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Regression modeling of electrodialytic removal of Cu, Cr and As from CCA treated timber waste: application to sawdust

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Abstract Waste of wood treated with chromated copper arsenate (CCA) is expected to increase in volume over the next decades. Alternative disposal options to landfilling are becoming more attractive to study, especially those that promote re-use. The authors have studied and modeled the electrodialytic (ED) removal of Cu, Cr and As from CCA treated timber waste. 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 electro dialysis. The technique was tested in eight experiments using a laboratory cell on sawdust of out-of-service CCA treated *Pinus pinaster* Ait. poles. The experiments differ because the sawdust was saturated with different assisting agents and different percentages of them. In order to select the best assisting agent in jointly removing the three metals and subsequently the best percentage of the selected assistant agent, a statistical analysis was made. First, three experiments were selected as being the best. Second, for the selected experiments, a polynomial model was found to describe the time evolution of the total concentrations of each metal in the electrolytes. Based on this modeling, a multi-treatment regression approach was further used to select the final range of experiments.

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Introduction

Chromated copper arsenate (CCA) is a water-borne preservative containing arsenic, chromium and copper 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 (Ribeiro et al. 2000). 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, promote re-use (e.g., for the manufacturing of wood-based composites).

The electro-dialytic (ED) process is an emerging remediation technique for removal of contaminants from polluted sites (Lageman et al. 1989; Probst and Hicks 1993; Ottosen et al. 1997). The efficiency of the ED technique is based on the movement of the charged particles towards electrode compartments (electrodes plus electrolyte solutions), if an external potential difference is applied between the electrodes, from where they may be easily removed. The potential advantages of the ED technique for removal of metals from CCA treated wood waste may be summarized as follows (Velizarova et al. 2002):

1. A low-level direct current can be used as a “cleaning agent”.
2. Ion exchange membranes allow regulating the direction and magnitude of the ion fluxes.
3. The metal removal degree can be controlled by adjusting the flow rates of the solutions contacting the membranes.
4. The metals (Cu, Cr and As) removed might be re-used.
5. The “cleaned” timber waste might be further recycled. The present study reports results from the application of the ED process to out-of-service Portuguese CCA treated poles.

Previous studies using oxalic acid as an “assisting agent” (Ribeiro et al. 2000) pointed to the neighborhood of 2.5% (w/w) as containing the optimal percentage. To widen the scope of this study, beside treatments with oxalic acid as an assisting agent, two other treatments, with formic acid and citric acid, were included as “assisting agents”. The aims of this study were to assess the comparative values of these new agents with oxalic acid, and moreover to check on the results of the percentage of oxalic acid.

We point out that the treatments that were compared are defined by the percentage of the “assisting agent” used to saturate the wood waste.

Multi-treatment regression design approach (Kendell et al. 1983; Mexia 1987) was used to compare different oxalic acid percentages. The main ideas of this approach are briefly presented in the [Appendix](#).

Experimental section

CCA treated timber waste

All of the experiments were carried out using sawdust (particles of average size 20 mesh diameter) prepared 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. The “total” Cu, Cr and As content was determined according to BS 5666: Part 3: Method 1 (BS 5666 1979).

Laboratory cell

All experiments were run in a batch laboratory ED cell for 30 days as developed at the Technical University of Denmark (Ottosen and Hansen 1992); this type of cell is described in detail elsewhere (Ribeiro and Mexia 1997; Ribeiro et al. 2000). The cell is divided into three compartments, consisting of two electrode compartments and a central one ($L = 3$ cm, internal diameter = 8 cm), in which the sawdust is placed (Fig. 1). The electrode compartments and the sawdust were separated by ion exchange membranes [cation exchange membrane (CAT): IC1-61CZL386, and anion exchange membrane (AN): IA1-204SXZL386, both supplied from Ionics Inc., USA]. Each electrode compartment contained 1,000 ml 10^{-2} M NaNO_3 , pH = 2 as electrolyte solution and was equipped with a circulation system. The pH value of the catholyte solution was adjusted to about three by periodic addition of concentrated HNO_3 . Platinum coated electrodes (Bergsøe AC, Denmark) were used as working electrodes. A power supply (Hewlett-Packard E3612A) was used to adjust the desired initial direct current (DC) and was monitored by a Fluke 37 multimeter.

Electrodialytic experiments

Eight laboratory experiments with differing experimental conditions were carried out (Table 1). Before being put in the cell, the sawdust was saturated with a solution of the potential assisting agent: distilled water (experiment 1); oxalic acid 1.0, 1.75, 2.5, 5.0 and 7.5% (w/w) in experiments 2–6, respectively; formic and citric acid 2.5% (w/w) (experiments 7 and 8, respectively). In all of the experiments, the current density was 0.2 mA/cm^2 and duration of treatment was approximately 30 days.

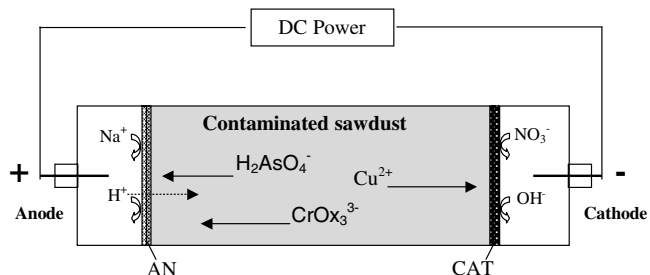


Fig. 1 The ED cell. AN anion-exchange membrane, CAT cation-exchange membrane

Table 1 Treatments

Experiment	1	2	3	4	5	6	7	8
Treatments	Water	1% Oxalic acid	1.75% Oxalic acid	2.5% Oxalic acid	5% Oxalic acid	7.5% Oxalic acid	2.5% Formic acid	2.5% Citric acid

For the purpose of the analysis the experiments will be considered as treatments. Treatment 1 (with water) is considered the control treatment—equivalent to 0% oxalic acid or representing the absence of an assisting agent. Treatments 2–6 (different percentages of oxalic acid) are considered levels of the first type of assistant agent, and treatments 7 and 8 (formic acid and citric acid) are two more different types of assistant agents with just one level.

Analytical methods

During each experiment, samples of the electrolyte solutions (catholyte and anolyte) were periodically collected and analyzed for Cu, Cr and As determination. At the end of each experiment, the concentration of these target 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. 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). Copper and chromium were determined by Atomic Absorption Spectrometry (Perkin-Elmer 300-AAS) and arsenic by inductively coupled plasma (ISA Jobin–Yvon 24-ICP).

Results and discussion

The initial estimated concentration of Cu, Cr and As in the sawdust was $3,251 \pm 199$ mg Cu/kg, $7,388 \pm 1,586$ mg Cr/kg, and $7,537 \pm 1,223$ mg As/kg (Table 2). These results fall in the wide range reported in the literature for CCA-treated sawdust (mg/kg): 1,176–4,285 for Cu, 2,280–11,909 for Cr, and 1,186–10,506 for As (Clausen and Smith 1998; Clausen 1997; Hudson and Murphy 1997; Helsen et al. 1997; Kamdem et al. 1998).

Copper was mobilized in the sawdust in all experiments. Copper electromigrates as a cation in treatment 1 because the cathode compartment presents an accumulation of this metal. In treatments with oxalic acid, Cu was removed to

Table 2 Metal concentrations in the sawdust before each experiment

Metal (mg/kg)	Experiment 1 and 4	Experiment 2, 3, 7 and 8	Experiment 5 and 6
Cu	3,057.8	3,456.0	3,240.3
Cr	7,935.6	5,600.6	8,627.2
As	8,822.9	6,387.7	7,400.2

both electrode compartments partly as a cation and partly as an anionic complex. The anionic complex is most likely to be CuOx_2^{2-} . Cu also reacts with the oxalic acid to form copper oxalate (CuOx), which has a limited water solubility and therefore precipitates in the wood, which may prevent Cu removal by the ED process.

Chromium mobilization in the cell only occurred in treatments 2–8, being dominated by the flux towards the anode compartment.

Arsenic moved in the ED cell mainly towards the anode compartment. Some low As concentrations were also obtained in the cathode compartment.

Joint analysis of data

Three different types of data were collected from the experiments: (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.

For the first data type, the anolyte concentrations, the catholyte concentrations and the sum of both (total concentrations) were analyzed.

The time evolution of the total concentrations in the electrolytes for Cu, Cr and As is presented in Fig. 2, grouped by treatments with oxalic acid and water (treatments 1–6) and treatments with formic and citric acids (treatments 7 and 8). The values of maximum concentrations thereby attained are presented in Table 3.

In Fig. 3a–c the three available types of data for Cu, Cr and As

- Removal efficiency percentages
- Maximum concentration in the electrolytes
- Accumulated amounts at the end of the experiments in the ion exchange membranes and electrodes are jointly presented for each treatment.

The central role of the removal efficiency is self-evident so that a first discussion will be centered on it. Thus when looking only to the removal efficiency percentages, the following comments can be made.

Copper

At the end of the experiments, the removal efficiency is high (around 91–97%). However, for treatments 5 and 6 (the highest percentages of oxalic acid) the removal efficiencies are very low (less than 40%). These results could be explained by the formation of copper oxalates, which are highly insoluble, avoiding Cu mobilization towards the cathode compartment at least for the experiment's time range. However, this low efficiency, in treatments 5 and 6, is probably apparent considering the time of experiments. Inside the cell, copper oxalates, copper cations and oxalate anions co-exist in chemical equilibrium. A consequence of this equilibrium is the existence of a removal ratio of copper and oxalate ions in opposite directions from the central compartment which is dependent on time and initial concentration of oxalic acid.

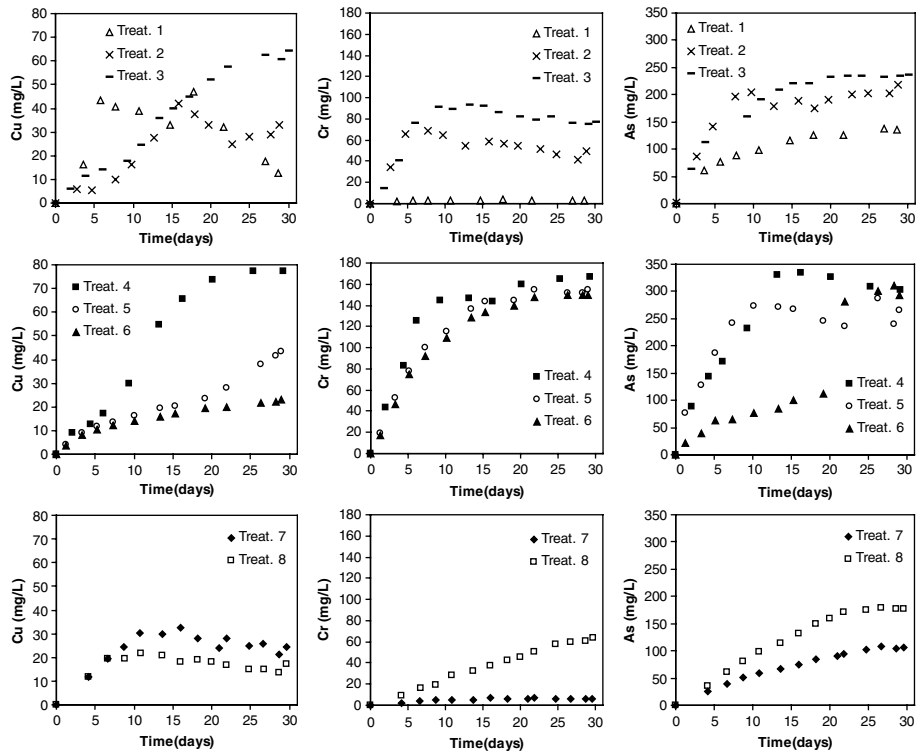


Fig. 2 Time evolution of total concentrations of Cu, Cr and As in the electrolytes (catholyte + anolyte)

Chromium

In opposition to Cu, chromium oxalates are highly soluble, the highest removal efficiencies for Cr are obtained with high percentages of oxalic acid. Such is the case for treatments 4, 5 and 6 with removal efficiencies around 94–96%, which are explained by the formation of soluble complexes between Cr and the oxalic acid. Treatments 2 and 3 also obtain good removal efficiencies (around 84%), though not as good as those for treatments 4, 5, and 6. For treatments 1, 7 and 8 the efficiency removal is very low (less than 40%).

Table 3 Maximum metal concentrations measured in the electrolytes (mg/L)

Treatment	1	2	3	4	5	6	7	8
	0%	1%	1.75%	2.5%	5%	7.5%	2.5%	2.5%
	Oxalic acid	Oxalic acid	Oxalic acid	Oxalic acid	Oxalic acid	Oxalic acid	Formic acid	Citric acid
Cu	47.1	42.2	67.4	77.5	43.2	23.0	32.6	21.8
Cr	3.8	69.1	93.4	167.3	155.0	149.8	7.1	63.6
As	137.5	217.5	235.5	334.8	287.5	310.9	107.7	178.5

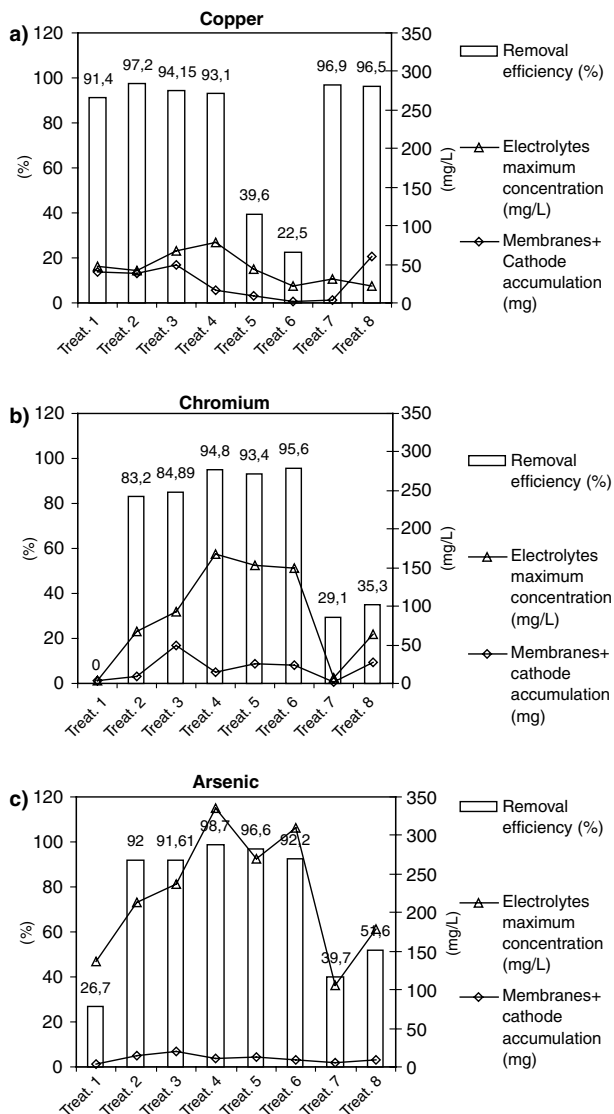


Fig. 3 Graphical presentation of the three types of data for Cu, Cr and As
Arsenic

The removal efficiencies of chromium and arsenic behave in similar ways. This fact suggests the existence of a relation between Cr and As removals. Indeed, the adjusted Pearson correlation coefficient for percentages y (As removal efficiency) and x (Cr removal efficiency) was $\rho=0.99$, thus suggesting the existence of a linear relation between y and x .

$$y = 0.74x - 26.7 \quad (1)$$

The value $R^2=0.98$ was obtained. Both removal efficiency percentages are presented in Fig. 4, where the linear relation is clearly displayed.

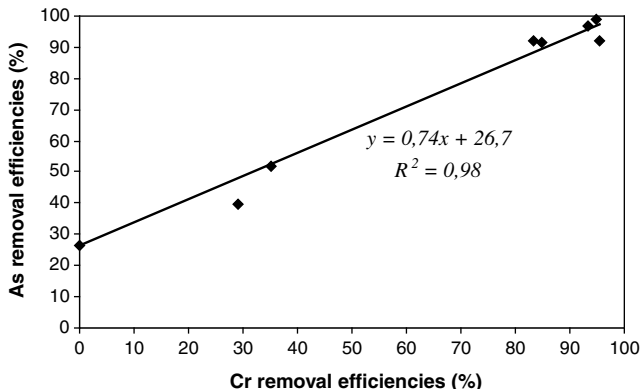


Fig. 4 Linear relation between the Cr and As removal efficiencies

Considering:

1. The percentage 26.7 (Fig. 4) as an initial removal of As
2. The value 0.74 (Eq. 1) as the proportion of As removal in the Cr removal, after 26.7% of the initial As removal
3. The atomic weights of Cr ($AW_{Cr} = 52.01$) and As ($AW_{As} = 74.91$) and the fact that the As does not complex with the oxalates, then, from the following calculations:

$$\frac{AW_{As}}{AW_{Cr}} p = 0.74 \Leftrightarrow \frac{74.91}{52.01} p = 0.74 \Leftrightarrow p \simeq \frac{1}{2}$$

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

When the removal of the three metals is derived, one is led to restrict to treatments 2, 3 and 4. The results for these treatments will be now described in more detail. From Fig. 3a–c, it can be observed for the three metals that:

1. The maximum concentration in the electrolytes increases from treatment 2 to treatment 3 and from treatment 3 to treatment 4.
2. The accumulation on the membranes and the cathode attains its maximum for treatment 3. Moreover, it can be observed that the As accumulation in the membranes and cathode is much lower than that of Cu and Cr. Since there is high As concentration in the electrolytes, these results point towards As as being more soluble than Cu and Cr.

Furthermore, for treatment 3 and mainly for Cu and Cr, considerably high amounts were collected in the membranes plus the cathode. This point will be looked into in further studies.

Time evolution of metal concentrations in the electrolytes

Pursuing the above analysis, it was decided to model the time evolution of the total concentrations in the electrolytes for treatments 2, 3 and 4. It is interesting

to point out that, considering all elements, a single assisting agent has to be considered: oxalic acid. Thus, the problem of treatment selection is considerably lightened since one has only to choose the percentage of the selected agent.

Using standard statistical techniques, namely least squares method and significance tests for individual regression coefficients (Montgomery 1997), 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:

$$y_i = \alpha_{i,2}t^2 + \alpha_{i,3}t^3 + \alpha_{i,4}t^4 (i = 2, 3, 4) \quad (2)$$

For Cr and As, 3rd degree polynomials of type

$$y_i = \alpha_{i,1}t + \alpha_{i,2}t^2 + \alpha_{i,3}t^3 (i = 2, 3, 4) \quad (3)$$

were a better fit, where t represents time in days, i the treatment number and $\alpha_{i,j}$, $j = 1, 2, 3, 4$ are the regression coefficients. Adjusted polynomials in Eq. 2 do not include the first-degree term, since it was shown that the corresponding coefficient was not significantly different from zero. Finally, there is no independent term in the adjusted polynomials since it is assumed that, at time zero, no heavy metals have been removed from the wood. The adjusted regression coefficients $\tilde{\alpha}_{i,j}$, with $j = 1, 2, 3, 4$; $i = 1, 2, 3$ and values for the coefficient of multiple determination R^2 are presented in Table 4.

The multi-treatment regression designs described in the Appendix can now be applied. Namely, the well known Scheffé multiple comparison method (Scheffé 1959; Mexia 1987) may be applied to find significant differences between same coefficients of pairs of treatments. These will be the coefficients for the same powers of time (t , t^2 , t^3 , t^4). The first coefficients, which correspond to the lower degree ($\alpha_{i,2}$ for Cu, and $\alpha_{i,1}$ for Cr and As) are especially interesting since they will be relevant in determining the initial speed (rate) of dissolution and mobilization into the electrolytes. This initial speed is very important since the aim of this study is to find the most efficient treatment for removal of heavy metals in the shortest possible time.

Copper

The evolution of the adjusted regression coefficients $\tilde{\alpha}_2$, $\tilde{\alpha}_3$ and $\tilde{\alpha}_4$ with oxalic acid percentage (treatments 2, 3 and 4) is presented in Fig. 5. It is interesting to observe that $\tilde{\alpha}_2$ and $\tilde{\alpha}_4$ have a similar evolution, which is symmetrical to the one for $\tilde{\alpha}_3$. The maximum value of $\tilde{\alpha}_2$ is attained for treatment 4, which is equivalent to say that treatment 4 (2.5% percentage of oxalic acid) is the treatment with the highest initial speed, followed first by treatment 2 and then by treatment 3.

Table 4 Regression coefficients from the adjusted polynomial regressions for treatments 2, 3 and 4

Treatment	Copper				Chromium				Arsenic			
	$\tilde{\alpha}_4$	$\tilde{\alpha}_3$	$\tilde{\alpha}_2$	R^2	$\tilde{\alpha}_3$	$\tilde{\alpha}_2$	$\tilde{\alpha}_1$	R^2	$\tilde{\alpha}_3$	$\tilde{\alpha}_2$	$\tilde{\alpha}_1$	R^2
2	0.00050	-0.02948	0.47199	0.85	0.01866	-0.99965	15.04778	0.54	0.04588	-2.40853	39.09511	0.81
3	0.00019	-0.01542	0.36456	0.98	0.01395	-0.86556	15.97298	0.92	0.01711	-1.20867	28.76647	0.97
4	0.00045	-0.03253	0.65406	0.99	0.02463	-1.40572	25.94324	0.92	0.01198	-1.30979	38.15238	0.95

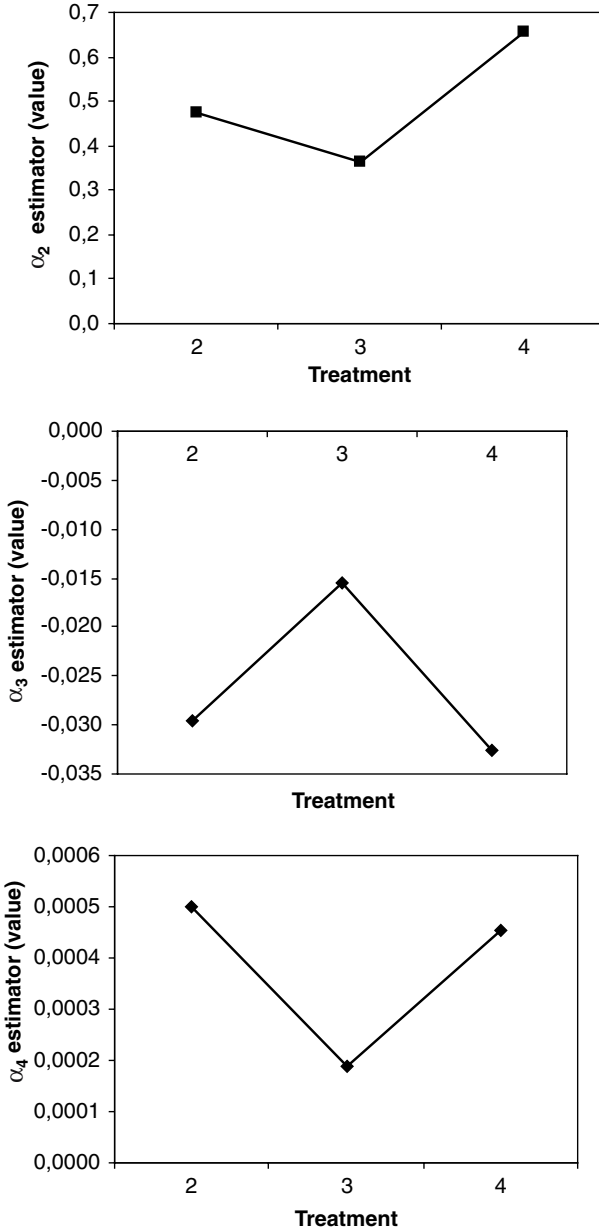


Fig. 5 Evolution of each regression coefficient with the percentage of oxalic acid for Cu

Moreover, through the use of the Scheffé multiple comparison method at a 5% confidence level, it was shown that:

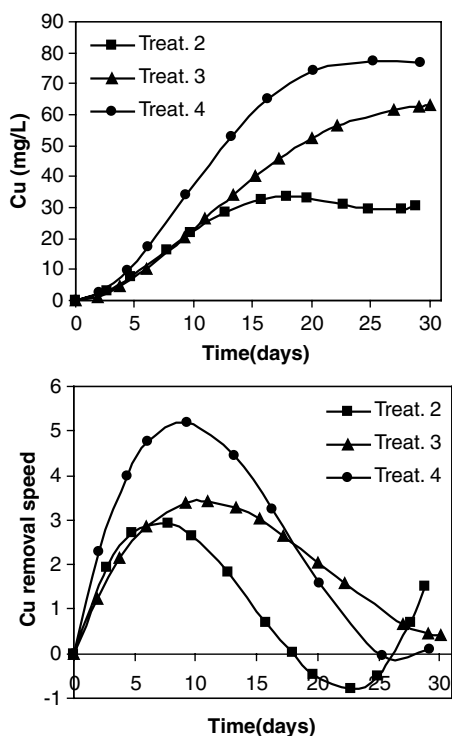
- For $\tilde{\alpha}_2$, there are significant differences between treatments 3 and 4.
- For $\tilde{\alpha}_3$, there are no significant differences between treatments.
- For $\tilde{\alpha}_4$, there are no significant differences between treatments.

The results enable us to separate significantly, at the 5% level, treatments 3 and 4.

In Fig. 6, the curves of the adjusted polynomials to the Cu concentrations for treatments 2, 3 and 4 are presented along with the curves for the instantaneous speed (rate) of Cu removal into the electrolytes, which is given by the first derivative of the polynomials.

Polynomials of the 4th degree may present either none or two inflection points. The first case happens when the second derivative has complex roots or real equal ones. While the second case occurs when both roots of the second derivative are real and distinct. Thus, when adjusting polynomials of the 4th degree, one would expect to find two or none inflection points. But actually one or both of these roots may fall outside the time range that is considered. It is important to point out that at the times corresponding to these points the behavior of the process changes from accelerating to decelerating or vice-versa. Treatments 2, 3 and 4 present a first inflection point at times 7, 10.6 and 8.9 (measured in days), respectively. At these inflection points, the process changes from accelerating to decelerating and the maximum speed (rate) of removal is attained there (Fig. 6). For treatments 2 and 4, a second inflection point is found at times 22.6 and 27. Treatment 3 has an estimated second inflection point slightly to the right of the considered time range (30.7). At these second inflection points, the process changes from decelerating to accelerating and a minimum speed (rate) of removal is attained there. The existence of two inflection points for Cu curves suggests that there may exist two simultaneous processes of Cu removal. In an attempt to uncover these two processes, it was

Fig. 6 Adjusted polynomials to Cu concentration in the electrolytes and corresponding Cu removal speeds for treatments 2, 3 and 4



decided to study separately the time evolutions of Cu concentration in the catholyte and in the anolyte. These evolutions are presented in Fig.7, which shows that, mainly for treatments 3 and 4, the Cu removals towards the anolyte and towards the catholyte do not differ very much. The Cu was removed towards the two electrolytes in different forms.

To model both removals, 4th degree polynomials were adjusted. The coefficients and R^2 values for these polynomials are presented in Table 5.

For the Cu removal towards the catholytes for treatments 3 and 4, a first inflexion point at times 16.9 and 13.7 was respectively found. No inflexion point inside the experiments time range was found for those two treatments when considering the removal towards the anolyte. Thus for these treatments (3 and 4) acceleration and deceleration of Cu removal appears to be dominated by removal towards the catholyte.

Moreover, for treatment 2 and from day 7 onwards, removal towards the catholyte is predominant (Fig. 7).

Despite the previous considerations at the beginning, the Cu removal towards the anolyte has a higher speed, which is shown by larger lower order coefficients (Table 5). Thus one may assume an initial phase of mainly removal towards the anolyte, followed by a phase in which Cu removal towards the catholyte predominates. For treatments 3 and 4 the global impact of the two phases is

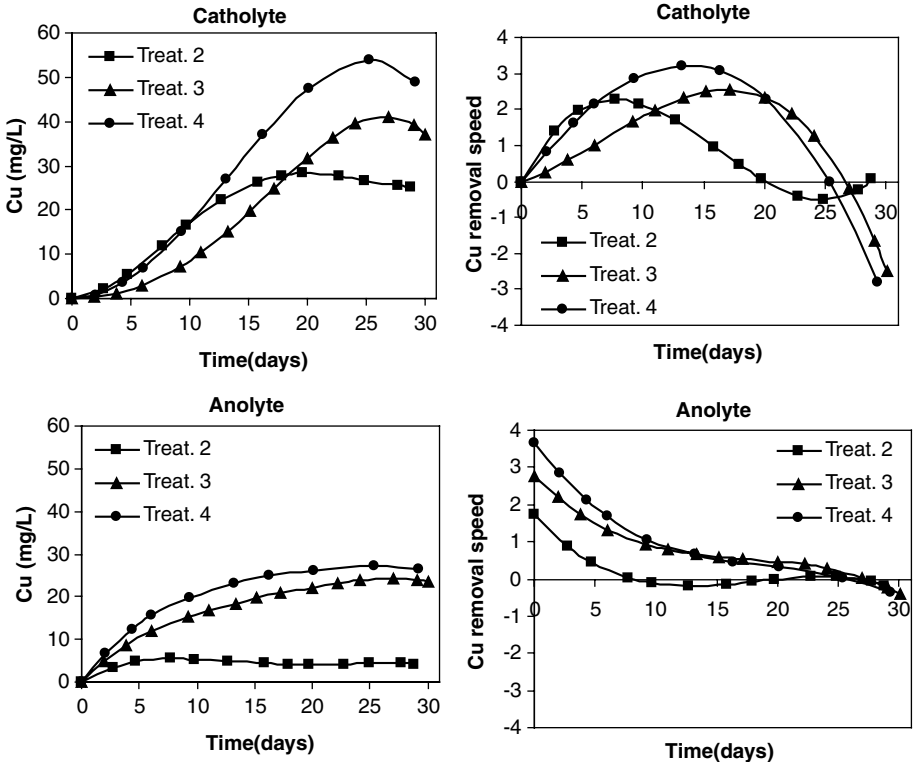


Fig. 7 Adjusted polynomials and corresponding removal speeds for Cu concentration in the catholyte (upper) and anolyte (lower), for treatments 2, 3 and 4

Table 5 Regression coefficients from the adjusted polynomial regressions to Cu concentration in the catholyte and anolyte for treatments 2, 3 and 4

Treatment	Catholyte				Anolyte				
	$\tilde{\alpha}_4$	$\tilde{\alpha}_3$	$\tilde{\alpha}_2$	R^2	$\tilde{\alpha}_4$	$\tilde{\alpha}_3$	$\tilde{\alpha}_2$	$\tilde{\alpha}_1$	R^2
2	0.00029	-0.01854	0.32696	0.85	-0.00010	0.00738	-0.18269	1.72482	0.64
3	-0.00017	0.00447	0.05598	0.98	-0.00008	0.00591	-0.16774	2.76899	0.96
4	-0.00006	-0.00344	0.21200	0.98	-0.00009	0.00700	-0.22182	3.67107	0.97

smaller while in treatment 2 the second phase is predominant. What separates these treatments is the oxalic acid concentration and, possibly, the pH (Probst and Hicks 1993). Since Cu is removed in different forms towards both electrolytes, and copper oxalates are insoluble, these differences may, perhaps, be explained through the influence of pH on solubility of negatively charged copper compounds. However, in treatment 7 and 8, high removal efficiencies were achieved for copper. According to Fig. 8, it occurs at a fast rate.

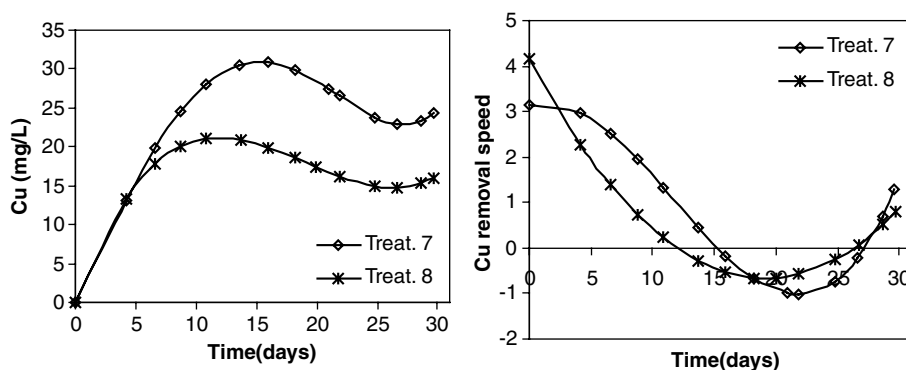
The results show that Cu removal is a gradual process towards both electrode compartments, the removal towards the anode compartment being much faster than the one towards the cathode. However, the total removal of copper in time, is conditioned by the movement towards the cathode compartment.

Chromium

The evolutions of the adjusted regression coefficients $\tilde{\alpha}_1$, $\tilde{\alpha}_2$ and $\tilde{\alpha}_3$ are shown in Fig. 9. The evolutions of $\tilde{\alpha}_1$ and $\tilde{\alpha}_3$ are inverse from the evolution of $\tilde{\alpha}_2$ and the maximum value of $\tilde{\alpha}_1$ is attained for treatment 4. Thus, it can be concluded that also for Cr, treatment 4 is the treatment with the highest initial speed (rate), followed by treatments 3 and 2 with much lower values.

Applying the Scheffé multiple comparison method to the coefficients, at the 5% level it was determined that:

- For $\tilde{\alpha}_1$, there are significant differences between treatment 4 and treatments 2 and 3.
- For $\tilde{\alpha}_2$, there are significant differences between treatment 4 and treatment 3.

**Fig. 8** Adjusted polynomials to Cu concentration in the electrolytes and corresponding Cu removal speeds for treatments 7 and 8

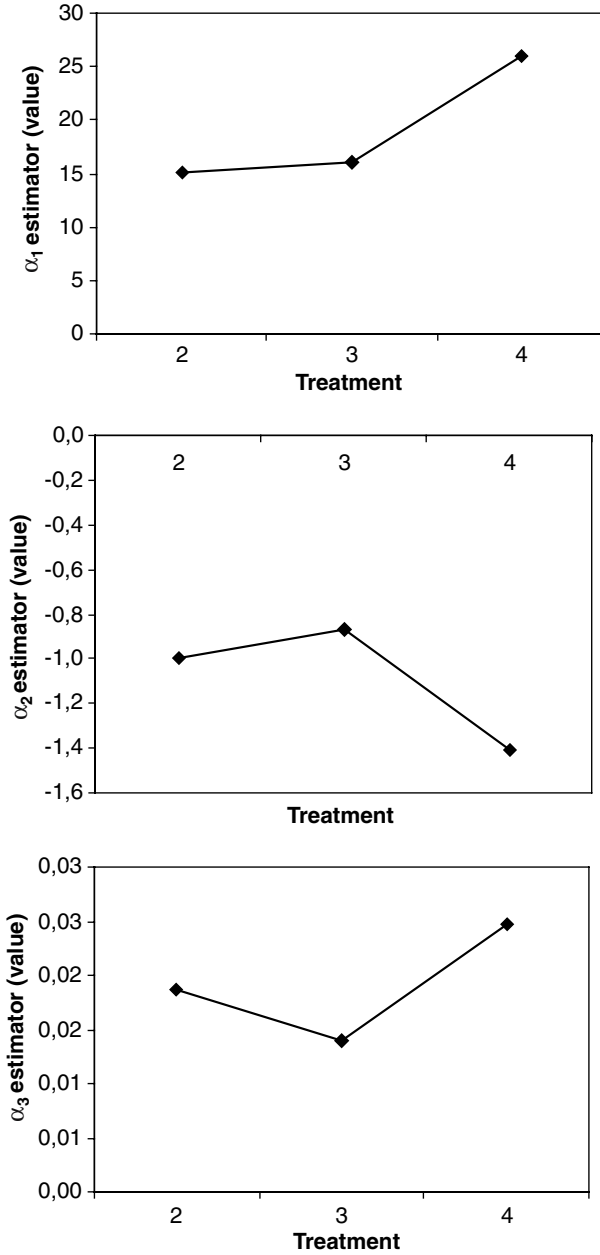


Fig. 9 Evolution of each regression coefficient with the percentage of oxalic for Cr

– For $\tilde{\alpha}_3$, there are no significant differences between treatments.

Given that $\tilde{\alpha}_1$ has much more weight in the regression than the $\tilde{\alpha}_2$ and $\tilde{\alpha}_3$ coefficients, it can be concluded from these results that there are no significant differences between treatments 2 and 3, but treatment 4 is significantly different from the other two.

In Fig. 10, the curves of the adjusted polynomials to the Cr concentrations for treatments 2, 3 and 4 are presented along with the curves for the instantaneous speed of Cr removal into the electrolytes.

Polynomials of the 3rd degree present just one inflection point that may fall inside or outside the time range that is considered. Treatments 2, 3 and 4 present inflection points at times 17.9, 20.7 and 19 (measured in days), respectively. It can be seen in Fig. 10 that for the three treatments at these inflection points the behavior of the process changes from decelerating to accelerating and consequently these points correspond to minimum speeds (rates).

Contrary to what happens with Cu concentrations in treatments 3 and 4, the Cr concentrations in the anolytes are significantly larger than the Cr concentrations in the catholytes. Chromium removal is fast and mainly towards the anode compartment (results not shown).

Arsenic

The evolutions of the adjusted regression coefficients $\tilde{\alpha}_1$, $\tilde{\alpha}_2$ and $\tilde{\alpha}_3$ are shown in Fig. 11. Again, the evolutions of $\tilde{\alpha}_1$ and $\tilde{\alpha}_3$ are inverse from the evolution of $\tilde{\alpha}_2$, but the maximum value for $\tilde{\alpha}_1$ is attained for treatments 2 and 4 which have almost the same value. Treatment 3 presents a considerably lower value.

Using the Scheffé multiple comparison method at 5% confidence level, it was found that:

- For $\tilde{\alpha}_1$, there are significant differences between treatments 2 and 3 and between treatments 3 and 4.
- For $\tilde{\alpha}_2$, there are significant differences between treatments 2 and 3 and between treatments 2 and 4.
- For $\tilde{\alpha}_3$, there are significant differences between treatments 2 and 3 and between treatments 2 and 4.

Given that $\tilde{\alpha}_1$ has much more weight in the regression than the $\tilde{\alpha}_2$ and $\tilde{\alpha}_3$ coefficients, it can be drawn from those results that there are no significant differences between treatments 2 and 4 but treatment 3 differs from the other two.

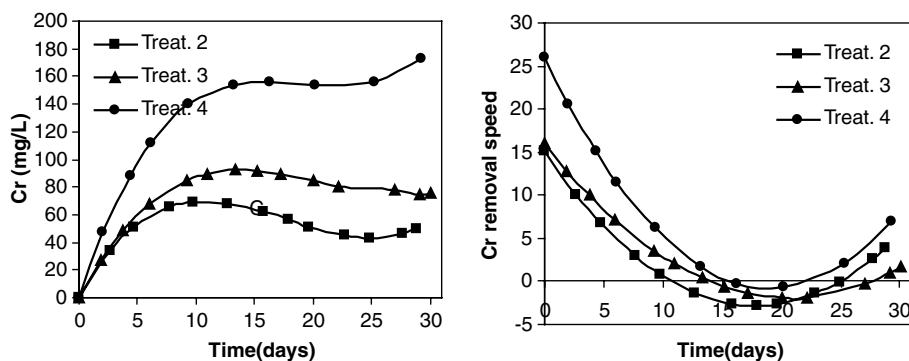


Fig. 10 Adjusted polynomials to Cr concentration in the electrolytes and corresponding Cr removal speeds for treatments 2, 3 and 4

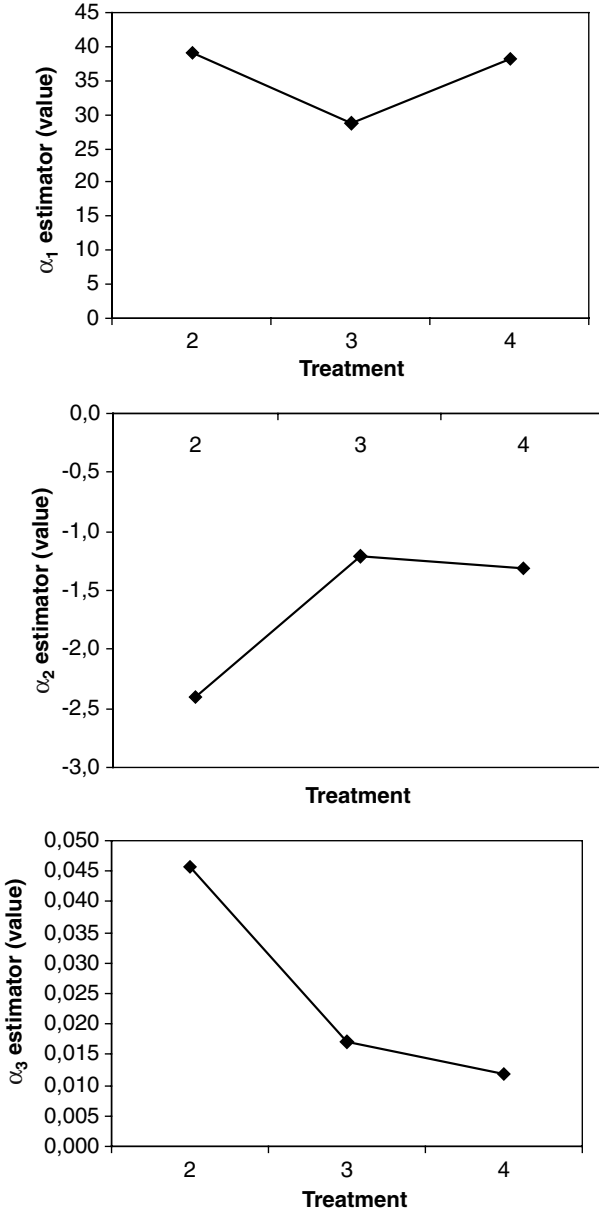
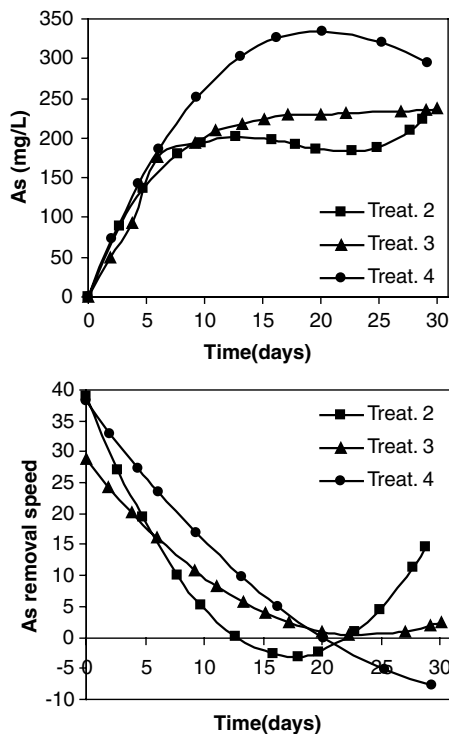


Fig. 11 Evolutions of each regression coefficient with the percentage of oxalic acid for As

Figure 12 presents the curves of the adjusted polynomials to the As concentrations in the electrolytes for treatments 2, 3, 4 and also the curves for the instantaneous speed of As removal towards the electrolytes.

Treatments 2 and 3 present inflection point at times 17.5 and 23.5, respectively, and for treatment 4 the inflection point is outside the range. As for Cr, it can be seen in Fig. 12 that for the three treatments at these inflection points the

Fig. 12 Adjusted polynomials to As concentration in the electrolytes and corresponding As removal speeds for treatments 2, 3 and 4



behavior of the process changes from decelerating to accelerating, thus corresponding these points to minimum rates.

As for chromium, arsenic removal is fast, mainly towards the anode compartment (results not shown).

Conclusions and future work

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

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

The copper removal was found to be described by a 4th degree polynomial regression with two inflection points. This behavior is apparently, in time, dominated by copper removal towards the cathode compartment. The copper removal towards the anode compartment is faster and apparently occurs in the first days of the process.

The chromium and arsenic removal in the process was found to be described by a 3rd degree polynomial regression with one inflection point. The removal of both elements is fast. Concerning the arsenic removal, a linear relation was found between its removal and the chromium removal.

The modeling carried out for the time evolution of heavy metal concentrations in the electrolytes also pointed to the range of near 2.5% as the best concentration of oxalic acid.

This conclusion must be refined through the study of oxalic acid percentages near 2.5.

Moreover, the possibilities of using mixtures of assisting agents must be studied. Actually, formic and citric acids showed a higher (albeit slight) efficiency and faster rate in copper removal. This suggests the use of combined assisting agents.

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Appendix

Multi-treatment regression designs

Let us consider a design with L treatments for each of which there is a sample of observations. If normality and equality of variances is assumed, it is straightforward to apply the well known ANOVA techniques and multiple comparison methods to analyze the data. When, instead of a sample for each treatment, there is a linear regression in the same variables, both controlled and dependent, then one has a multi-treatment regression design. Now instead of the action of the treatments on the sample mean values, the action on the regression coefficients is studied. If for all regressions there is the same matrix X for the values of the controlled variables, the ANOVA algorithms and multiple comparison methods are easy to adapt (Mexia 1987). It suffices to replace the sum of sums squares of the residuals to the mean for the L samples by the sum of sums of squares of residuals for the L regressions, as sum of squares for error. The number of degrees of freedom for error will, instead of $L(r-1)$, be $L(r-1)(n-k)$, with n being the number of points per regression, r the number of replicates and k the number of controlled variables.

When studying the action of the treatments on the i th coefficient, the dimension r of the samples must be replaced by the i th principal element of matrix $(X^t X)^{-1}$ in all formulas. Once these substitutions are carried out, exactly the same algorithms can be applied, which is highly convenient.

These designs have a wide field of application, for instance, in horticultural trials in which the controlled variables will be powers of time and the dependent variables are biometric.

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