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Optimization by Experimental Design of Copper Adsorption on Natural Clay

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Abstract: *Natural clay from the Felix geothermal area was used to assess the possible removal of heavy metals from wastewaters. Several experimental conditions, including pH, contact time and temperature, depending on the initial concentration were studied. The design of experiments method was applied in order to get the highest percentage of adsorbed copper. The factorial experiments were performed according to the matrix program developed by Design Expert. The obtained mathematical model assessed the optimal values of the factors that influence the adsorption of copper, taking into account maximum productivity, as well as economic criteria. The estimated values were in accordance with the experimental research.*

Keywords*:adsorption, Felix natural clay, heavy metal, experimental design*

1. Introduction

A thermomineral water deposit which has been used for therapy is located in the northwest of Romania [1]. The geothermal gradient in this region is higher than in other areas with similar structure, allowing infiltrated water to emerge as thermal water [2-4]. There are two well-known resorts in this area, 1 Mai and Felix, which contain plenty of indoor and outdoor treatment facilities, the waters of these resorts being known since Roman Empire. There is also natural clay used to treat several diseases. Following medical research and experiments, chronic inflammatory rheumatism, degenerative rheumatic diseases, and associated diseases of these main profiles are treated in these resorts [5]. In addition, there are some natural springs useful in the treatment of internal diseases.

The Pannonian geothermal aquifer is multi-layered, confined and is located in the sandstones from the basement of the upper Pannonia, on an area of 2500 km^2 along the western border of Romania. The Oradea aquifer and the Felix-1 Mai aquifer are hydrodynamically connected and are part of the active natural water circuit. They are mainly located in limestones and dolomites [6].

Natural products as unique chemicals or as plants extracts, oils, mineral waters, clays, etc. have been used since ancient times to treat different diseases. Natural products have been the most successful source of potential drugs. In addition, many of these natural products have the potential to become remedies with lower side effects [7-10]. Therapeutic mineral waters as drinking waters or bath treatments are successfully used in gynecological, respiratory or digestive disorders, allergies, skin, rheumatologic or chronic inflammatory diseases. Mineral waters enhance the quality of life and are frequently used in preventive medicine and wellness. Balneotherapy, through the use of mineral waters or clays, can be proposed as an alternative, safe and natural treatment for various illnesses [11, 12].

In the last decades, heavy metals have become a public health concern. Industrial effluents loaded with heavy metals as a result of the automotive industry, corrosion protection such as copper coating, can have a negative impact on the environment. Due to their tendency to accumulate in organisms and cause diseases, their presence in the environment is not desirable. Different chemical treatments have been tried to avoid water pollution, such as chemical precipitation [13], chemical reduction [14], extraction [15], adsorption [16, 17].

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Among the various methods of removing heavy metal ions from waters are adsorbent technologies. A known adsorbent is activated carbon. It has long been used to treat wastewater due to its specific surface. Natural clays have recently been investigated as possible adsorbents. They are abundant, therefore their cost is low and they have no toxicity to the environment. Within the clay minerals with a proven efficiency in removing pollutants, they include: kaolinite [18], smectite minerals [19, 20], sepiolite [21], perlite [22].

The purpose of this paper is to investigate whether the natural clay mineral, taken from the area of geothermal resorts, could be used as adsorbent for heavy metals. In this respect, the adsorption capacity of the mineral from the Felix-1 Mai geothermal aquifer in the removal of heavy metals from aqueous solutions was assessed. Another aim of this paper is to optimize the parameters of the adsorption process of copper from wastewater, using the factorial experiment method.

The analytical methods involve detailed knowledge of the system to be modelled, so that a considerable number of time-consuming tests are required for data processing, and the costs of experiments can also be high [23]. These considerations highlight the high interest in the programming of experiments in order to optimize the costs regarding the experimental data obtained.

2. Experimental part

2.1. Materials and methods

Prior to the realization of the factorial experiments, preliminary experiments were performed, in which the influence factors were highlighted, as well as the tendency of increasing the adsorbed copper concentration by changing these three factors.

The natural clay mineral from Felix resort was first cleaned for experiments by repeated dispersion, sedimentation and siphoning. The fine solid fraction was dried at 70°C, ground and sieved to pass 140 mesh [24]. The solid sample from natural clay was performed using a Philips PW1710 diffractometer with filtered Cu k-alpha radiation.

Pin AAcle 900T Atomic Absorption Spectrometer, Perkin Elmer manufacturer, was used for copper analysis from the waters. The standard solutions were prepared starting with the standard copper solution, $Cu(NO_3)_2$ in HNO_3 0.5 mol/L, 1000mg/L Cu CertiPUR®, Merck Millipore manufacturer. Solutions with initial copper concentrations ranging from 25 to 300 mg Cu^{2+}/L were prepared, starting with the standard 1000 mg/L solution. Successive dilutions were performed according to the recommended domain of absorbance-concentration linearity for copper.

A laboratory stirrer provided with a heating system was used to supply the conditions for the copper ion solutions to be in contact with the adsorbent in order to carry out the adsorption process. After the adsorption process has reached equilibrium, the mixture was centrifuged and the supernatant was quantitatively analyzed. The copper concentration retained in the adsorbent was calculated. The copper concentrations in the water samples after adsorption were determined by atomic absorption spectrometry at 324.75 nm. Experiments were carried out to establish the effect of adsorption on the removal of copper ions. The effects of the initial concentration of copper in water on the adsorption process, the pH, the water temperature and the contact time with the solid mineral as adsorbent were studied.

2.2. Experimental design

Table 1 presents the factors and their values used within the factorial experiments. The three factors represent independent variables with different levels of variation. As can be seen from Table 1, the factor: "Contact time" (X_1) was tested at four levels, the factor "Temperature" (X_2) at three levels, and the factor "pH" (X_3) at nine levels.

To determine the optimum adsorption conditions, a second-order factorial program was used since the linear regression equation becomes inadequate (the curvature of the surface is accentuated, and the interactions are significant). The method of processing the data is similar to the one from the factor programs of the first order, but there are changes regarding the orthogonality of the program matrix.

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Table 1. The influence factors of the adsorption process.

Factor	Code	Values								
Contact time [min]	X_1	30		60		90			120	
Temperature [°C]	X_2	30			40				45	
pH	X_3	4	4.5	5	6	6.5	7	7.5	8	8.5

The processing of the experimental data involves the following stages:

- Determining the regression coefficients
- Analysis of the significance threshold of the regression coefficients
- Analysis of the model's suitability

The general shape of the model is:

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j \cdot X_j + \sum_{\substack{j,u=1 \\ u \neq 1}}^{k} \beta_{ju} \cdot X_j \cdot X_u + \sum_{j=1}^{k} \beta_{jj} \cdot X_j^2 \qquad (1)$$

where:

Y – objective function (response);

X_j, X_u – influencing factors;

β_0, β_j, β_{jj}, β_{ju} - regression coefficients.

The experimental determinations aim to obtain the necessary data for the calculation of the coefficients of the adopted model, the number of coefficients determining the number of experiments. In order to reduce the effort for carrying out these experiments, a factorial program [23] was used.

3. Results and discussions

The X ray diffraction analysis of the natural clay mineral indicated that the crystalline phase consists of dolomite (Figure 1).

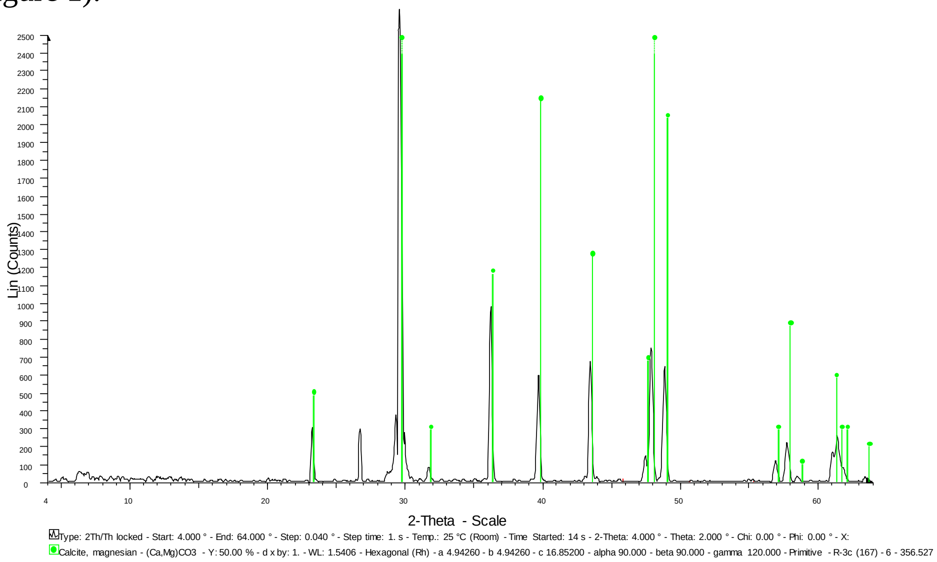


Figure 1. The XRD diagram of the solid sample.

This natural mineral was tried as adsorbent in the experiments. The natural clay mineral (0.1 g) was stirred with 100 mL of water sample with initial copper concentration ranging from 25 to 300 mg/L, at temperature of 30°C for 30 min. Based on the calibration curve (Figure 2) were obtained the copper ion concentrations in the waters before and after the adsorption process. The copper ion concentrations retained on the adsorbent were obtained knowing the initial copper concentration and the copper concentration in the aqueous solution after adsorption process. Then the percentage of copper ion removal was calculated. The results are illustrated in Figure 3.

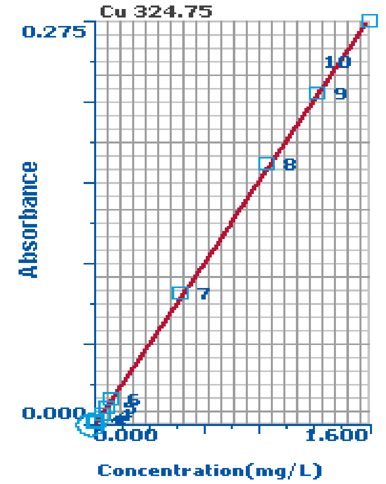


Figure 2. Calibration curve for AAS analysis of copper.

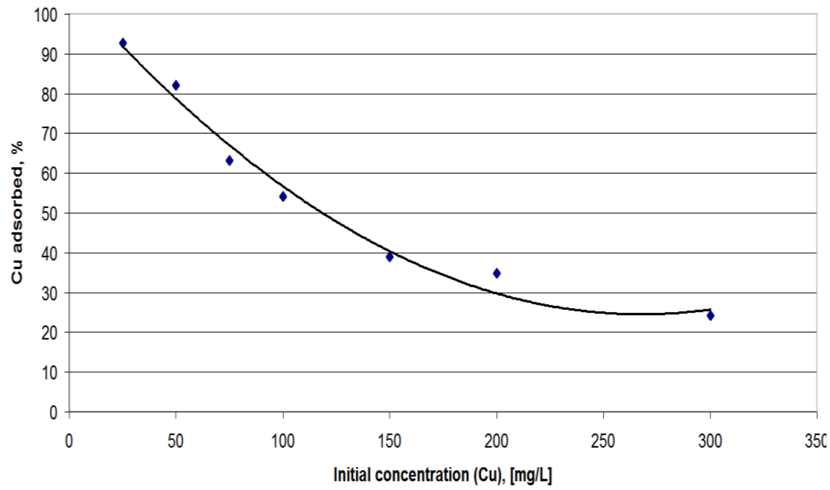


Figure 3. Influence of initial copper concentration on the adsorption process.

As can be seen in the Figure 3, a high percentage of copper is adsorbed from the solution with the concentration of 25 mg Cu^{2+}/L. Due to the limited adsorption capacity of the adsorbent, the percentage of adsorbed copper decreased at higher concentrations. For this reason, the other experiments were conducted for the lowest initial copper concentration. The program matrix and the results obtained in the experiments are presented in Table 2.

Table 2. The matrix of the factorial experiments.

Run	Contact time [min]	Temperature [ºC]	pH	Cu adsorbed [%]
1	60	45	5.0	75.6
2	60	30	7.0	87.8
3	120	45	7.5	93.1
4	120	30	4.0	68.5
5	30	40	5.0	75.4
6	30	30	8.5	81.1
7	30	40	8.5	81.2
8	120	30	8.5	83.5
9	60	40	4.0	68.8
10	30	30	4.0	68.4
11	120	40	6.5	90.3
12	60	30	5.0	77.7
13	90	45	8.5	85.0
14	30	45	6.0	79.3
15	120	45	4.0	71.5

In order to study the significance of the parameters: contact time, temperature, and pH on the concentration of adsorbed copper, it was performed the analysis of experimental data.

The data resulting from the experiments were processed by the Design Expert application (trial version). Typically, ANOVA (analysis of variance) is used to test the significance of the regression model and the importance of the model coefficients. ANOVA is a statistical descriptor of the scattering of values of a measurable parameter, that allows highlighting the most important influence factors and also focusses on their quantitative influence.

In Table 3 are presented the results of the analysis of Variance test (ANOVA).

Table 3. Analysis of variance of the regression model ANOVA.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	p value	Comments
Model	0	9	0.000001695	148.45	< 0.0001	significant
X_1	0.000001103	1	0.000001103	96.63	0.0002	
X_2	5.928E-10	1	5.928E-10	0.0519	0.8288	
X_3	0.000009827	1	0.000009827	860.67	< 0.0001	
$X_1 \cdot X_2$	5.693E-07	1	5.693E-07	49.86	0.0009	
$X_1 \cdot X_3$	1.396E-08	1	1.396E-08	1.22	0.3191	
$X_2 \cdot X_4$	2.642E-08	1	2.642E-08	2.31	0.1887	
X_1^2	5.777E-09	1	5.777E-09	0.5059	0.5087	
X_2^2	7.249E-08	1	7.249E-08	6.35	0.0532	
X_3^2	0.000003728	1	0.000003728	326.49	< 0.0001	
Residual	5.709E-08	5	1.142E-08			

The Table 3 provides the test value "F" for the studied model (F value = 148.45). The "F" test represents the ratio between "Mean Square" and "Residual". Value for F_{critic} = 4.77246561. The calculated F-value of the model is 148.45. This means that the model is significant. This report is used to calculate the significance test value "p". Values lower than the significance threshold "p" (the default value accepted for the significance threshold $\alpha = 0.05$) indicate that there is a significant effect.

Following the calculations, the statistical values regarding the suitability of the model are obtained (Table 4).

Table 4. Adecvance of the model

R^2	0.9963
Adjusted R^2	0.9896
Predicted R^2	0.9702
Adeq Precision	35.9494

Thus, the coefficient of determination R^2 has a high value ($R^2 = 0.9963$), which indicates a good correlation between the experimental model and the regression model, adjusted R^2 which represents a measure of the amount of variation around the mean explained by the model, correlated for the number of terms in the model. The values indicated in Table 3 means that only 1.04% of variation can not be explained by the regression model.

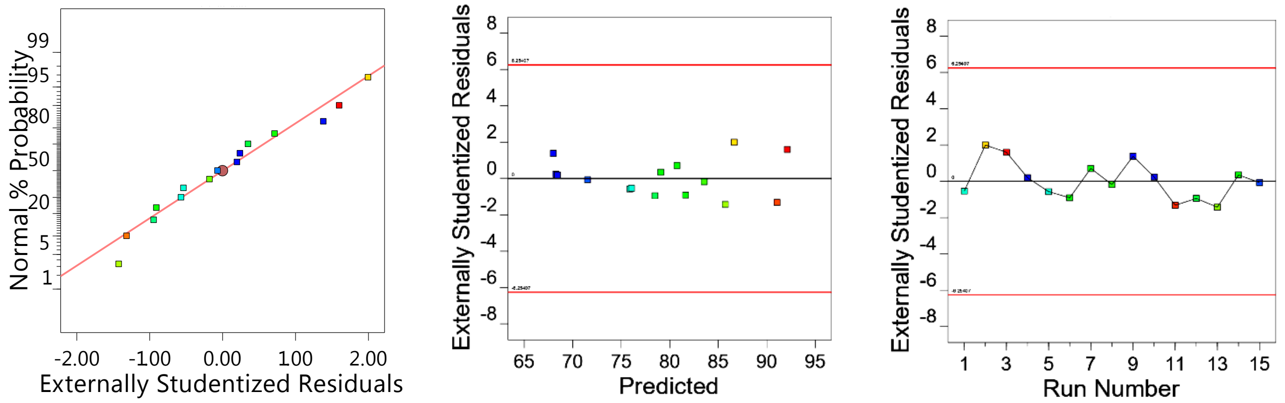
The high value of predicted R^2 (0.9702) shows how well the obtained regression model can predict the response value for different input data. Between the predicted value of R^2 and the adjusted value of R^2 must not be a difference greater than 0.2. As can be seen from Table 3, the difference between the predicted R^2 value (0.9702) and the adjusted value (0.9896) is 0.0194, which means a reasonable agreement.

The Adeq Precision measures the ratio signal: noise, that must be greater than 4. The range of predicted values is compared with the model obtained with the average prediction error (the range of the predicted values at design indicates the average prediction error).

After modelling the system, the coefficients β_0, β_j, β_{jj}, β_{ju} are replaced by the values determined after processing the experimental data. In this way they move from the real model to the empirical model. The polynomial form of the regression model according to the coded term is given by the relationship:

$$Y = 87.14 + 2.8X_1 - 0.097X_2 + 7.75X_3 + 2.29X_1X_2 + \\ +0.4428X_1X_3 + 0.6325X_1X_2 - 0.2425X_1^2 - 1.63X_2^2 - 9.89X_3^2 \quad (2)$$

The plot of residuals is shown in Figure 4. The distribution of points is approximately linear and the graphs show that the errors are normally distributed.



a) b) c)

Figure 4. The plot of residuals
a) – Normal plot vs residuals; b) - Residuals vs. Predicted; c) - Residuals vs. run

The graph of the real answers compared to the predicted answers is shown in Figure 5. As can be seen, the points have a distribution approximately equal to the 45 degree line.

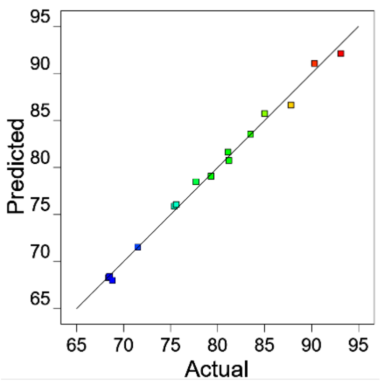


Figure 5. Predicted vs. actual.

In Figure 6 is shown the response surface of the adsorbed Cu concentration, depending on the process parameters. The response surface represents the link between several response variables to highlight the optimal area for the response function (in this case, adsorbed copper).

Figure 6, a) shows the dependence of adsorbed copper on the variation of the factors temperature and contact time. In Figure 6, b) is shown the dependence of Cu adsorbed vs. pH and contact time, and in Figure 6, c) is presented Cu adsorbed vs. pH and temperature. From the analysis of these figures, it is observed that temperature and contact time have a lower influence on the adsorption process (Figure 6, a), that is reflected when modifying the two factors, by a slight change of adsorbed copper concentration. The pH factor has the greatest influence on the process, as shown in Figures 6, b), and 6, c).

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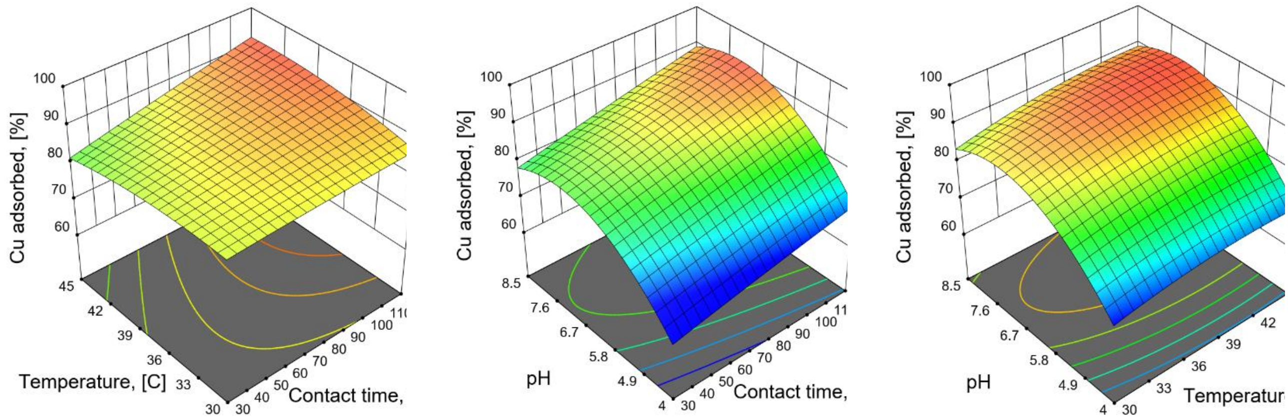
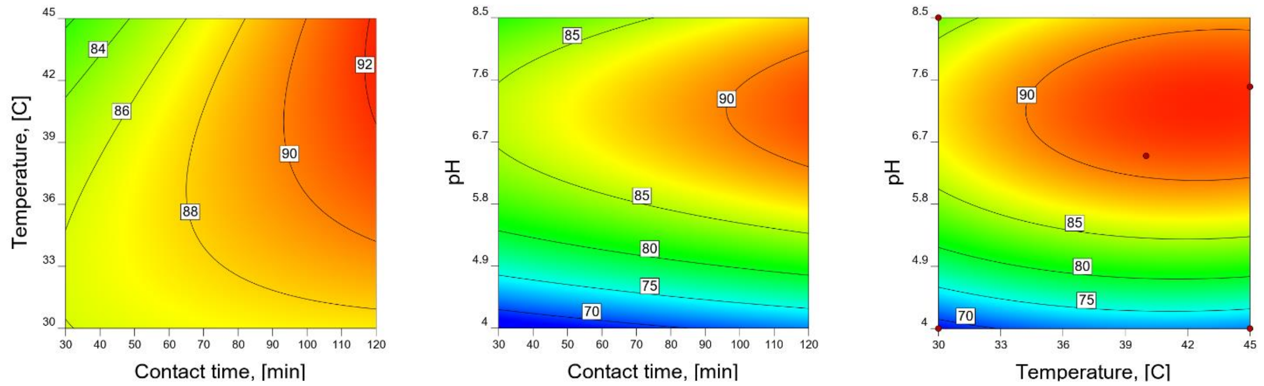


a) b) c)

Figure 6. The response surface of the adsorbed Cu concentration, depending on the process parameters. a) – Cu adsorbed vs. Temperature and Contact time; b) - Cu adsorbed vs. pH and Contact time; c) - Cu adsorbed vs. pH and Temperature

To conclude with, there is a higher dependence of the percentage of copper adsorbed on the *p*H increase and a lower dependence on temperature and contact time. By indicating the value of a parameter, the contour plot allows you to view the 3D response area on the plane defined by other process influence parameters.

In Figure 7 is presented a contour plot in which the optimal area of the studied process is highlighted (the red one), depending on the process parameters. In Figure 7, a) the optimum area is presented according to temperature and contact time, at pH = 7.33, in Figure 7, b) the optimum area according to contact time and pH at temperature 44 ^{o}C, and in Figure 7, c) according to temperature and pH factors at a time of 120 min.



a) b) c)

Figure 7. Highlighted the optimal area (the red one) depending on the process parameters.
a) – Temperature vs. Contact time; b) - pH vs. Contact time;
c) - pH vs. Temperature

The process can be optimized according to several criteria: by maximizing the percentage of adsorbed copper or by minimizing the costs related to the temperature and working time for the process. Optimization involves identifying a combination of levels of the influence factors, which allows simultaneous constraints imposed to the factors and the response.

Based on the model created and the values of the working parameters, the application can achieve the optimization of the process according to the mentioned criteria. The working parameters for maximizing the percentage of adsorbed copper are shown in Figure 8. Figure 9 shows the percentage of adsorbed copper under the minimum working time conditions and the temperature at which the adsorption process can occur.

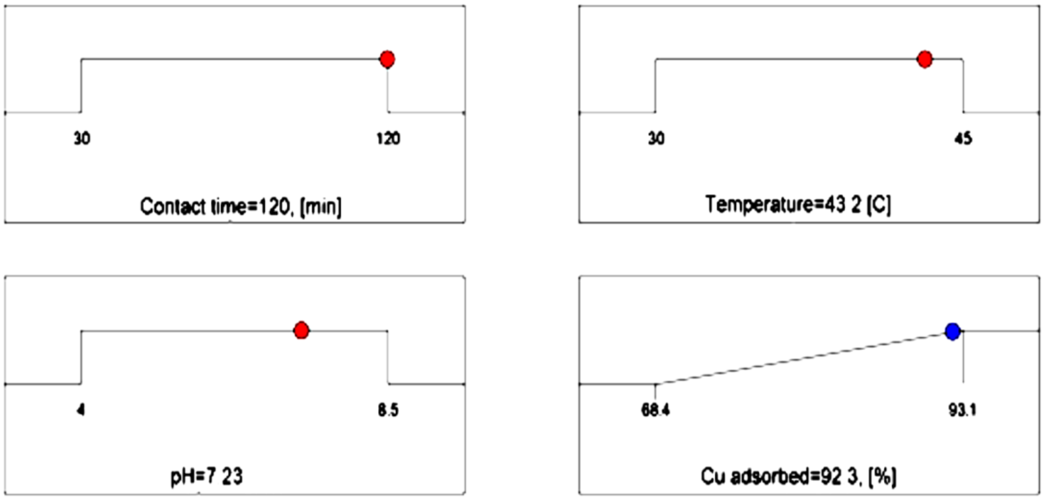


Figure 8. The working parameters for maximizing the percentage of adsorbed copper

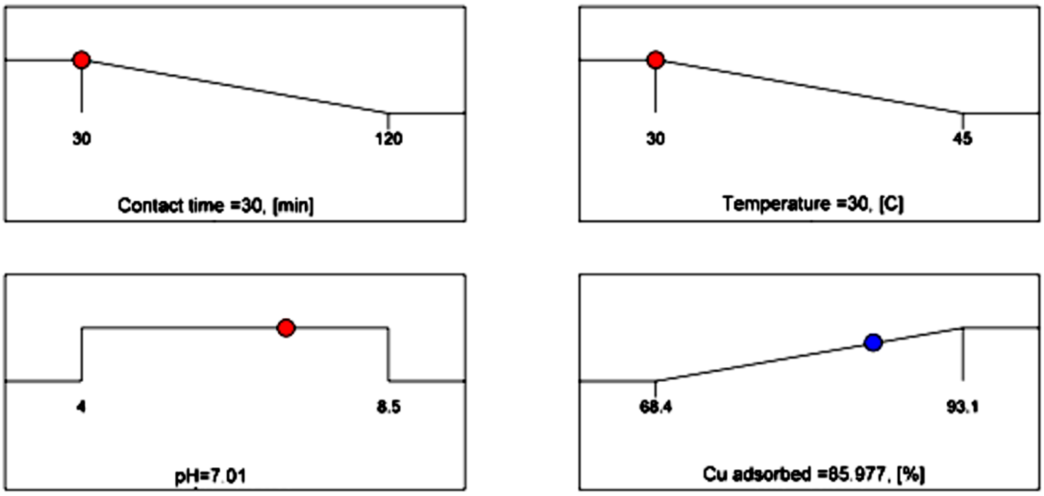


Figure 9. The optimization of the percentage of adsorbed copper by minimizing the working time and the temperature of the process.

In the first option (Figure 8), the working parameters are: time 120 minute, temperature 43.2 ^{o}C, pH 7.23, the percentage of adsorbed copper being estimated at 92.3%. To obtain the maximum percentage of copper under minimum working conditions and temperature (Figure 9), it is assumed that the following working parameters are required: time 30 min, temperature 30 °C, pH 7.01. The percentage of adsorbed copper was estimated at 85.9%.

In Figure 10, a) is shown a parallel plot for the optimization process solutions to maximize the percentage of adsorbed copper, and Figure 10, b) presents a parallel plot for the optimization process solutions to maximize the percentage of adsorbed copper at the minimum temperature and the minimum working time required for the process development. Both figures show the combinations used in the calculation for optimization, and highlight the optimal combination of parameters according to the required criterion.

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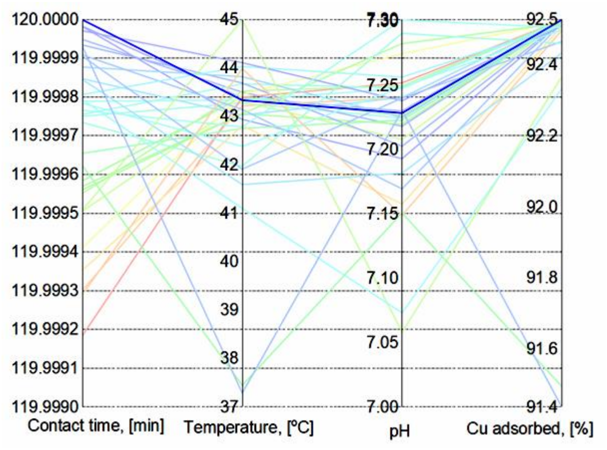

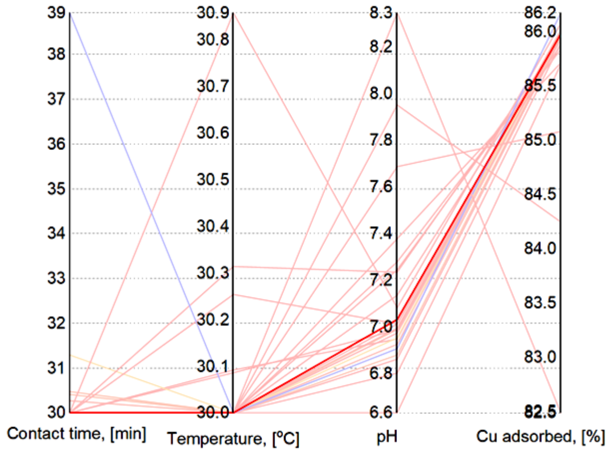

a) b)

Figure 10. The optimal solutions
a) for maximum adsorbed concentration;
b) for minimum cost and maximum adsorbed concentration

In the working conditions found by design experiment for maximum productivity, respectively maximum economic efficiency were performed three experiments for each optimization criterion, in order to check the accuracy of the optimization procedure. By first criterion the adsorbed copper percent was 91.8% compared to the result of optimization procedure, 92.3% and by second criterion was 85.2% compared to 85.977%, the difference between the estimated values by the programme and the experimental results being 0.5%, respectively 0.8%.

4. Conclusions

A natural clay from the Felix geothermal area has been identified as a potentially attractive adsorbent for the treatment of copper ions from aqueous solutions. The adsorption ability was revealed by different initial copper concentrations and, for the best adsorption percentage, experimental tests were performed by changing the pH and temperature of aqueous solutions, as well as the variation of the contact time between these solutions and the natural clay.

The factorial experiments confirmed the influence of the factors on the response function. Based on the obtained model, an estimated correlation between the three influence factors from the range of studied values could be made. The model allows obtaining data that can be used to predict the behaviour of the adsorption process. It also allows obtaining information that will guide the process to the optimal area.

Two variants of process optimization were studied both in terms of maximum productivity and in terms of minimum cost. All the results were achieved in Design Expert, obtaining the optimum value of the three factors in order to get the highest percentage of adsorbed copper of 92.3%, respectively taking into account both the adsorption optimization process and the economic factor, working on a minimum contact time and temperature for 85.9% adsorbed copper.

The values estimated after the optimization were validated by subsequent experiments. Considering the results, the natural clay from Felix may be used as an adsorbent with lower costs for removing copper from wastewaters.

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