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## FULL FACTORIAL DESIGN APPLIED TO REMOVAL COPPER IONS FROM SOIL

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*Abstract. In many areas in the world, the soil has been seriously contaminated, due practical of inadequate disposal and pollutant industrial activities. This contaminated soil becomes a threat to the environment for presenting toxic substances, as the heavy metals. It is important to consider that metals, besides causing damages to the environment, also offer serious risks to the human health. New techniques are being developed in the attempt to extract these contaminants from the soil, being one of them the technique of electrokinetic remediation, which has been considered promising because it presents an excellent potential of recovery of places contaminated by heavy metals. The objective of this work was to apply experimental design in the removal of copper ions from soil by electrokinetic remediation. The reactor performance was evaluated by the following variables: potential e time of remediation. Since there are almost no mathematical models fitting to the system and due to their complexity, it was decided to use a statistical technique, the full factorial design, for the attainment of the desired responses (removal efficiency) as empirical functions. However, this model was not able to accurately represent the experimental data, indicating that the remediation of copper contaminated soils is not a first order function.*

**Keywords:** *Electrokinetic remediation, Heavy metal removal, Full factorial design, Copper ions, Design of experiments.*

### 1. INTRODUCTION

Soil contamination by heavy metals can occur in several ways: natural, geological and also through activities performed by men (mining, industry and transport). Unfortunately the industrial activity coupled with the increase of municipal waste dump, has brought a considerable increase in the amount of metals in soil (Mavropoulos, 1999). Resulting in reduction of crop fields and agricultural contamination of water sources (Chaves, 2008).

The copper ions (Cu) can be found in different organs of human body, acting as an important nutrient for human health and the immune system (MACÊDO, *et. al.* 2010), as well as extremely important for animals and essential for plants. High concentrations of Cu ions in contaminated soils may be justified by natural and anthropogenic processes. When in high concentrations, copper may have negative impacts on several ecosystems. It has a cumulative essence in soil at different levels, which can lead to a reduction of agricultural cultivation, as well as risks to the food chain. In addition to other elements, such as phosphorus (P), it may become even more harmful (Santos *et. al.* 2012; Mantovani, 2009).

There are various technique for soil remediation as: precipitation, incineration, phytoremediation, electrochemical processes, etc. All based on two processes in situ and ex situ.

The electrokinetic remediation is an in situ technique consists of applying a direct current of low intensity (mA/cm<sup>2</sup>) or applying a potential between the electrodes located on the soil. The contaminants are mobilized in the form of charged species, particles or ions. Applied current mobilizes species electrically charged particles and ions in the soil. One consequence of this technique is the occurrence of parallel reactions such as reduction of hydrogen or oxygen generation, reducing the process efficiency.

Statistical analysis is a very important tool in validating the data, as well as to the appropriate extrapolation of the results obtained (Normando *et al.*,2010). A full factorial design should include all possible combinations of the levels of the factors of the experiment. The aim of this study is to evaluate the efficiency of removal of copper ions using the technique of electrokinetic remediation in contaminated soils. The variables that will be studied are: applied potential

and time of remediation. In order to verify the influence of these variables was used the full factorial design to obtain the desired response (removal efficiency) as empirical function.

## 2. DEVELOPMENT

### 2.1 Copper

Copper is an essential element for life. The total content of this element in the soil can vary between 2 and 100 mg kg<sup>-1</sup>. It can occur in different forms, (Cu<sup>+2</sup>), (Cu<sup>+</sup>) and metallic form, the first being the most important (Pais and Jones, 2000). According to Kabata-Pedias (2001), it tends to associate with sulfides, forming insoluble compounds. All soil minerals, such as iron (Fe), manganese (Mn) and aluminium (Al), clay and humus have the ability to absorb in a specific way Cu ions of the solution. The copper ions, when high soil concentration, can precipitate with anions, carbonates and hydroxides of sulphides, especially at Ph above 6,0. In addition, various organic substances form complexes with the Cu ions.

Copper ions has good absorption by soil particles and has a low mobility compared to other metals. Due to low mobility, it tends to accumulate on the soil. Leaching phenomena can occur with this metal when the soil retention capacity is exceeded (CCME, 1999b).

Although essential for some of the vital processes of humans, both in food and in enzymatic processes, large amounts of Cu ions become toxic. The effects of such toxicity may include anemia and disturbances in the central nervous system and cardiovascular system (CCME, 1999b).

### 2.2 Soil

The soil makes up an essential part of the landscape, preserves parts of the past and is itself a relevant part of the cultural heritage. In addition to the base provides about 90% of all human food, animal feed, fiber and fuel, it also contributes more than productive functions. The preservation of the soil is a respectable issue worldwide (Jones, 2010).

The importance for a wide variety of human activities makes them more vulnerable to the damages and the exhaustion caused by them. The soil having the provisions of buffer, filtration and absorption of the contaminants, means that the damages, are not often detectable until they are already in a fairly advanced state (European Environment Agency, 2000).

Soil is a complex system with ecological, economic, social and cultural roles that play a relevant role for human activity and for the survival of ecosystems and life in general (EP Solos e Sedimentos, 2012).

### 2.3 Electrokinetic Remediation

Electrokinetic remediation, electrokinetic soil processing, electromigration, electrokinetic descontamination, or electrocorrection, can be used in the extraction of heavy metals and some types of organic residues of soils and sediments (Acar *et. al* apud Guaracho, 1995).

The principle of this technique consists in the application of a direct current, of low intensity, in the order of mA/cm<sup>2</sup>, or of a potential through the ground between two or more electrodes. The contaminants are mobilized in the form of charged species, particles, and ions in the soil (Fig. 1) (Schultz, 2003; Guaracho, 2005).

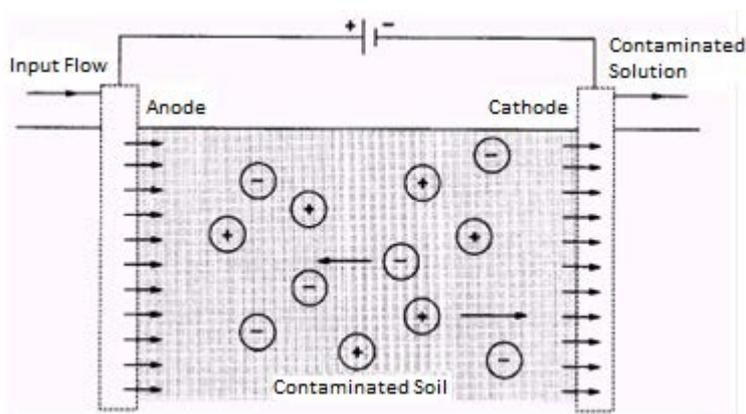


Figure 1: Systematic diagram of the Electrokinetic Remediation process (Schultz, 2003; Guaracho, 2005).

The electrochemical treatment becomes increasingly viable, since the most used treatments have a high cost, they can use a great quantity of chemical reagents and generate by-products, besides the storage of the sludge that is formed. In the electrokinetic remediation, the highest costs are in the generation of low intensity current to be used, and the greatest challenge is to increase the efficiency of the process, because, depending on the time of application of the electrokinetic remediation method, copper repair capacity is lost and the process is reduced to mass transport (Schultz, 2003).

Through remediation, contaminants can be isolated by reducing the permeability of the residue. However, select the most appropriate method of soil remediation depends on factors such as local characteristics, metal concentrations and types of these pollutants (Mulligan *et al.*, 2001).

Among the main advantages of electrokinetic treatment, are the acquisitions of products in their metallic form, the minimization of contaminated sludge, and their simple and compact application (Schultz, 2003).

## 2.4 Statistical Method

The statistical analysis of the results obtained in a given study is a tool of great importance in the validation of the data, as well as for the adequate extrapolation of the obtained results (Normando *et al.*, 2010).

A full factorial design should include all possible combinations between the levels of the experiment factors. The order of experiments is randomized because it is essential for adequate conclusion, where the experimenter can't be certain of all the variables that influence the experiment, so we make sure that a greater number of external variables to the experiment influence in an equal way. Even by identifying and controlling some of these variables, unplanned complications can occur. Randomization doesn't avoid complications, but it has some protection against the addition of the experiment (Box *et al.*, 1978; Neto *et al.*, 1996).

Analysis of variance (ANOVA) is a procedure used to compare three or more treatments. It is a collection of statistical models where the sample variance is divided into several components due to different variables. A variance analysis allows the comparison of several groups simultaneously, with the use of continuous variables (Box *et al.*, 1978; Neto *et al.*, 1996).

## 3. MATERIALS AND METHODS

### 3.1 Reactor Electrokinetic

The electrokinetic reactor was assembled based on the Yeung *et al.* (1997). It is constituted in a PVC body of 19 cm in length and 9 cm in diameter, where the contaminated soil was compacted, and, acrylic chambers with 2 cm of width at their ends were coupled, having two filters for passage of the electrolyte support. Inside the acrylic chambers, at the ends of the reactor, as a current feeder plate is the cathode and as an electrode the anode. The fixation of the base set with metal plates (anodic and cathodic compartments) and cylinder were carried out by means of 8 steel screws, being sealed later with silicone glue.

The electrodes used were a Ti/Ru-Ir plate (anode) produced by the DSA® process (dimensionally stable), known by the trade name Denora and a stainless steel plate 304 (cathode).

The concentration was obtained through the UV spectrophotometer Femto Cirrus 80.

For the assembly of the reactor used in the experiment the following steps were performed: a copper sulfate solution (CuSO<sub>4</sub>) of 1000 ppm molar concentration was prepared first, using a 1000 mL pycnometer and a 0.001g precision balance.

The soil was dried in a greenhouse with controlled temperature of approximately 35 °C. The soil was contaminated with a concentration of 1000 ppm of copper ions. This contaminated material remained in rest for 24 hours prior to remediation.

A support electrolyte, a 0.5 molar solution of sulfuric acid solution, was introduced to the soil with a peristaltic pump of the brand Milan, model BP200 and with adjustable flow control from 3 mL/min to 5 mL/min.

In performing the remediation, a source was used, which was coupled to the electrolytes and passed different potentials. Aliquot withdrawals were made at the start of the experiment and at the end of the experiments. Figure 2 shows the schematic of the experimental apparatus.

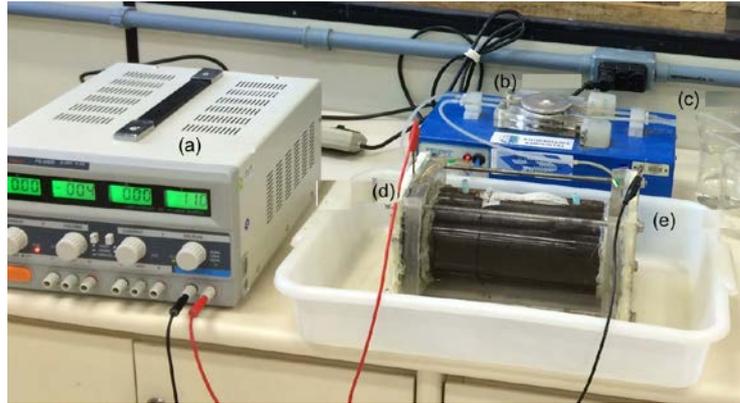


Figure 2: Experimental apparatus: (a) Power Supply, (b) Peristaltic doser pump, (c) supporting electrolyte, (d) anode, (e) cathode

### 3.2 Statistical Techniques

The techniques used was factorial statistical design - especially the full factorial design with two levels (-1 and 1) and two variables ( $2^2$ ), with three repetitions of the central point (0). The coded values are shown in Table 1 and the experiment matrix in Table 2.

Factorial design has been widely applied in basic and technological research and is classified as a simultaneous type method, where the variables of interest that actually have significant influences on the response are evaluated at the same time. One of the favorable aspects of this type of design is the realization of few experiments (Kaminari *et al.*, 2005, 2007).

For this work, 2 variables (factors) were selected to evaluate the influence of copper ion removal efficiency. These factors were the potential and the time of remediation.

Table 1. Coded variables.

Variables	-1	0	1
Potential (V)	5	7	11
Time (h)	2	3	4

The values presented in Table 2 were chosen based on results of Guaracho, 2005 and Iryoda, 2008.

Table 2. Matrix of experiments.

Experiment	Time (t)	Potential (E)
1	-1	-1
2	-1	1
3	1	-1
4	1	1
5	0	0
6	0	0
7	0	0

#### 4. RESULTS

Removal efficiency (R) was calculated based on the follow equation.

$$R = \frac{(C_i - C_f)100}{C_i} \quad (1)$$

where:

R = Removal efficiency (%);

C<sub>i</sub> = Initial Concentration (ppm);

C<sub>f</sub> = Final Concentration (ppm).

The results obtained according to the planning matrix are shown in Table 3.

Table 3. Results for the removal of copper.

Experiment	Potential (E)	Time (t)	R (%)
1	-1	-1	15,00
2	1	-1	53,10
3	-1	1	57,68
4	1	1	66,86
5	0	0	25,58
6	0	0	23,29
7	0	0	25,58

Using the least squares method and with the statistical software, the coefficients ( $\beta$ ) for Equation 2 were estimated.

$$R = \beta_0 + \beta_1 E + \beta_2 t + \beta_{12} Et \quad (2)$$

The coefficients obtained, as well as the respective standard errors, Student's t-tests and significance levels (p) are in Table 4.

Table 4. Estimated coefficients for Equation 2.

Coefficient	Estimated Value	Standard deviation	t of Student	p
$\beta_0$	38,15457	0,500390	76,2496	0,000172
$\beta_1$	11,81730	0,661954	17,8521	0,003123
$\beta_2$	14,11037	0,661954	21,3162	0,002194
$\beta_{12}$	-7,23114	0,661954	-10,9239	0,008276

Adopting a level of 10% of significance, it can be observed that the coefficients presented levels of significance lower than 10%. This means that these coefficients present statistically significant values, will only be considered statically significant when the level of significance calculated is smaller than the one adopted. All coefficients that presented a level of significance lower than 10% should be maintained in the adjustment. What can be visualized through the Pareto Diagram (Fig.3).

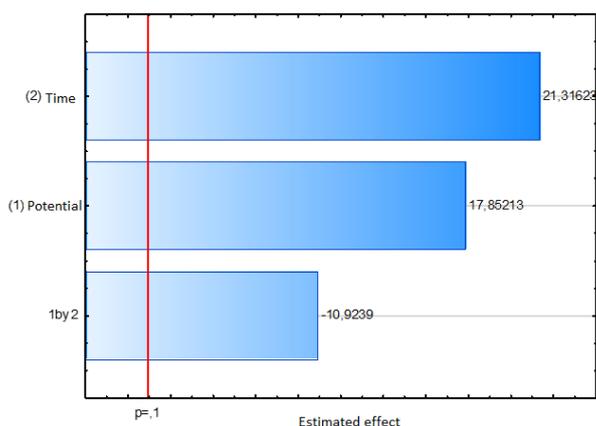


Figure 3: Pareto diagram.

Thus, the equation to be adjusted presents the form of equation 3.

$$R = 38,16 + 11,82E + 14,11t - 7,23Et \quad (3)$$

The p-value in the Analysis of Variance (ANOVA) was less than 10% of the computed F-values ( $F_c$ ) obtained for R was smaller than the F-value in the statistical table ( $F_t$ ) (Tab. 5), indicating that the model was not significant at a high confidence level (90%).

Table 5. Analysis of the variance (ANOVA) for Equation 3.

Source	Sum os Square	Degree os Freedom	Mean Square	$F_c$
Regression	1564,163	3	521,388	1,668
Residue	937,629	3	312,543	
Lack of adjustment	934,124	1	934,124	533,024
Pure error	3,505	2	1,7525	
TOTAL	2501,792	6		

$$R^2 = 62.52\%;$$

$$F_t = 49.5$$

Through the F test of the lack of adjustment, one can test the following hypotheses:

$H_0$ : the linear model is suitable (there is no lack of adjustment)

$H_1$ : the linear model is not suitable (there is no adjustment)

As the value of F calculated resulted in a value greater than the table F, we reject the hypothesis  $H_0$  and conclude that there is no fit. This can be observed in Fig. 4, through the dispersion of the obtained points. Therefore, it can be concluded that the linear model does not seem to be adequate for this process.

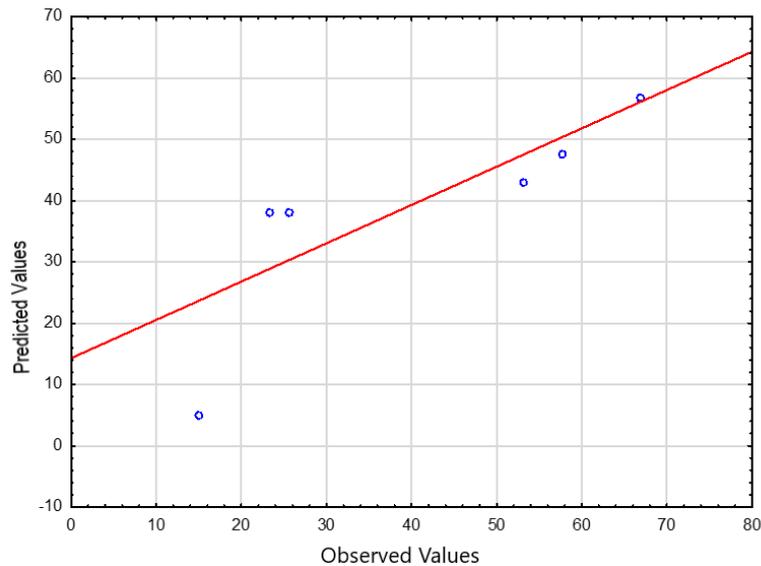


Figure 4: Predicted values x observed values.

The determination coefficient ( $R^2$ ) was 62.52% indicating that the model could not represent the experimental data. Figure 5 provides a good visualization of this adjustment, in which it is verified that the values for the experimental copper removal are far from the values found by the adjustment Equation 3. This means that approximately 62% of the total variation around the mean is explained by the regression, leaving 38% with the residuals.

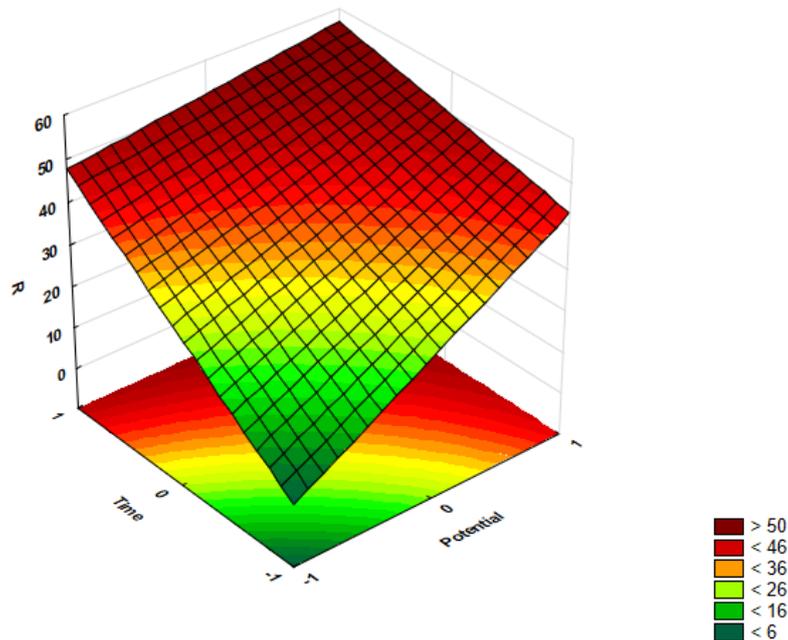


Figure 5: Surface of the experimental data.

## 5. DISCUSSION

There were several variables that were not possible to be measured in the soil, such as the amount of organic matter, the ions present in the soil and etc because no more detailed analysis was performed, since the proposal of this research did not cover such details.

The peristaltic pump used was not in perfect condition, besides being used by other students and collaborators during the period of the research, causing in the alteration of its calibration and in its state, making difficult the development of the work, taking time higher for project execution. In addition to the reactor leakage every time it was

assembled, because of the impossibility of sealing areas in contact with the solutions, requiring more time for silicone bonding and greater care. The change in the reactor design to address these problems is being studied in the future.

There was a change from the previous research, while taking samples, there was no difficulty as previously reported. The execution time of the electrokinetic races was increased as proposed, guaranteeing improvement in the withdrawal of the initial and final aliquots.

Again, it was possible to observe that the electrokinetic remediation technique is favorable and can be used for the remediation of soil contaminated by heavy metals, such as copper.

## 6. CONCLUSION

In the execution and development of the project some difficulties were encountered, such as problems of reactor leakage and assembly. Also, because the laboratory was not used exclusively for this research, but rather shared with several students and collaborators, there was sharing in the use of equipment and utensils, which could lead to alteration of the calibration and perfect functioning of the same, affecting the quality of research execution and Acting as factors of influence on the results obtained.

Even with such problems, it was concluded that the use of the electrokinetic remediation technique in soils with organic traces contaminated with the heavy metal copper can be used, since its concentration was reduced after the application of the same and presented regular results until the time of the research.

The mathematical model that represents this process was obtained through adjustments in the design and the remediation time as proposed in the planning. However, this linear model could not represent the experimental data, an adjustment with a higher-order model must be performed.

Changes in the project are studied to remedy such difficulties and the adjustment in the proposed model for the satisfactory representation of its experimental data.

## 7. ACKNOWLEDGEMENTS



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