# Central Composite experimental design applied to removal of lead and nickel from sand

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## ABSTRACT

The aim of this study was to apply Central Composite experimental design in the removal of lead and nickel ions from sand by electrokinetic remediation. Sand was used for an initial study since it is inert, thus making it possible to analyze the parameters influencing the process. Central Composite Design was used to create an experimental program to provide data to model the effects of various factors on removal efficiency. The variables chosen were ion concentration ($C$), applied potential ($E$) and time ($t$). The mathematical relationship between removal efficiency and three significant independent variables can be approximated by a second-order quadratic model. Response Surface Methodology (RSM) was used to describe the individual and interactive effects of three variables at five levels, combined according to a Central Composite Design. This study has shown that Central Composite Design can be applied to the removal of lead and nickel ions from sand, and it is an economical way of obtaining the maximum amount of information with the fewest experiments.

## 1. Introduction

In many areas of the world, the ground has been seriously contaminated due to inadequate disposal practices and polluting industrial activities [1]. The polluted soil becomes a threat to the environment because it contains toxic substances, such as heavy metals. It is important to take into consideration that, in addition to the damage inflicted to the environment; metals also offer serious risks to human health. These metal contaminants include lead, nickel, chromium, arsenic, zinc, cadmium, copper, and many others. Among the technological options available to mitigate the problem, electrokinetic remediation has been considered a good choice [2–6].

Electrokinetic remediation has been known to be an in situ method. This method can be used to remove contaminants, such as heavy metals, by inserting electrodes into the soil and applying a low level of DC power between the electrodes [5,7]. Electrokinetic remediation is based on three principal mechanisms: electromigration, electroosmosis and electrophoresis [2].

In the electrokinetic process, the pH of the aqueous solution in the anodic reservoir decreased due to the electrolysis of water. The solution becomes acid at the anode because hydrogen ions are produced and oxygen gas is released, while the pH could drop to values as low as 2. At the cathode, the solution becomes basic, hydroxide ions are generated, and hydrogen gas is released; pH may increase to values as high as 12. Both cases depend on the total current applied [8,9]. The acid front migrates from the anode to the cathode [10,11]. The acid front movement, by a migration process, results in the desorption of contaminants from the soil.

The objective of the present work was to study the removal of lead and nickel ions from sand by electrokinetic remediation by using Central Composite Design. The design experiments were already used to recover metals from industrial effluents [12–14]. Basically the optimization process involves three major variations: performing the statistically designed experiments, estimating the coefficient in a mathematical model, and predicting the response and checking the adequacy of the model [15]. Response Surface Methodology (RSM) was used to describe the individual and interactive effects of three variables at five levels on removal efficiency ($R$), combined according to a Central Composite Design.

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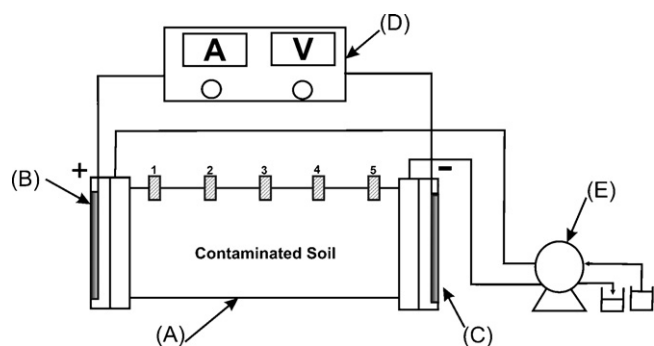[3] Tel.: +55 41 33613197; fax: +55 41 33613197.

**Fig. 1.** Schematic representation of the experimental units: (A) electrochemical reactor, (B) anodic compartment, (C) cathodic compartment, (D) power supply, and (E) peristaltic doser pump.

**Table 1**
Coded level values for lead.

| Variable | −1.68 | −1 | 0 | 1 | 1.68 |
|---|---|---|---|---|---|
| $C_{Pb}$ (ppm) | 2240 | 2750 | 3500 | 4250 | 4800 |
| $E$ (V/cm) | 0.39 | 0.56 | 0.83 | 1.11 | 1.28 |
| $t$ (h) | 16 | 24 | 36 | 48 | 60 |

**Table 2**
Coded level values for nickel.

| Variable | −1.68 | −1 | 0 | 1 | 1.68 |
|---|---|---|---|---|---|
| $C_{Ni}$ (ppm) | 530 | 800 | 1200 | 1600 | 1900 |
| $E$ (V/cm) | 0.39 | 0.56 | 0.83 | 1.11 | 1.28 |
| $t$ (h) | 16 | 24 | 36 | 48 | 60 |

## 2. Materials and methods

### 2.1. Materials

The arrangement of equipment used in the experiments is schematically shown in Fig. 1 and the actual experiment design is listed in Table 3. The sand is placed in a PVC tube about 18 cm long and 9 cm in diameter. The porosity of the bed was approximately 0.4 (fixed bed). The sphericity of particles of sand was approximately 0.9.

The reactor consisted of five holes so that samples of electrolyte could be drawn during the experiment. Samples (approxi-

mately 1 mL) were drawn to measure the concentration and the pH.

The reactor consists of two electrode compartments and two electrode reservoirs. At one of its ends are located the cathode, a lead-plate, and as anode a 304 stainless steel plate.

Washed sand was used with an average particle size of 0.25 mm; it was left to rest for 24 h in a 10% sulfuric acid solution to remove organics. Then, it was washed again with deionized water and dried under vacuum. The soils were prepared with sand mixed with a lead nitrate solution to simulate contamination with lead ions, and with nickel sulfate to simulate contamination with nickel ions, at the concentrations determined for each experiment. A peristaltic pump was used to control deionized water circulation with an outflow of 20 mL h$^{-1}$ to assist in electroosmotic flow. A spectrophotometer (model FEMTO 600 PLUS) was used to analyze lead concentration during each experiment. The sample to be analyzed was diluted until a band could be detected by the equipment. A Spectr AA-200 spectrophotometer (Varian) was used to determine the concentration of nickel ions.

### 2.2. Methods

#### 2.2.1. Experimental design

Prior knowledge of the procedure is generally required to produce a statistical model [16–18]. The three steps used in the experimental design included statistical design of experiments, estimation of coefficients through a mathematical model with prediction of response, and analysis of the model's applicability. The experiment was conducted with one response variable in a Central Composite Design (CCD). Removal efficiency (R) was selected as dependent variable in the experiment. Three independent parameters were chosen as variables: ion concentration; applied potential; and time. The pH was not chosen as an experimental variable due to the difficulty in maintaining this value constant. This may affect the final result, because the pH is a variable that contribute in movement of the contaminant in the soil. For this reason the behavior of pH was studied separately.

The low, middle and high levels of each variable were designated as −1.68, 0 and +1.68, respectively, and the corresponding actual values for each variable are listed in Tables 1 and 2.

The correlation between the independent variables and the response was calculated by a second-order polynomial equation

**Table 3**
The Central Composite Design for the three independent variables.

| Trial no. | Ion concentrations | Potential | Time | Removal efficiency ($R_{Pb}$) (%) | Removal efficiency ($R_{Ni}$) (%) |
|---|---|---|---|---|---|
| 1 | −1 | −1 | −1 | 98.55 | 30.50 |
| 2 | −1 | −1 | 1 | 99.56 | 67.00 |
| 3 | −1 | 1 | −1 | 98.92 | 37.00 |
| 4 | −1 | 1 | 1 | 96.70 | 71.50 |
| 5 | 1 | −1 | −1 | 92.42 | 32.79 |
| 6 | 1 | −1 | 1 | 99.04 | 55.38 |
| 7 | 1 | 1 | −1 | 98.84 | 38.00 |
| 8 | 1 | 1 | 1 | 98.97 | 76.24 |
| 9 | −1.68 | 0 | 0 | 97.36 | 54.96 |
| 10 | 1.68 | 0 | 0 | 98.85 | 56.24 |
| 11 | 0 | −1.68 | 0 | 98.90 | 66.53 |
| 12 | 0 | 1.68 | 0 | 95.40 | 76.80 |
| 13 | 0 | 0 | −1.68 | 96.52 | 21.60 |
| 14 | 0 | 0 | 1.68 | 99.27 | 77.93 |
| 15 | 0 | 0 | 0 | 98.31 | 47.67 |
| 16 | 0 | 0 | 0 | 98.39 | 48.25 |
| 17 | 0 | 0 | 0 | 98.67 | 43.50 |
| 18 | 0 | 0 | 0 | 98.05 | 46.31 |
| 19 | 0 | 0 | 0 | 98.82 | 47.86 |
| 20 | 0 | 0 | 0 | 97.75 | 49.25 |
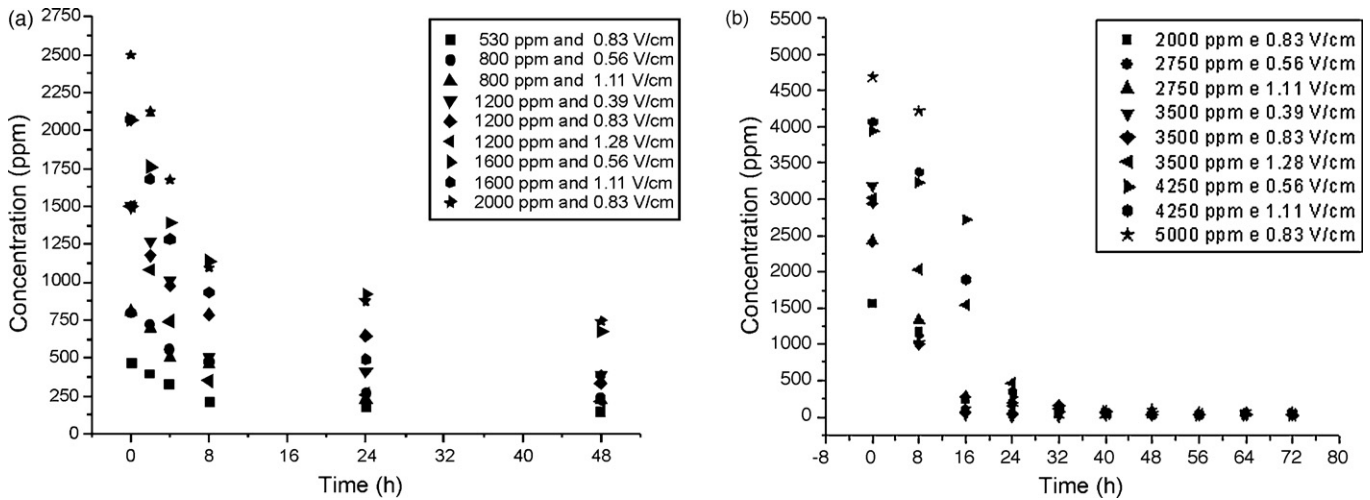
**Fig. 2.** (a) Ni concentration versus time curves. (b) Pb concentration versus time curves.

(Eq. (1)), using the least squares method, as shown below:

$$Y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_1^2 + \sum_{i=1}^{3} \sum_{\substack{j=1 \\ i<j}}^{3} b_{ij} X_i X_j + \xi \quad i \neq j \qquad (1)$$

where $Y$ is the predicted removal efficiency ($R$) response; $X_i$ represents the variables in the coded forms of the input variables; $b_0$ is the model's intercept (constant); $b_{ii}$ denotes the regression quadratic coefficients, $b_{ij}$ is a cross-product coefficient and $\xi$ is the stochastic term, which is supposed to have Gaussian distribution $[\xi \sim N(0, \sigma^2)]$ and is estimated by the difference between the $Y$ value predicted by the model and the observed $\hat{Y}$ value.

Twenty experiments are needed to estimate the coefficients for removal efficiency using multiple linear regression analysis. All experiments were performed in duplicate.

### 2.2.2. Response Surface Methodology (RSM)

RSM is a combination of a mathematical and a statistical technique used for developing, improving, and optimizing the processes, and is used to evaluate the relative significance of several factors affecting the system even in the presence of complex interactions. RSM usually contains three steps: (1) design and experiments; (2) response surface modeling through regression; (3) optimization. The main objective of RSM is to determine the optimal operational conditions of the process or to determine a region that meets the operating specifications [19].

### 2.2.3. Data analysis

The results of the final concentration (electrolyte samples drawn of cathode compartment) obtained in the experimental design were used to calculate the removal efficiency ($R$) based on the following equation:

$$R = \frac{(C_i - C_f)100}{C_i} \qquad (2)$$

where $R$ is the removal efficiency (%); $C_i$ is the initial concentration (ppm); $C_f$ is the final concentration (ppm).

## 3. Results and discussion

The model applied to the experiments resulted in the following equations:

$$R_{Pb} = 97.96 + 1.49t + 2.21C_{Pb}E + 1.99C_{Pb}t - 2.43Et \qquad (3)$$

$$R_{Ni} = 47.61 + 7.96E + 33.18t + 13.63E^2 \qquad (4)$$

Eq. (3) shows the great difficulty in the analysis of the direct influence of the variables on the efficiency of removal of Pb because some terms of the equation are inter-related.

Eq. (4) shows that the $C_{Ni}$ was not significant. This occurred because the process of removal of nickel ions is very effective due to the duration (approximately 8 h) of the remediation process for all the concentrations used in this paper, as shown in Fig. 2. The $C_{Ni}$ did not change significantly with time after 8 h.

The $p$-value in the Analysis of Variance (ANOVA) was less than 5% of the computed $F$-values obtained for $R_{Pb}$, and $R_{Ni}$ was greater than the $F$-value in the statistical table, indicating that both models were significant at a high confidence level (95%). The $p$-value probability was also relatively low ($p < 0.05$), indicating the model's significance. The $R$-squared coefficient of variation for $R_{Pb}$ was $R^2 = 0.70$, while for $R_{Ni}$ it was $R^2 = 0.92$, therefore indicating a moderate degree of correlation between the response and the independent variables in $R_{Pb}$ (Fig. 3), and a high degree of fitting for $R_{Ni}$ (Fig. 4). Figs. 3 and 4 demonstrate this correlation between predicted and experimental values.
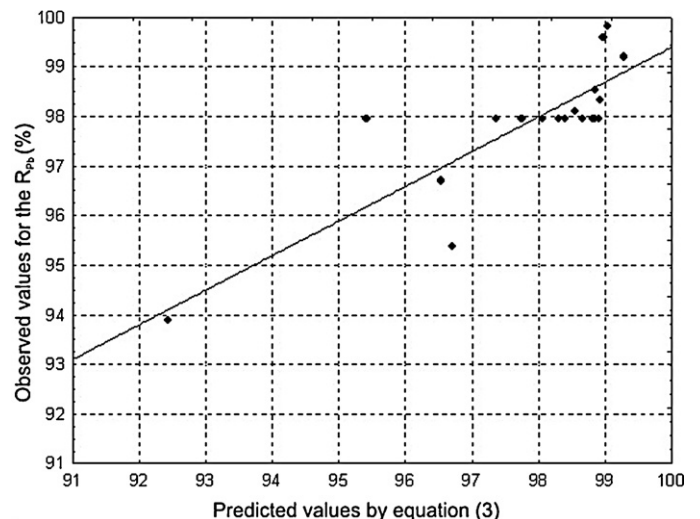


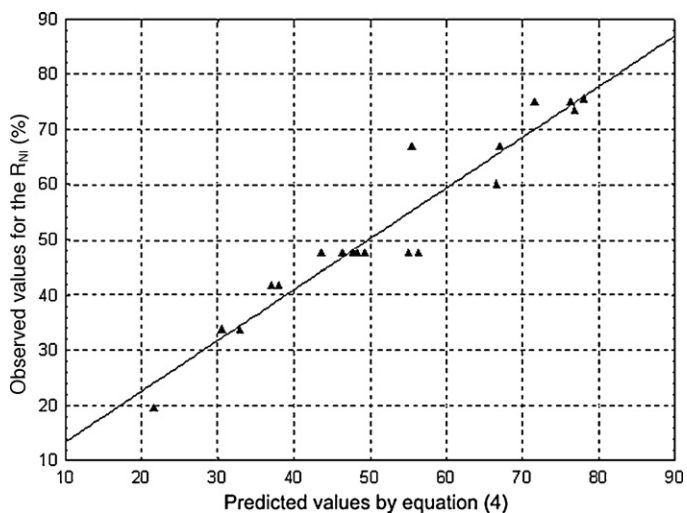**Fig. 3.** Experimental values and values predicted by Eq. (3).

**Fig. 4.** Experimental values and values predicted by Eq. (4).

### 3.1. Effect of pH

The values measured at the pH measuring point during the experiment are show in Fig. 5. It is important to control the pH in the sand and in the conductive solution during removal of toxic metals since it affects the solubility of heavy metals. This was done by adjusting the dimensions of the soil and the concentration of the solution. It is observed that the pH value rises and it keeps constant this means that the Ni and Pb are stable thus avoiding the occurrence of parallel reactions. According to Li et al. [20], this could be an indication that the position of the pH jump moves towards the anode during the experiments. At the beginning of each experiment, hydroxides are consumed by forming precipitates with heavy metal. Thus the advance of the base front is reduced, and the pH jump, established as the acid front and the base front meet each other, is closer to the cathode.
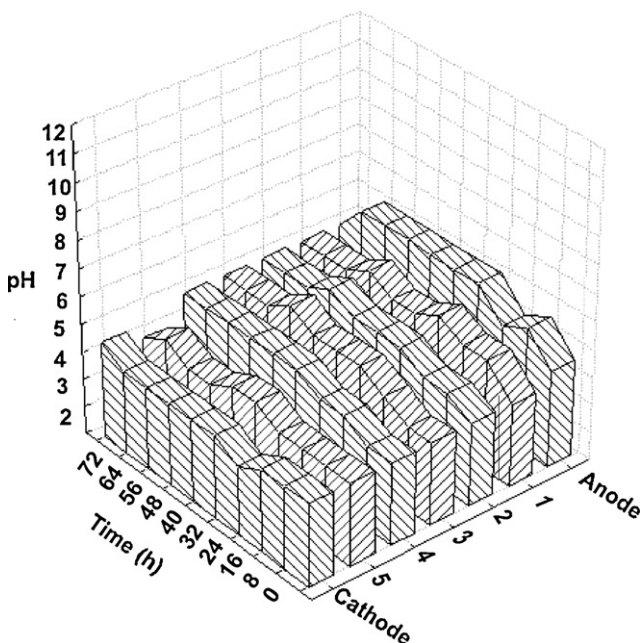


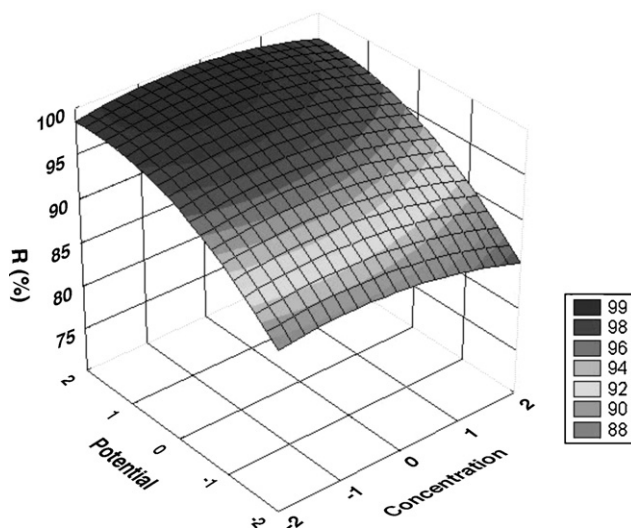**Fig. 5.** pH measured in the experiments for Pb removal.



**Fig. 6.** Removal efficiency for lead—$E = -1.68$.

### 3.2. Response surface estimation for maximum removal of lead

The Response Surface Methodology (RSM) is a statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations simultaneously [21]. RSM is used to determine the optimal response for lead- and nickel-removing processes ($R_{Pb}$ and $R_{Ni}$). Response surfaces can be visualized as three-dimensional plots that display the response as a function of two factors while keeping a third factor constant.

The results presented in Fig. 6 show $R_{Pb}$ as a function of concentration and time for the lowest potential value. The removal efficiency obtained is practically constant, at the highest time level, having a possible optimal point when the concentration is at an intermediate level. This result probably occurs because the reactions that were taking place under that condition did not reach saturation. The same behavior is observed in Fig. 7 ($R_{Pb}$ as a function of concentration and potential for the lowest time value).

The results presented in Fig. 8 show $R_{Pb}$ as a function of time and potential for the highest concentration value. Removal efficiency is practically constant at the highest time level, having a possible optimal point when the concentration is at an intermediate level.
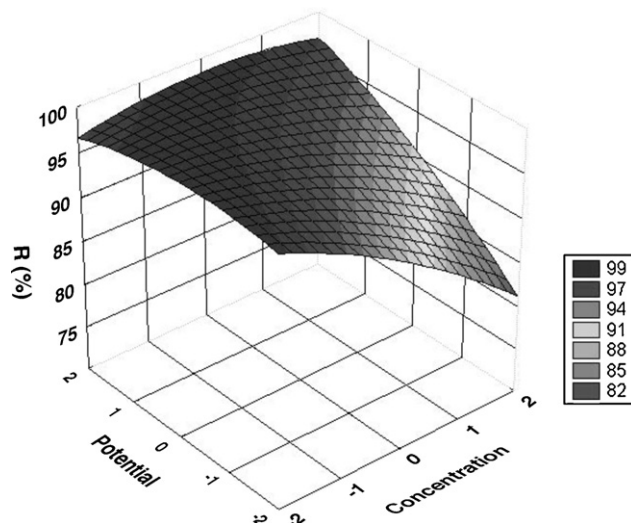


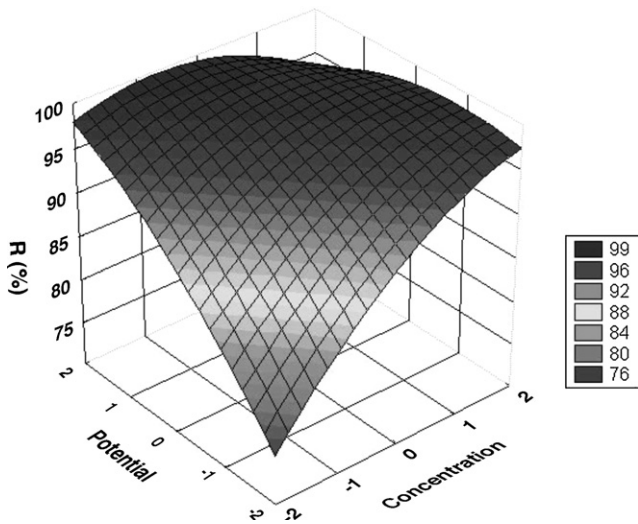**Fig. 7.** Removal efficiency for lead—$t = -1.68$.

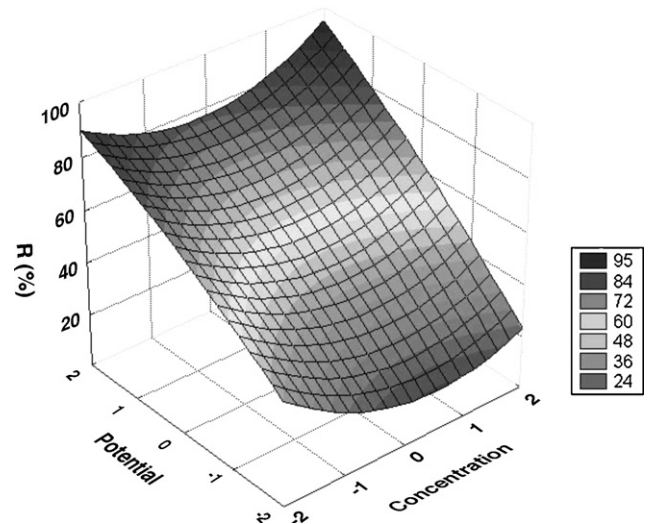**Fig. 8.** Removal efficiency for lead—$C$ = 1.68.
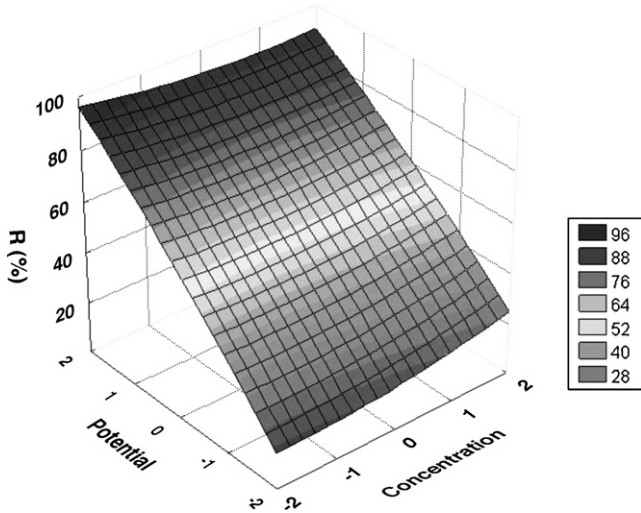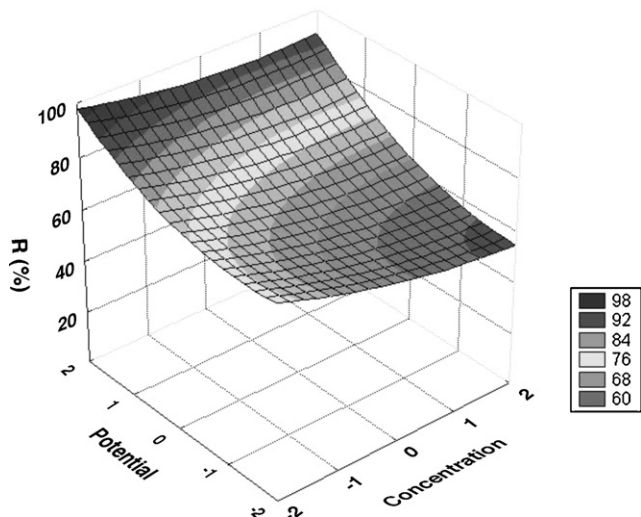


**Fig. 11.** Removal efficiency for nickel—$C$ = −1.68.

### 3.3. Response surface estimation for maximum removal of nickel

The results presented in Fig. 9 show $R_{Ni}$ as a function of concentration and time for the lowest potential value. Removal efficiency is practically constant at the longest times. The same behavior is displayed in Fig. 10 ($R_{Ni}$ as a function of concentration and potential for the longest time value).

The results presented in Fig. 11 show $R_{Ni}$ as a function of time and potential for the lowest concentration value. The highest $R_{Ni}$ is obtained at the highest potential and time.

### 4. Conclusions

The electrokinetic remediation process applied in this study demonstrated good performance in removing lead and nickel from simulated contaminated soils. The CCD, regression analysis, and response surface method were effective in identifying the optimal conditions for maximum removal efficiency for the analyzed metals. The obtained coefficient of variation $R$-squared for $R_{Pb}$ was $R^2$ = 0.70, while for $R_{Ni}$ it was $R^2$ = 0.92, indicating a moderate degree of correlation between the response and the independent variables in $R_{Pb}$ and a high degree of fitting in $R_{Ni}$.

### Acknowledgement

**Fig. 9.** Removal efficiency for nickel—$E$ = −1.68.



**Fig. 10.** Removal efficiency for nickel—$t$ = 1.68.

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