times of experiment will have to be carried out. When the soil pH decreases the electrokinetic removal of Cu increases (Eq. (4)).

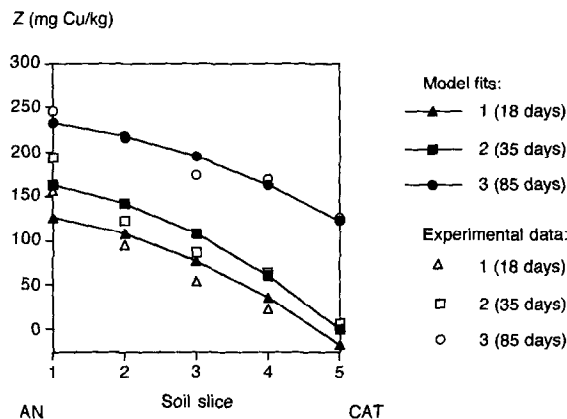


Fig. 5. Second degree parabolas of the Z data (mg Cu/kg) vs. distance from anion exchange membrane for experiments 1 (18 days), 2 (35 days) and 3 (85 days). AN - anion exchange membrane; CAT - cation exchange membranes.

The detailed study of the variables which control the process corroborated the above points and allows us to state that: 1- for the considered soil, the removal of Cu by electrokinetics (essentially Cu subjected to electromigration) depends on the release of metal from different soil fractions (defined by sequential extraction) and, to a certain extent, on the duration of the process (time being the less important) (results of F tests in Table 9). Cu attached to 'organic matter' and to 'amorphous Fe-oxides' (respectively sequential extraction steps c) and d)), are the most relevant removal steps. However, it is not possible to distinguish between these two fractions in terms of importance. The removal of Cu from the soil is local (depends on the distance from AN), and pH play an important role (results of F tests in Table 10). 2- Neither of the variables time (duration of treatment), step of sequential extraction, or distance from AN should be discarded, as they are all important to control the process. The results show the removal process to be governed by the interaction between time of treatment and distance from AN. A good degree of fit was obtained between the percentage of the total charge passed carried by Cu (P_{Cu}), and the Z_{total} ($Z_1 + Z_2 + Z_3 + Z_4 + Z_5$) in each experiment (Eq. (5)).

5. Conclusions

The authors have studied the removal of Cu from an industrially heavy-metal-contaminated soil, using the application of electric current. Three aspects of the study contribute to its originality: (i) the use of a actual contaminated soil, rather than a spiked soil sample; (ii) the use of a sequential extraction procedure to monitor changes in the chemical associations of Cu during the electrokinetic treatment of the soil; and (iii) the presentation of a dynamic model based on a biregional design which enables a joint analysis of experiments which were carried out in a laboratory cell.

Although there is some discussion about possible uncertainties with sequential chemical extraction procedures, this technique is believed to be one of the most reliable ones available for predicting metal leaching rates as well as transformations induced in the soil by the application of electric current.

The dynamic model proposed enables us to draw the following statistically significant conclusions: the electrokinetic removal of Cu from the soil is time dependent, local (depends on the distance from AN), and depends on the release of metal by different soil fractions (defined by the steps of sequential extraction). The process is also very much a result of the interaction between time (duration of treatment) and distance from AN. In the process of releasing Cu from the soil, the 'organic matter' and 'amorphous Fe-oxides' fractions (respectively steps c) and d) of the sequential extraction) are the most relevant, although it is not possible to distinguish between them in terms of importance.

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