

STATISTICAL MODELING OF COPPER IONS BIOSORPTION ONTO SUNFLOWER HULLS

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Abstract

The statistical modeling of the copper ions biosorption onto sunflower hulls is presented in this work. The analysis was conducted using the Response Surface Methodology coupled with the Box-Behnken Design. The software experimental design, consisting of 17 experiments, was applied to optimize the biosorption process. The obtained results indicated that the used model is statistically significant, and that the optimal conditions for copper ions biosorption onto sunflower hulls are: 0.7 g sunflower hull sample mass, 0.1 g dm⁻³ initial copper ions concentration, and pH of the solution 5. The analysis indicated that all three analyzed parameters are significant model terms.

Keywords: Response surface methodology; Box-Behnken design, biosorption, sunflower hull

1. INTRODUCTION

In recent years, rapid industry growth accelerated the discharge of large amounts of pollutants into the surface and groundwater. Wastewater polluted with heavy metals is a serious worldwide environmental issue. Heavy metals are non-degradable pollutants, that tend to accumulate in living organisms, and cause a wide array of diseases and disorders. These pollutants are present in discharges from various industries, including metal processing, mining, surface treatment of metals, energy sector, etc. [1,2].

As a trace element, it is essential in living organisms as it participates in the synthesis of different types of enzymes. However, in bigger concentrations it is toxic to living organisms, as it affects the metabolism, cell growth, and other processes [3].

On the industrial scale, many technologies have been used to treat wastewater and remove toxic pollutants, including electro dialysis, chemical precipitation, adsorption, chemical precipitation, membrane separation, and others. These technologies come with several limitations and difficulties, that include high operating costs, high reagent usage, sludge production, high energy requirements, and inefficiency when it comes to low heavy metal concentrations [1,2].

Biosorption, i.e. the adsorption of toxic pollutants using biological materials as adsorbents (biosorbents) has become a popular alternative method to conventional technologies. Biosorbents are economically and environmentally friendly, and have shown, to some extent, selectivity towards heavy metals, and can be used in a wide range of physico-chemical conditions [2].

2. EXPERIMENTAL

The sunflower hulls were ground and then sieved through a set of laboratory sieves, and the fraction (-1+0.4) mm was used for the Cu²⁺ biosorption experiments. The experiments were performed using synthetic copper solutions prepared using CuSO₄ · 5H₂O (p.a. purity). The pH value of the solutions was adjusted with 0.1 M KOH, and 0.1 M HNO₃. The chemicals used were manufactured by LACHEMA (Czech Republic).

The RSM-BBD experimental design, which was used to optimize the biosorption process, consisted of 17 experiments. The design was applied comparing three selected factors: biosorbent mass (A), initial copper ion concentration (B), and pH value of the solution (C). The test series and their values are listed in Table 1.

Table 1. Experimental ranges and their levels

Factors	Range level		
	-1	0	1
A – biosorbent mass, g	0.3	0.5	0.7
B – initial copper ion concentration, g dm ⁻³	0.1	0.2	0.3
C – pH of the solution	3	4	5

3. RESULTS AND DISCUSSION

The biosorption process was optimized using Response Surface Methodology (RSM) coupled with the Box-Behnken Design (BBD). The process optimization experimental design, given in Table 1, was applied to optimize the copper biosorption process onto sunflower hulls. The matrix of the experimental design, and the obtained results (response R – biosorption degree) are shown in Table 2.

Table 2. Experimental ranges and their levels

Run	A – biosorbent mass, g	B – initial copper ion concentration, g dm ⁻³	C – pH of the solution	R – biosorption degree, %
1	0	1	1	24.036
2	0	-1	-1	52.564
3	0	1	-1	15.433
4	-1	0	-1	11.726
5	1	0	-1	18.613
6	0	-1	1	75.396
7	0	0	0	40.007
8	-1	-1	0	64.556
9	0	0	0	30.026
10	0	0	0	32.221
11	-1	0	1	27.351
12	-1	1	0	15.537
13	1	-1	0	74.086
14	1	1	0	35.557
15	1	0	1	45.475
16	0	0	0	32.377
17	0	0	0	35.348

A polynomial equation (1) was fitted in order to describe the correlation between the independent variables: linear ($\beta_1, \beta_2, \beta_3$), quadratic ($\beta_{11}, \beta_{22}, \beta_{33}$), interaction terms ($\beta_{12}, \beta_{13}, \beta_{23}$) and the response (R) [4]:

$$R = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} AA + \beta_{22} BB + \beta_{33} CC + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (1)$$

The results obtained are shown in Table 2. The copper ions biosorption onto sunflower hulls can be expressed as:

$$R = 33.99 + 6.82A - 22.01B + 9.24C + 2.62A \cdot B + 2.81A \cdot C - 3.56B \cdot C - 1.31A^2 + 14.75B^2 - 6.89C^2 \quad (2)$$

The ANOVA statistical analysis was performed to determine the statistical significance of the applied model. The obtained results are given in Table 3. The significance of the individual coefficients is analyzed by the F-values and p-values. The coefficient is more significant as the F-value is higher and p-value lower. p-values below 0.0500 indicate a highly significant regression at a confidence level of 95 % [5,6].

Table 3. ANOVA analysis for the Response Surface model for copper ions biosorption onto sunflower hulls

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	6116.00	9	679.56	61.42	< 0.0001	significant
A-A	372.11	1	372.11	33.63	0.0007	
B-B	3873.72	1	3873.72	350.12	< 0.0001	
C-C	683.06	1	683.06	61.74	0.0001	
AB	27.51	1	27.51	2.49	0.1588	
AC	31.57	1	31.57	2.85	0.1350	
BC	50.62	1	50.62	4.57	0.0697	
A ²	7.27	1	7.27	0.6570	0.4443	
B ²	916.31	1	916.31	82.82	< 0.0001	
C ²	199.92	1	199.92	18.07	0.0038	
Residual	77.45	7	11.06			
Lack of Fit	17.95	3	5.98	0.4024	0.7598	not significant
Pure Error	59.49	4	14.87			
Cor Total	6193.44	16				

The obtained F- and p-values (61.42 and < 0.0001) indicate that the model is significant, with further indication that there is only a 0.01% chance that this F-value appeared due to noise. The model fit was also confirmed by the regression coefficients of the predicted and experimental values ($R^2 = 0.940$ and $\text{adj-}R^2 = 0.971$).

P-values above 0.1000 indicate that the analyzed model terms aren't significant. In this case, A-A, B-B, C-C, BC, B² and C² are significant model terms.

The plot of actual vs predicted responses (shown on Figure 1) can also give insight into the significance of the applied model [6]. The obtained results show a good agreement between the experimental and the model predicted responses.

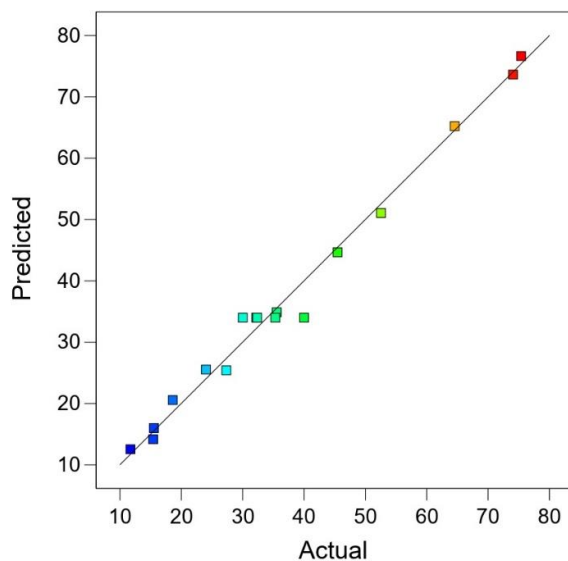


Figure 1. Actual vs model predicted responses

3D surface plots, illustrating the influence of the analyzed parameters on the system response (R) are shown on Figure 2.

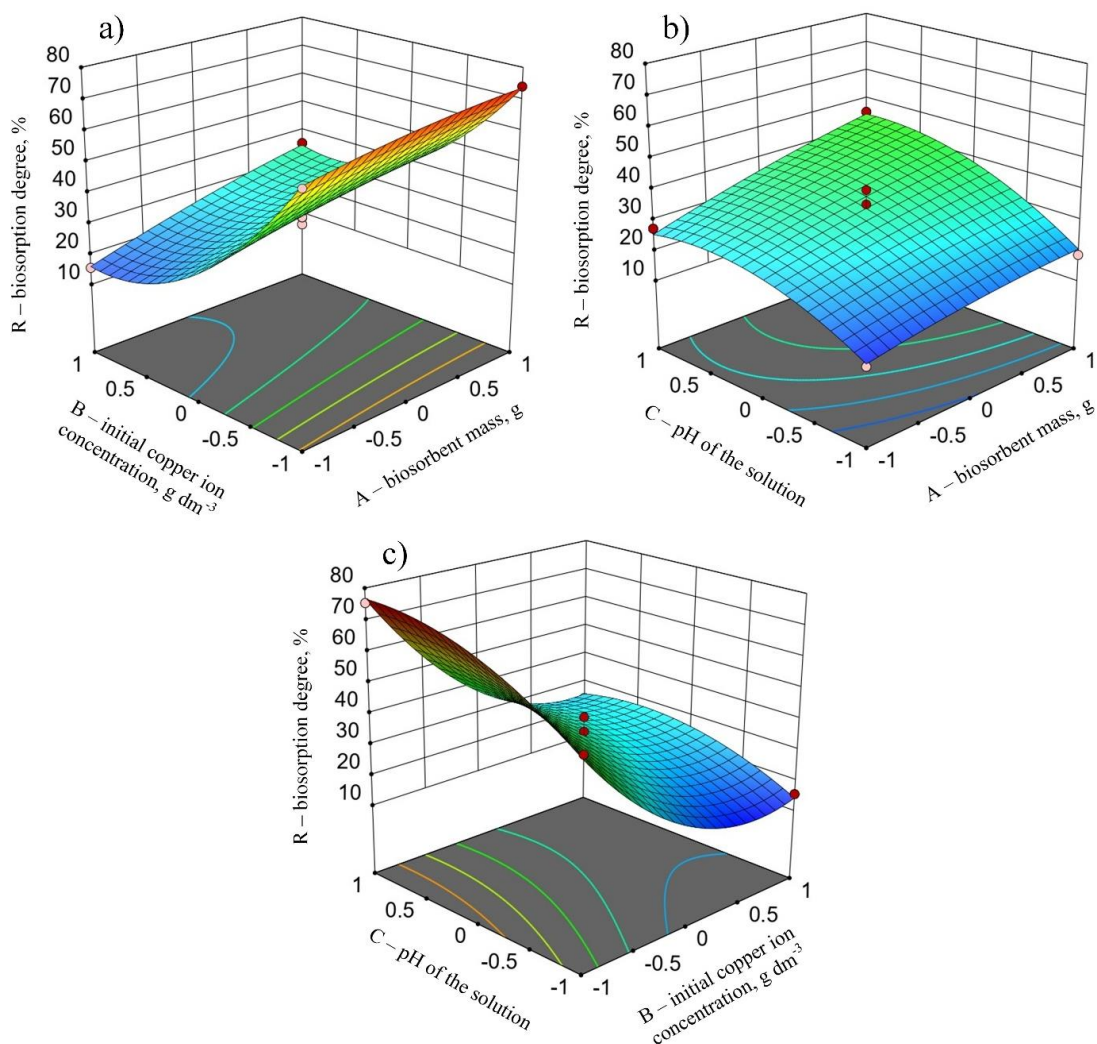


Figure 2. Response surface plots showing the interaction and influence on the biosorption rate (R) of (a) biosorbent mass (A) and initial copper ions concentration (B); (b) biosorbent mass (A) and pH of the solution (C); (c) initial copper ions concentration (B) and pH of the solution (C)

Figure 2a indicates that low initial copper concentrations in combination with high biosorbent mass led to a high response (biosorption degree). The interaction between the biosorbent mass and pH of the solution is shown on Figure 2b. It can be seen that higher biosorbent mass along with higher pH value of the solution led to a higher response, i.e. biosorption degree. Figure 2c (interaction between initial copper concentration and pH of the solution) indicated that lower initial copper concentrations in combination with higher pH values of the solution gave higher system responses, i.e. higher biosorption degree.

4. CONCLUSIONS

The optimization of the copper ions biosorption onto sunflower hulls was performed using the RSM-BBD method. The influence of three process parameters, i.e. the mass of the biosorbent, the initial copper ion concentration, and the pH of the solution was evaluated. The used model was determined to be statistically significant. The performed analysis suggested that the optimal conditions for copper ions biosorption onto sunflower hulls are: 0.7 g biosorbent mass, 0.1 g dm⁻³ initial copper concentration, and pH of the solution 5.

ACKNOWLEDGEMENTS

The research presented in this paper was done with the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade - Technical Faculty in Bor, according to the contract with registration number 451-03-137/2025-03/200131.

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