ORAL PRESENTATION

2^3 Full factorial design approach to the optimization of copper removal from aqueous solutions with bio-nano material

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Abstract

It is known that the high amounts of copper in water are harmful to the living system and the environment. The removal or recovery of Cu(II) in water is important in many respects, such as being a precious metal. In this study, a bio-nanocomposite material was produced from bio-waste material and silver nanoparticles and used as a bio-adsorbent for the removal of Cu(II) from model aqueous solutions. Since the optimization study of many factors affecting the removal process with bio-adsorption will cause long time and financial loss with classical methods, the effect of factors on bio-adsorption and the interaction between factors have been carried out with the Experimental design method. With 2^3 full factorial design models, the effects of 3 factors (time, amount of bio-adsorbent, initial Cu(II) concentration) on the bio-adsorption process were examined and their optimum values were found. From the results obtained, the percentage of Cu(II) removal of the bio-nanomaterial from aqueous solutions and the capacity of the bio-adsorbent were determined

Keywords: copper, full factorial design, bio-nano material

INTRODUCTION

As a result of increasing industrial studies in recent years, aqueous environments are polluted with heavy metals. It is not surprising that copper, one of the most used heavy metals in daily life and industry, is found in aqueous environments. A certain level of copper is an essential element for living organisms. However, this level depends on what the living organisms are varied (Bozbaş K. and Boz 2016). The presence of copper in low concentration levels in the human body is necessary for many conditions such as enzyme synthesis, tissue, and bone development; however, high copper concentration has toxic and carcinogenic effects. Various reports in the literature indicate acute copper poisoning/toxicity causing stomach and intestinal disorders such as nausea, vomiting, diarrhea, and stomach cramps (Taylor et. al. 2020). WHO sets the permissible copper level in drinking water as 0.02 mg/L (Chain V. 2011).

Many methods and studies are carried out for the recovery and removal of copper(II) from aqueous environments. Methods such as chemical precipitation and filtration, electrochemical methods, ion exchange, reverse osmosis, evaporation and adsorption have been used for the removal and recovery of copper from aqueous media. Among these methods, the most preferred method is the adsorption method, which has many advantages such as easy applicability, use for all metals, and cheapness.

There are many materials used as adsorbent in the adsorption method. Some of these are newly synthesized materials, some are waste materials, some are bio-materials found in nature. The material to be used as an adsorbent is expected to be easy to obtain, cheap and reusable (Karayunlu Bozbas 2013, Zanin 2017)

The bio-nanomaterial used in this study consists of the powder of seashells collected from the seaside and silver nanoparticles. Ball milling method was chosen for the bio-nanomaterial we obtained. This material was used to remove the copper (II) ion from model aqueous solutions. The percent removal success and optimization conditions in the copper(II) removal of the material we obtained were realized with the 2^3 full factorial design method.

MATERIALS AND METHODS

Materials

Copper was prepared from standard 1000 mg L-1 Cu(II) ion solutions nitrate salts (Merck, Germany). The Ag ion was obtained from $AgNO_3$ (Merck). Different types of seashells we collected from the seaside were first brushed and washed in tap water to purify them from external pollution. The washed peels were kept overnight in deionized water. It was then dried at 100 °C for 24 hours. Clean and dry shells were crushed into small pieces with hard materials such as hammers, then ground and sieved down to 45 µm. These powders are mixed with an $AgNO_3$ solution. The mixture crushed with ball-milling for 2 hours. After ball milling, the mixture was washed with distilled water, centrifuged for 5 minutes and then washed with ethanol. It was dried in vacuo overnight. The bio-nanomaterial was stored in airtight acid-washed polyethylene containers at room condition.

A Perkin Elmer Model AAnalyst 800 flame atomic absorption spectrophotometer (FAAS) was used for determine the Cu(II) concentration after bio-adsorption process.

All the chemicals used in the work were of analytical reagent grade.

Methods

Factors such as metal concentration, pH, amount of bio-adsorbent, time and temperature affect adsorption. With the Full Factorial design, the total number of experiments required in traditional methods is reduced and the best optimization values are found. It is seen in the literature that experimental design methods are used for many studies with advantages such as improving quality, reducing costs and increasing the reliability of the results. A two-level full factorial design with three experimental factors was modeled to determine the optimum levels of effective factors in determining the maximum percentage of removal in the bio-adsorption process.

Using 20 mL of copper(II) solution at pH 5.5 at room temperature and at a stirring speed of 300 rpm; Factors such as time, copper (II) concentration and amount of bio-nanomaterial and their interaction effects were investigated.

All experiments were performed in 50 mL dark glass bottles containing 25 mL of Cu(II) solution. The bio-adsorption process was started by adjusting the amount of bio-nanomaterial, copper (II) concentration and time values specified in the design for each experiment. After reaching equilibrium, metal concentrations in the supernatant solutions were measured in FAAS (diluted if necessary). The percent removal of adsorbent was calculated from the following equation:

$$\%R = \left(\left(C_0 - C_e\right)/C_0\right)x100 \quad (1)$$

where %R is the percentage removal of Cu(II), C_0 and C_e are initial and equilibrium concentrations of Cu(II) in the solution (mg/L), respectively.

For the 2^3 experimental design, the high and low levels of the three independent factors and the results are listed in Table 1. Appropriate choices of high- and low-level values for the factors and other parameters were determined during previous experiments.

Table 1. Appropriate choices of high- and low-level values for the factors and other parameters were determined during previous experiments

Run	Bio-nanomaterial amount (g)	Cu(II) concentration (mg/L)	Time (min)	R (%)	R (%)
1	0.05	50	10	49.060	48.825
2	0.30	50	10	60.980	61.100
3	0.05	200	10	65.095	66.010
4	0.30	200	10	65.390	64.670
5	0.05	50	150	44.360	44.030
6	0.30	50	150	87.886	88.920
7	0.05	200	150	65.365	64.780
8	0.30	200	150	66.825	67.230

Using MINITAB 15 statistical software, 2^3 full factorial design tables were created and the results were analyzed. The results were created by averaging the %R results of two parallel experiments. The order in which the experiments were carried out was chosen randomly to avoid systematic errors.

RESULTS and DISCUSSION

Effects of optimum conditions and factors on the percentage of Cu(II) removal from model aqueous solutions by bio-nanomaterial; Eight parallel experiments were conducted and main effects were evaluated by Pareto plot, interaction plot, surface plot and analysis of variance of experiments.

Statistical parameters with analysis of variance (ANOVA), the quality of interactions between the independent factors and the model was performed based on a 95% confidence level P-value (Hines and Montgomery 1990). In Table 2, the singular effects of the factors and the two- and three-way interaction effects, the coefficients of the model (Coef.), the standard error (SE Coef) coefficients, Student test values (T) and probability (P) results are given.

Table 2. Estimated Effects and Coefficients for R (%) (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		63.158	0.1102	573.06	0.000
Bio-nanomaterial amount (g) (A)	14.434	7.217	0.1102	65.49	0.000
Cu(II) concentration (mg/L) (B)	5.026	2.513	0.1102	22.80	0.000
Time (min) (C)	6.033	3.017	0.1102	27.37	0.000
Bio-nanomaterial amount (g)* Time (min) (A*C)	13.718	-6.859	0.1102	-62.24	0.000
Bio-nanomaterial amount (g)* Cu(II) concentration (mg/L) (A*B)	8.647	4.324	0.1102	39.23	0.000
Cu(II) concentration (mg/L)* Time (min) (B*C)	-5.274	-2.637	0.1102	-23.93	0.000
Bio-nanomaterial amount (g)* Cu(II) concentration (mg/L)* Time (min) (A*B*C)	-7.408	-3.704	0.1102	-33.61	0.000

S = 0.44 PRESS = 6.2191, R-Sq = 99.94% R-Sq(pred) = 99.75% R-Sq(adj) = 99.88%

In the Table 2, Effects were found significant at a 5% probability level ($P < 0.05$) in case all factors and factors interactions. In addition, the corrected regression coefficient R-Sq(adj) value of 99.88% was obtained, which shows the compatibility of the model with the experimental data (Tizi et al. 2013). Model equation for Cu(II) extraction by the new bio-nanomaterial:

%R= 63.158 + 7.217A+ 2.513 B +3.017 C -6.859 A*C + 4.324 A*B -2.637 B*C -3.704 A*B*C

The three independent factors examined according to the recovery equation formed from the table and all interactions between the factors are effective on the model. The negative and positive coefficients in the above equation indicate high or low factor settings (Mathialagan and Viraraghavan 2005).
The interaction plots, shown in Figure 1, show the significant interactions of the factors studied for the percent removal of Cu(II) from aqueous solutions. These graphs are used to understand the importance of different interactions on the bio-nanomaterial, in a sense to determine operating conditions.

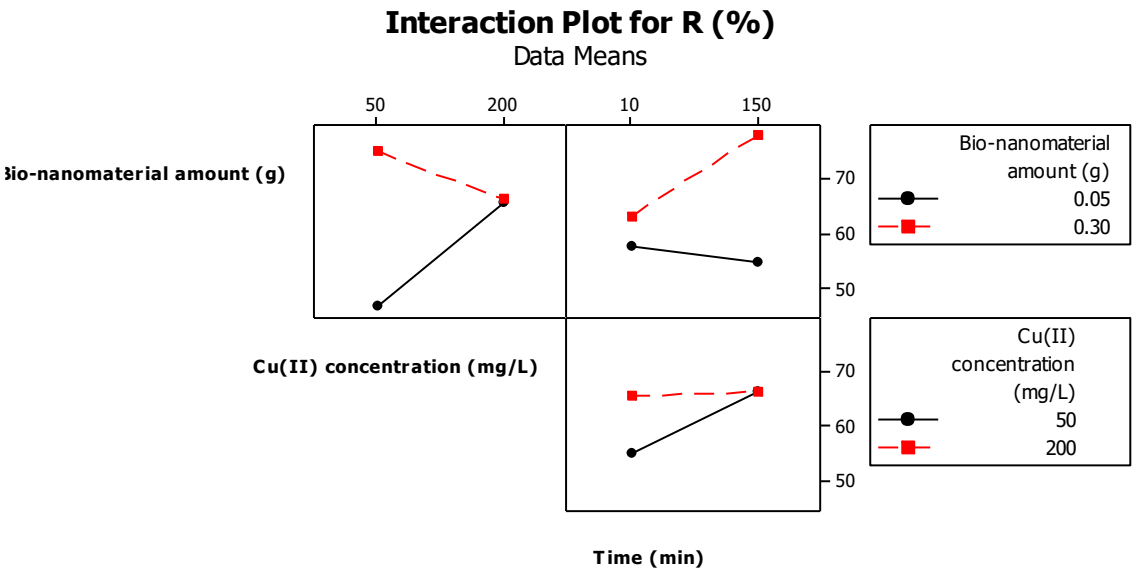


Figure 1. Interactions plot of factors

The MINITAB program plots the response for each combination of factors from the generated design and connects the points for the low and high level of the factor plotted on the x-axis. The variation of a factor's response from low to high, depending on the level of a second factor, tells us whether the factors are effective or not. If the lines are not parallel, it is concluded that the investigated factors are effective on bio-adsorption. It is seen that when the Cu(II) concentration is low, the highest %R value is obtained when high time is applied at low Cu(II) concentration and high bio-nanomaterial amount, again at high bio-nanomaterial amount. Cu(II) concentration and amount of bio-nanomaterial, Cu(II) concentration and time, time and amount of bio-nanomaterial; It was determined that the bilateral interactions were effective on the recovery percentage in this case.

The main effects of the three selected factors for the removal of Cu(II) from model aqueous solutions by the bio-adsorption process on the bio-nanomaterial on the recovery percentage with a change in the main factor level are shown in Figure 2. The sign of the selected factors defines whether the effect is positive or negative on the outcome (Srinivasan and Viraraghavan 2010).

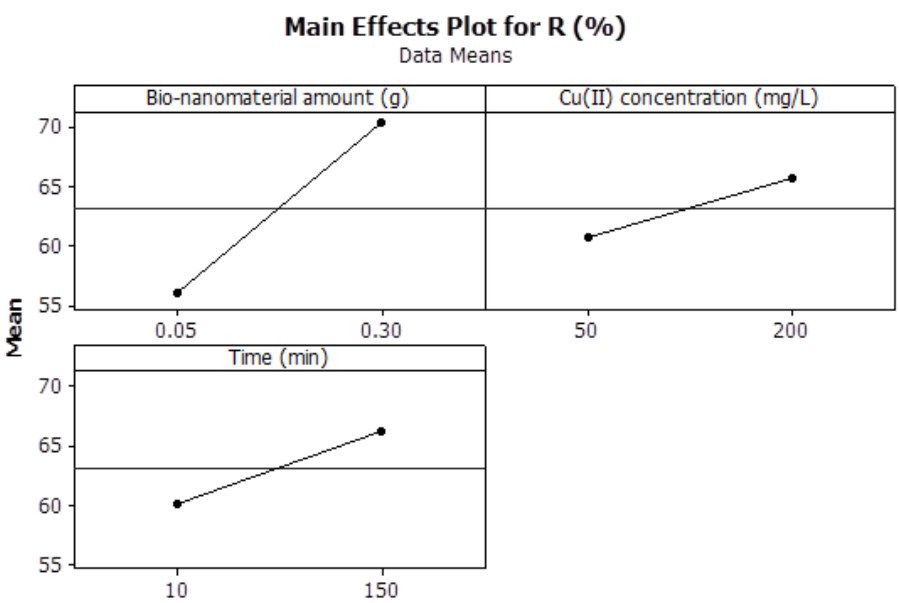


Figure 2. Main Effects of Each Factor

As seen in the figure above, while the effects of time and Cu(II) concentration on the bioadsorption process were similar, it was determined that the effect of the amount of bio-nanomaterial was more effective.

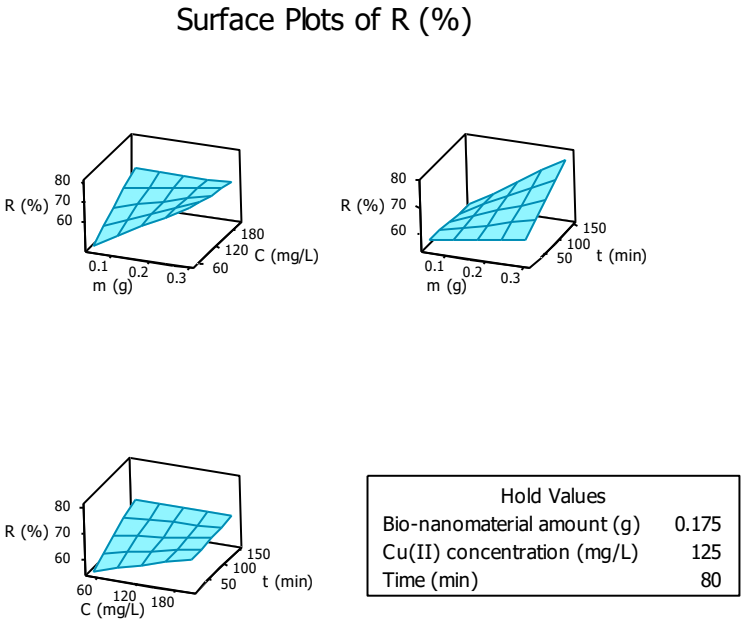


Figure 3. Surface plots for median of three factors

Response surface method was used to determine the optimum parameter values for the removal of Cu(II) from model aqueous solutions. The surface graphics of the design are as in Figure 3.
As seen in the graphs drawn based on the median values of the two interactions of the three factors, the highest R % value was determined to be below 90.
According to the optimization values given by the model, it was determined that the highest percent recovery value was 88.40% in the amount of 0.30 g bio-nanomaterial in 50 ppm Cu(II) concentration in 150 minutes. When the experiment was repeated with these optimization values, our test result was determined as 87.56%.

CONCLUSION

As a result, the use of composite nanomaterial consisting of seashell powder and silver nano-particles as an adsorbent has been tried. The optimization values of the bio-adsorption process of the bio-nanomaterial were carried out by the experimental design method. The highest recovery percentage of the bio-nanomaterial in the removal of Cu(II) from model aqueous solutions was determined as 88.40%. This value was obtained at a concentration of 50 ppm Cu(II) and 0.30 g of bio-nanomaterial in 150 minutes.

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