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APPLICATION OF BIREGRESSIONAL DESIGNS TO ELECTRODIALYTIC REMOVAL OF HEAVY METALS FROM CONTAMINATED MATRICES

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Abstract

Given a base design with quantitative factors and a primary linear regression to each of the treatments, we may adjust secondary regressions of linear combinations of the adjusted coefficients on the primary regressions on the factor levels, thus obtaining a biregressional model.

A biregressional design was established for a set of treatments, defined from quantitative factors and a linear regression in the same variables. Afterwards the action of the regression coefficients and their linear correlations was analysed.

This approach was used to study the electrodialytic process (ED), a decontamination technique for removal of heavy metals from polluted matrices. The method uses a low-level direct current as the "cleaning agent", combining the electrokinetic movement of ions in the matrix with the principle of electrodialysis.

The authors have studied the removal of heavy metals from industrially heavy-metal-contaminated soil, preserved wood waste and fly ash from municipal solid waste incinerators using the application of the electrodialytic process. In this paper we show how statistics may support the development of a research line.

The removal of heavy metals was found to be described, in all studies, by low degree polynomials with null independent terms. The coefficient [twice the coefficient] of the first [second] degree terms measuring the initial rate [acceleration] of removal. Our approach enabled the study of the action of the factors defining the treatments on these, and other, coefficients of the polynomials.

Keywords: contaminated soil, preserved wood, fly ash, electro-remediation, birregressional design.

2000 Mathematics Subject Classification: 00A06, 00A71.

1. Introduction

The electrodialytic process (ED) is a decontamination technique for removal of heavy metals from polluted matrices [1]. It has mainly been applied to polluted soils [2–3], impregnated wood waste [4–9], fly ash from straw combustion [10] or municipal solid waste incinerators fly ash [11]. The method uses a low-level direct current as the "cleaning agent" to remove matrix contaminants. The applied electric field present when a direct current (dc) is passed between a pair of electrodes placed in contaminated matrix leads:

1) to the electrolysis of water at the electrodes, generating an acidic medium at the anode, which promotes an acidic front that advances across the cell towards the cathode, and a basic medium at the cathode, which promotes an alkaline front towards the anode;
2) and to the mobilization of the pollutant species, driven towards one of the electrodes, mainly due to:
   - electromigration, the movement of charged species,
   - electroosmosis, the mass flux of pore fluid (water) due to dipolar interactions between water molecules and contaminated matrix surfaces, which is responsible for the removal of uncharged compounds,
   - and electrophoresis, the movement of charged particles.

The pollutants are then transported towards one of the electrode compartments where they will become concentrated. The general principle of the ED is presented elsewhere and several authors have critically reviewed its state of knowledge [1, 3, 7].

The application of biregressional design was studied to analyzee the ED on the removal of heavy metals from three different matrices: an industrially heavy-metal-contaminated soil, preserved wood with chromated copper arsenate (CCA) and fly ashes from municipal solid waste incinerators.

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 [l2]. Soils act as traps for heavy metals that are mobilized in the environment. In the case of copper (Cu), for example, Bowen [13] 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 is to be expected [2].

CCA is a water-borne preservative containing arsenic (As), chromium (Cr) and copper (Cu) that is used for the long term protection of wood against insects, fungi or marine borers. Due to its excellent fungicidal and insecticidal properties, CCA became the most widely used wood preservative. In spite of its usefulness extending the productive life of wood and reducing the demand for forest resources, the components of CCA are hazardous to human health and present a potential threat to the environment. An increase in the amount of waste from wood treated with CCA is expected over the next decades [4–7]. This raises an increasing concern about the environmental issue of treated wood waste management. Both legislation and drawbacks of the traditional disposal method (landfilling) are promoting research studies on alternatives for recycling and re-use of CCA-treated wood waste, particularly those that, after extraction of CCA below a certain level, as well as re-use (e.g., for the manufacturing of woodbased composites) [4].

Incineration of residues is a current practice in many countries, which produces fly ash, considered hazardous waste (172/2007/EC). Despite of their classification, the municipal solid waste incinerators (MSWI) fly ash represent valuable outputs due to their mineral content and potential fertilizing value, relying on its K, Mg and P content [14] if their hazardous components could be removed.

The main goal of this research line is to study and modeling the heavy metal behavior in electrodialytic treatment and to analyze the influence of different imposed conditions on these contaminated matrices, in the efficiency of the remediation process. In this paper we show how statistics may support the development of a research line, with papers previously published elsewhere, mainly through the following references [2, 8–10].

In biregressional models a primary linear regression is adjusted for each of the treatments of a base design. The factors of the base design must be quantitative so that we may adjust regressions on these levels of the adjusted coefficients of the primary regressions. These will be the secondary regressions and the complete model is considered a biregressional one.

In applying biregressional models we must start by deciding the regression models to use. In the following curves these were low degree polynomials with null independent terms. The nullity of these terms among, form the fact that at time 0 no migration thus occurred. Besides this, low degree polynomials adjusted quite well to the data.

The initial speed [acceleration] of the migration is thus measured by the coefficient [twice the coefficient] of the first degree [second degree] term.

2. Experimental section

2.1. Contaminated matrices

2.1.1. Soil

The contaminated soil was sampled at a Portuguese wood preservation site, at Famalicão, in the north of Portugal. The soil sampling was done at a storage area for freshly treated wood, which was the source of pollution by Cu, in addition to As and Cr.

The soil characteristics are presented in Table I.

2.1.2. Treated wood waste

The experimental samples were sampled from 8 years out-of-service CCA treated *P. pinaster* Ait. poles. The poles came from Leiria, near the central Atlantic coast of Portugal. The CCA formulation, as well as the treatment scheme used for the poles is unknown. All experiments were performed with poles sawdust.

The wood characteristics are presented in Table I.

Table I. Characteristics of the soil and sawdust wood.

	Soil	**Treated wood waste**
Depth	0 – 10 cm	–
pH(H2O)	7.15	–
pH(KCl)	6.10	–
Particle size	coarse sand = 49.4% fine sand = 24.4% silt = 21.7% clay = 4.5% loamy sand texture	20 mesh average diameter
Organic matter	70.9 g/kg	–
Cation exchange capacity	12.75 cmol(c)/kg	–
“total” metal mg/kg ± sd	Cu – 322 ± 21 (n = 9)*	Cu – 3251 ± 199** Cr – 7388 ± 1586** As – 7537 ± 1223**

*“total” Cu by HNO-HClO-HF extraction; **“total” Cu, Cr and As content determined according to BS 5666: Part 3: Method 1 (BS 5666 1979).

2.1.3. Fly ash

Fly ash samples were collected from VALORSUL MSWI, which serves the great area of Lisbon, Portugal, during a period of 3 weeks. The experimental samples consist of ashes composites collected at the boiler and air pollution control devices.

2.2. Experimental setup

2.2.1. Electrodialytic cell

All experiments were run in a batch laboratory electrodialytic cell (ED) developed at the Technical University of Denmark [15]; this type of cell is described in detail elsewhere [2, 4]. The cell is divided into 3 compartments, consisting of two electrode compartments and a central one, in which the contaminated matrix is placed (Figure 1). The electrode compartments and the central were separated by ion exchange membranes (cation exchange membrane [CAT]: ICl-61CZL386, anion exchange membrane [AN]: IAl-204SXZL386, both from Ionics, Massachusetts, USA).

Each electrode compartment contained an electrolyte solution (Table II) and was equipped with a circulation system. Power supplies were used to maintain a constant current and the voltage was monitored. Anolyte and catholyte solutions were maintained constant in all experiments.

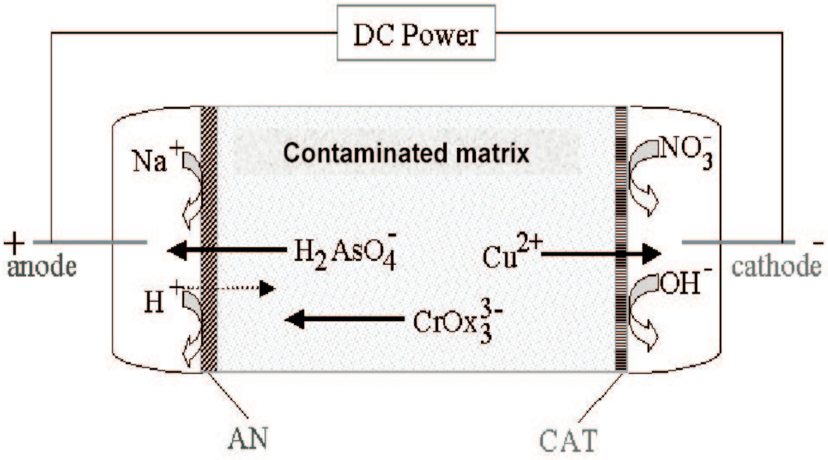

Figure 1. Schematic representation of the cell used in the experiments. AN - anion exchange membrane; CAT - cation exchange membrane.

Table II. Characteristics of the electrolytes used in the experiments.

Matrix	Anolyte	Catholyte
Soil	10^{-2}M $NaNO_3$ (pH = 3)	10^{-2}M $NaNO_3$ (pH = 3)
Wood	10^{-2}M $NaNO_3$ (pH = 2)	10^{-2}M $NaNO_3$ (pH = 2)
Fly ash	0.25M ammonium citrate in 1.25% NH3	10^{-2}M $NaNO_3$ (pH $\approx$ 2)

2.2.2. Electrodialytic experiments

The electrodialytic experiments were carried out with several variables (quantitative factors): Central compartment length, remediation time, applied current, studied metal and assisting agent used. For fly ash experiments the ash dilution percentage was also considered. Table III describes the variables used in the experiments.

Table III. Description of the variables used in the carried out experiments.

Matrix	**Variable**	
Soil	Central compartment length remediation time applied current studied metal assisting agent (w/w) number of experiments	15 cm 18, 35 and 85 days 0, 20 mA/cm^2 Cu water 3
Wood	Central compartment length remediation time applied current studied metal assisting agent (w/w) number of experiments	3 cm 30 days 0, 20 mA/cm^2 Cu, Cr and As Oxalic acid: 1.0, 1.75, 2.5, 5.0 and 7.5 % Formic acid: 2.5 % Citric acid: 2.5 % water 8
Fly ash	Central compartment length remediation time applied current studied metal assisting agent (w/w) ash dilution percentage number of experiments	3 and 10 cm 14 and 21 days 0, 20, 40, 60 and 80 mA Fe, Mn, Cu, Zn, Cd, Cr, Pb and Ni 0,25M ammonium citrate in 1,25% NH_3 50, 75, 90 and 100% 18

2.2.3. Analytical methods

All the reagents used in the experiments were '*pro analysis*' grade.

2.2.3.1. Soil

Copper contents were determined by Atomic Absorption Spectrophotometry (AAS) (Perkin Elmer 5000) after a six-step sequential chemical extraction procedure described in [2].

2.2.3.2. Treated wood waste

Copper and Cr were determined by AAS (Perkin-Elmer 300) and As by inductively coupled plasma (ISA Jobin–Yvon 24-ICP). The final "total" amount of Cu, Cr and As in the sawdust after the experiments was also analyzed according to method 1 of the British Standard (BS 5666 1979). The concentration of the metals in the ion-exchange membranes was determined in the filtrates (after immersing the membranes for 48 h in 1 M HCl solution). Metals deposited on the electrodes were analyzed in solutions, obtained after immersing each electrode in 1 M HCl solution and applying a potential reversal against a clean electrode.

2.2.3.3. Fly ash

Quantification of heavy metal contents, total concentrations and respective ratios between final and initial concentrations were performed using the *aqua-regia* (HNO_3/HCl) procedure, following AAS analysis.

2.2.4. Data treatment

2.2.4.1. Soil

The "total" Cu content in the soil was sub-divided into six different fractions [2]: 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'.

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. The pH was measured and the Cu content was estimated for each soil slice. Both measurements were made in order to establish the concentration profiles of pH and Cu in the various fractions in relation to the distance from the anode. The fractions from where Cu had been removed where identified by comparing its contents in the soil before and after the passage of the current. The experimental data has not been rounded off to indicate the expected precision, since most of the data is used for subsequent calculations. For modulation purposes it was assumed that a positive current goes from anode to cathode within the cell and that Cu is mainly in the form of Cu^{2+} and moving towards the cathode. As there is no replication of the experiments it was assumed that there is no interaction present between variables.

2.2.4.2. Treated wood waste

Different types of data were collected from the experiments and used for modulation: (1) concentrations of Cu, Cr and As in both electrolytes (anolyte and catholyte) during the experiments; (2) percentage of removal efficiency derived from the concentrations of Cu, Cr and As in the sawdust before and after the experiments; (3) amounts of Cu, Cr and As accumulated at the end of the experiments in both electrolytes, ion exchange membranes and electrodes. A joint analysis of data and individual analysis Cu, Cr and As data was performed. It was assumed that, at time zero, no heavy metals have been removed from the wood.

2.2.4.3. Fly ash

Total concentrations of metals (initial and final) in fly ash and its electrolyte concentrations along the experimental time were used as the raw data. The data was modeled, adapting the methodology applied in [9], using the SPSS program, developed by Apache Software Foundation and Microsoft Office tools.

3. RESULTS

3.1. Industrially heavy metal contaminated soil

3.1.1. A model for the electrokinetic removal of Cu

A dynamic model based on biregressional designs was proposed.

The independent and dependent variables considered as starting points for the model are shown in Table IV.

Table IV. Independent and dependent variables considered on the biregressional designs for the electrokinetic removal of Cu from contaminated soil.

Matrix	Independent variable	Dependent variable
Soil	Time Distance (AN to each soil slice)	soil pH “total” Cu Cu contents from 6-step sequential extraction % of the total charge carried by $Cu^{2+}= P_{Cu}$

The first set of regressions adjusted, per treatment, resulted in quadratic expressions without linear terms (second degree parabolas) showing that Cu removal (Z_i) from the soil was a function from the distance to anion exchange membrane (AN).

(1) $Z_i = \alpha_i + \beta_i x^2$ ($i =$ experiments; $x =$ distance from AN in cm).

The application of Scheffé's method found that only a differed significantly between experiments.

Cu removal from the soil (α) in the first set of regressions (Eq. (1)) can be considered as a location parameter for the curves and thus when this parameter varies the parabola moves parallel to itself and in the same sense (Figure 2).

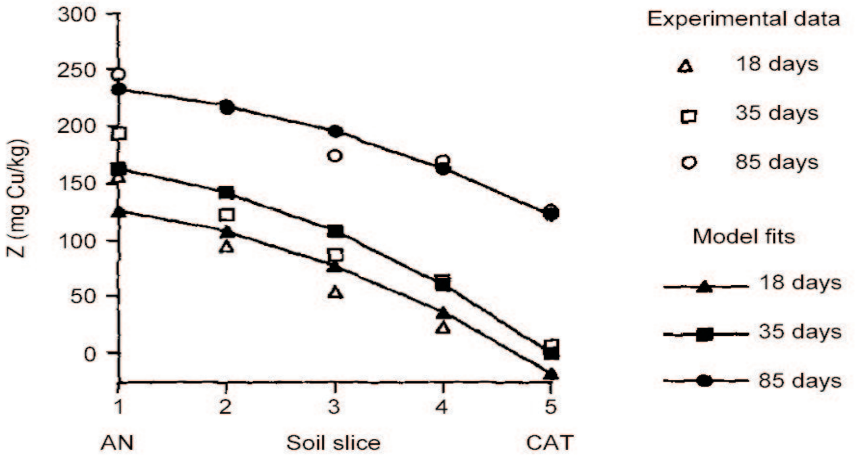

Figure 2. Second degree parabolas of Cu removal (mg Cu/kg) vs. distance from anion exchange membrane for experimental time. AN - anion exchange membrane; CAT - cation exchange membranes [2].

A second phase regression was carried out only for a expressing the effect of the duration of experiment on the coefficients of the adjusted regressions. The results showed a linear relation with the time of experiment.

(2) $\alpha = 108.48 + 1.53t\,(t = \text{time of experiment } \geq \text{ 18 days}),\text{ with } r^2 = 0.986.$

The second phase regression shows how this location parameter a varies with time (Eq. (2)). The good fit obtained points towards a cumulative process (Eq. (2)).

The first conclusion obtained was that Cu removal is a local phenomenon, dependent from the distance to anion exchange membrane and controlled by the time.

Soil pH is also an important variable, in the process and it was decided tried to adjust second degree parabolas and study its influence.

(3) $pH_i = \alpha'_i + \beta'_i x_2\,(i = 1, 2, 3\,\text{experiments}; x = \text{distance from AN in cm}).$

The influence of pH measured by a' on the amount of Cu removed, as expressed by a was found to varied linearity following the relation:

$$\alpha = 657.45 - 151.85\alpha' \text{ with } r^2 = 0.911. \tag{4}$$

Showing up that Cu removal is also controlled by the pH. When the soil pH decreases the electrokinetic removal of Cu increases (Eq. (4)).

In order to study the efects of pH, time and distance on the coefficients a of the initial regressions, a second set of regressions was adjusted considering the individual Cu removal rates for each soil slice subdivided into the $\sum$Cu quantities of the six sequential extraction steps (initial and final values). Five linear regressions were obtained between α (expressing Cu removal per sequential extraction step) and the time of experiments.

A two two-way ANOVA without replication were performed over the α values, considering the factors time (days) and removal by a certain step of sequential extraction and over the pH values, considering the factors time (days) and distance from AN. For the F tests and the Scheffé's method the sum of squares for the interaction as sum of squares for the errors was used. The results of F tests shown that the differences among steps of sequential extraction were highly significant ($p = 0.00l$), and that the differences among time of treatment are significant for a level of 0.05, but not for a level of 0.01 ($p = 0.026$).

The ANOVA was completed through the use of Scheffé's multiple comparison method applying the critical 5% differences. The findings shown that Time 18 is significantly different from Time 85 and that the steps c) (organic matter) and d) (attached to amorphous Fe-oxides) of sequential extraction are the most important in the removal of Cu from the soil but without being possible to distinguish between them in terms of importance. The results of F tests presented also shown that the differences among distances from AN in the cell were highly significant ($p = 0.008$), and that there was no differences among times of treatment ($p = 0.102$). Concerning the pH the ANOVA completed through the use of Scheffé's multiple comparison method shown that it is significantly different from slices 1 and 2 and slice 5.

A three-factor ANOVA involving time, sequential extraction step and slice distance was used in order to test the possibility of discarding one or more of the controlled variables [2]. The results of F tests presented shown that the differences among times of treatment, steps of sequential extraction and distances from AN in the cell are all very highly significant ($p < 0.001$). The interaction between time and distance in the cell is also very highly significant, but not the interaction between time and step. The interaction between step and distance is barely significant.

The result shown that Cu removal from the soil is a function of its content on each soil fraction (5 fractions) and that can be expressed by equation 5.

$$Z_{ij} = \alpha_{ij} + \beta_{ij} x^2 \ (i - \text{time};\ j - \text{extraction step}). \tag{5}$$

Being Z the Cu removal and b the distance from each slice to the anion exchange membrane.

3.2. Preserved wood waste with CCA

3.2.1. A model for the electrokinetic removal of Cu, Cr and As

In these experiments the behavior of the Cu, Cr and As in the system is controlled by the role of the assisting agents. Cu electromigrates as a cation to the cathode compartment when using water as "assisting agent". When using oxalic acid Cr presents a fast mobility due do the high solubility of chromium oxalates. In opposition copper oxalate (CuOx) has limited water solubility and therefore precipitates in the wood, preventing Cu mobility in the initial experiment's time range. The removal efficiencies of As show a similar pattern with those of Cr, suggesting the existence of a relation between them. The adjusted Pearson correlation coefficient for percentages y (As removal efficiency) and x (Cr removal efficiency) was p=0.99, supporting the existence of a linear relation between y and x, estimated as:

$$y = 0.74x - 26.7 \quad \text{with } r^2 = 0.98 \tag{6}$$

Cr and As removal efficiency percentages are shown in Figure 3, where the linear relation is clearly displayed.

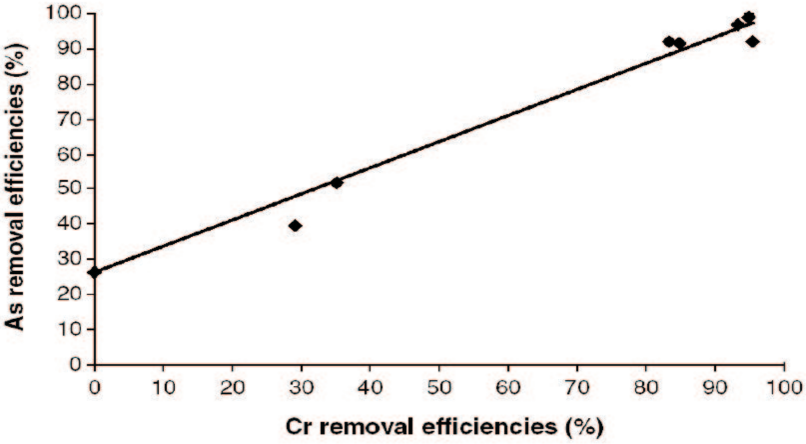

Figure 3. Linear relation between the Cr and As removal efficiencies.

The percentage value of 26.7 may correspond to the As that is not bounded and thus is frst mobilized into the electrolytes. The following removal may correspond to the As that bonds with Cr and forms soluble arsenic chromates. It was estimated that after removing 26.7% of the As, for two Cr removed one As is simultaneously removed.

The results obtained for Cu, Cr and As on global efficiencies have shown that, for the experimental time, oxalic acid is a better assisting agent than either formic or citric acid.

The modeling of the time evolution of the total concentrations in the electrolytes, considering all elements and the percentage of the assisting agent oxalic acid was performed.

Using least squares method and significance tests for individual regression coefficients [16], it was shown that for Cu the model that better described the relationship between concentration and time course of the experiments was a 4th degree polynomial regression of the following type:

(7) $y_i = \alpha_{i,2}t^2 + \alpha_{i,3}t^3 + \alpha_{i,4}t^4$ ($i = 2, 3, 4$ experiments; t – time in days).

The first derivative of the 4th degree polynomials, give the instantaneous speed (rate) of Cu removal into the electrolytes, which may present either none or two inflection points after adjusting. Two inflection points have been found for the experimental data. The existence of the two inflection points for Cu curves suggests that there may be occurring two simultaneous processes for Cu removal meaning that it is a gradual process. At the first inflection points, the process changes from accelerating to decelerating and the maximum speed (rate) of removal is achieved. At the second inflection points, the process changes from decelerating to accelerating and a minimum speed (rate) of removal is reached.

The XV multiple comparison method [17–18] was applied to find significant differences between the $\alpha_{i,j}$ coefficients of pairs of treatments for the same powers of time (t, t^2, t^3, t^4). The frst coefficients, which correspond to the lower degree ($\alpha_{i,2}$ for Cu) are relevant in determining the initial speed (rate) of dissolution and mobilization of metals into the electrolytes and thus to find the most efficient treatment for removal of heavy metals in the shortest possible time.

The results of the Scheffé's multiple comparison method at a 5% confidence level, shown that only a2 presents significant differences between treatments (1.75 and 2.5% oxalic acid) for Cu.

The data shown, that Cu was removed towards the two electrolytes in different forms. In an initial stage Cu removal is mainly observed towards the anolyte, following by a phase in which its removal towards the catholyte predominates. In an attempt to uncover these two processes, the time evolutions of Cu concentration in the catholyte and in the anolyte were study separately. To model both removals, 4th degree polynomials were adjusted. Inflexion points, inside the experiments time range, were only found for the Cu removal towards the cathode (1.75 and 2.5% oxalic acid treatments). These results suggested that Cu removal in time is a gradual process towards both electrode compartments that is dominated by its removal towards the catholyte.

For Cr and As, the best fit were achieved with 3^{rd} degree polynomials of the type:

$$y_i = \alpha_{i,1}t + \alpha_{i,2}t^2 + \alpha_{i,3}t^3 \ (i = 2, 3, 4 \text{ experiments}; \ t - \text{time in days}). \tag{8}$$

The Scheffé's multiple comparison method [17–18] was applied to find significant differences between the $\alpha_{i,j}$ coefficients of pairs of treatments for the same powers of time (t, t^2, t^3). The first coefficients, which correspond to the lower degree ($\alpha_{i,1}$ for Cr and As) are relevant in determining the initial speed (rate) of dissolution and mobilization of metals into the electrolytes and thus to find the most efficient treatment for removal of heavy metals in the shortest possible time.

For Cr it was found that α_1 and α_2 presents significant differences between treatments with 1.0 and 2.5 % and 1.75 and 2.5 % oxalic acid, respectively.

Polynomials of the 3^{rd} degree present just one inflection point when adjusted. For the experimental treatments at these inflection points the behavior of the process turns from decelerating to accelerating and consequently these points correspond to minimum speeds (rates). Contrary to what happens with the Cu concentrations in treatments with 1.75 and 2.5% of oxalic acid, the Cr concentrations in the anolytes are significantly larger than the Cr concentrations in the catholytes. Chromium removal is fast and occurs mainly towards the anode compartment.

For As it was found significant differences for all the coefficients a in relation to treatments with 1.0, 1.75 and 2.5% oxalic acid. For As a1 has much more weight in the regression than the a2 and a3 coefficients. This observation means that there are no significant differences between the treatments with 1.0% and 2.5 % oxalic acid but that treatment with 1.75% differs from the other two.

As for Cr, in the inflection points the behavior of the process changes from decelerating to accelerating and thus these points corresponding to minimum rates.

As for chromium, arsenic removal is fast, mainly towards the anode compartment.

The model results supported the importance of the concentration of assisting agent in the efficiency of the process and pointed to oxalic acid, at the range of near 2.5 %, as the best assisting agent.

The results show that when using oxalic acid, Cr and As removal is fast, while Cu removal is a gradual process.

3.3. Fly ash from municipal solid waste incinerators

3.3.1. A model for the electrokinetic removal of Cd

By means of Scheffé's multiple comparison tests, the final/initial concentrations ratios of the metals were analyzed in order to determine which of the variables ("ash percentage", "applied current", "time" or "central compartment length") have a significant effect on the efficiency of electrodialytic process.

From this analysis it was estimated that the variables *applied current*, *ash percentage*, *central compartment length* and the *metal to be removed* are all highly significant variables that influence electrodialytic remediation efficiency. The remediation time is not a significant variable, meaning that there is no difference between using 14 or 21 days in the process efficiency.

The Scheffé's multiple comparison method was also used to compare differences between the applied current and the ash dilution (%), in the efficiency of the electrodialytic process.

No significant differences between applying 20 and 40 and 60 mA of current in electrodialytic remediation or applying 0 and 80 mA.

Significant differences were found between the use of 50/75/90% o and 65/100% ash in the process.

A biregressional design approach was used to study the metals behavior over experimental time.

The independent and dependent variables considered as starting points for the model are shown in Table V.

Table V. Independent and dependent variables considered on the biregressional designs for the electrokinetic removal of metals from contaminated fly ash.

Matrix	Independent variable	Dependent variable
Fly ash	Current Ash (%) Remediation time Cell length	Metal Concentration ratio - $C_{\text{final}}/C_{initial}$ Δ Metal Concentration - C_{final} - C_{initial}

An ANOVA analysis, carried out for the concentrations ratios shown that the cell length has a negative influence on the process efficiency being the only variable with representative effect on Cd, Cu, Fe and Mn removals. Considering Cfinal - Cinitial , significant variables found were ash % (Cr and Ni), remediation time (Mn) and length (Fe and Ni). The variable current presented no significance in the removal rates.

F test carried out at a significant level of $p<0.05$, for the concentration rations of each metal, estimated that the applied current, Ash % and cell length affects significantly the removal of some of the metals (Table VI). The variable remediation Time, as expected, has no effect on the process. Fe, Mn and Ni were not affected by any of the studied variables.

Table VI. Removal of metals from contaminated fly ash: Significant variables (F test).

Matrix	**Significant variable**	**Affected Metal**
Fly ash	Current	Cr, Cu, Pb and Zn
	Ash (%)	Cu, Pb and Zn
	Cell length	Cd, Cu, Pb and Zn

The Cd, Cu, Pb and Zn migration to the electrode compartments were studied thought the remediation time and 4th degree polynomials were adjusted to each metal (Eq. 9).

$$(9)\ Y_i = \alpha_0 + \alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3 + \alpha_4 t^4 \quad (I - \text{experiments};\ t - \text{time in days}).$$

The estimated parameters α_0, α_1 and α_2 have a physical interpretation representing for each metal, respectively, the initial concentration ($t = 0$), the initial rate of migration (velocity at which metal enters the electrolyte compartment) and the initial acceleration ($\alpha_2 > 0$) or deceleration ($\alpha_2 < 0$) of the migration.

The estimated α_1 were overall positives showing that the metals increase their concentrations in the electrolyte compartments over time. The estimated α_2 did not show a specific trend meaning that the rates at which metal changes its migration velocities is an individual “property”.

A second regression series was adjusted for the same controlled variables being the dependent variables the first regression adjusted coefficients α. 4^{th} degree polynomials were adjusted for each metal and its migration electrolyte compartment (catholyte or anolyte) (Eq. (10)).

(10) $Y_i = \alpha_0 + \alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3 + \alpha_4 t^4 I -$ experiments; $t -$ time in days).

The results show that globally different variables have different effects on each metal. No significant effect was observed for any variable on Pb removal for both compartments and on Cd and Zn removals for the cathode. The influence of the studied variables on the estimated parameters α_0, α_1, and α_2 can be observed on Table VII.

Table VII. Removal of metals from contaminated fly ash: Significant variables (2nd regression series).

Matrix	**Significant variable**	**Affected metal at the anode**	**Affected metal at the cathode**
Fly ash	Current	Cu; Zn ($\alpha_0, \alpha_1, \alpha_2$)	Cu; Pb ($\alpha_0, \alpha_1, \alpha_2$)
	Ash (%)		Cu ($\alpha_0, \alpha_1, \alpha_2$)
	Cell length		Cu (α_1)
	Remediation time	Cd (α_2); Zn	

Final Remarks

We hope it is now clear the interest of the use of biregressional designs in studying the dynamics of ions migration (movement of species) when we work with quantitative factors. Namely we are able to quantify the action of the factor levels in the initial speeds and acceleration of such migration.

Our study also enabled us to consider separately the different heavy metals under study.

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