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The biosorption of Co(II) by *Homalothecium sericeum* from aqueous solutions under batch conditions: response surface methodology optimization and *Daphnia magna* bioassay

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ABSTRACT

In the present work, *Homalothecium sericeum* biomass was used for removal of Co(II) from aqueous solution. The effects of process parameters (contact time, biosorbent amount, and initial Co(II) concentration) on the response (Co(II) % removal) were investigated using a batch adsorption system optimized with response surface methodology/central composite design method. Under optimized conditions the maximum Co(II) removal efficiency achieved is 94.07% at an initial Co(II) concentration of 2.05 mg/L, a *H. sericeum* amount of 0.34 g/50 mL, and a process time of 36.09 min. In this study, the toxicity of the medium after biosorption carried out under optimized conditions was also tested with *Daphnia magna* bioassay. When mortality results with *D. magna* were evaluated, although a removal efficiency of 94.07% was obtained after biosorption, this was not sufficient to reduce mortality of *D. magna*.

Keywords: Biosorption; Co(II); Response surface methodology; *Daphnia magna*

1. Introduction

Cobalt is widely preferred in industrial and technological applications, especially in the manufacture of lithium-ion batteries. The mass production of tablet-type mobile phones and laptop screens containing lithium-ion batteries has increased the demand for cobalt even more in recent years, and as a result, industrial waste has accumulated on a global scale in the world. As a result of this accumulation, it was inevitable that cobalt should be separated from industrial wastes and purified afterwards [1].

In addition to these, the emergence of cobalt levels exceeding the environmental limit values has brought along problems in the proper functioning of the living activities of organisms. This has led to the conclusion that it shows signs of toxicity not only to plants or animals, which are the first component of the food chain, but also to the accumulation of cobalt amounts. This situation also put the later trophic levels at risk [2,3].

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Adsorption, ion exchange, oxidation process and irradiation methods are some of the commonly used physical methods that produce good results and are used for the treatment of wastewater containing dyes [4]. Biodegradation (i.e., bioremediation) is economically feasible, environmentally friendly and produces less sludge compared to other physicochemical techniques [5,6].

The widespread use of biosorption processes has recently gained momentum. Because these processes are less costly than other complex processes and these processes are environmentally friendly technology processes.

Biosorption processes occur by the transfer of chemicals from aqueous solutions to biological materials by biological, physical, and chemical methods [7]. Biosorption is a process that is responsible for heavy metal concentration by inanimate biomass in cases where the metabolic activity required for intracellular metal accumulation is lacking [8]. In this process, trace amounts of heavy metal ions can be quantitatively adsorbed on organisms such as bacteria, and algae. Most of the studies on the biosorption of heavy metals come from the immobilization of microorganisms on various adsorbents [9]. In recent years, international studies have focused on improving the adsorption processes by developing or replacing powerful, efficient, and inexpensive adsorbents with high absorbency [10].

Algae are widely preferred as an indicator organism of heavy metal pollution in many pollutions removal studies, since they cover approximately 23,000 species of all land plants in the world. According to the results obtained from these studies, the adsorption capacities of different algae species obtained from different regions should be emphasized to determine the pollution levels in an objective way [11]. The focus of much research on these issues in recent years has been the development of environmentally friendly methods/processes for the removal of pollutants. It is obvious that many types of organisms have important consequences when used as biosorbent against agricultural wastes and their residues [12].

Algae are sensitive biomarkers of heavy metal contamination and are also used as indicator organisms due to these properties. Algae have some properties due to their use as indicators. These; (1) Since they do not have cuticles or cuticles, the passage of metal ions through the cell walls is easy. (2) Lack of organelles to take minerals from the substrate.

It allows it to meet the minerals from precipitation. (3) Algae provide information about the concentration of most metals as a function of the amount of atmospheric precipitation [13]. Since mosses do not have a well-developed root system, the necessary minerals for their nutrition are mostly met from atmospheric accumulation [14].

Response surface methodology (RSM) is a statistical technique and because of this feature it is widely preferred to provide optimum process parameters based on the design of experiments [15]. RSM has several design techniques including full factorial, Box–Behnken and central composite design (CCD). CCD is one of the most preferred design types for RSM, especially in situations involving more than two (2) factors. CCD, on the other hand, provides a better fit of a quadratic model by providing superior predictions about how inputs affect outputs and what the interaction between several factors consists of in a complex process [16]. RSM can evaluate individual process variables, develop optimization models, and identify the interaction between each parameter visualized with the 3D response surface and contour plots. Such traditional approaches can be suppressed by optimizing process parameters together with statistical experimental design using RSM [17,18]. RSM stands out as an effective tool for constructing the empirical model, which can determine the useful static relationship between all variables in the experimental design. Although RSM was used for this statistical analysis, estimation of optimum conditions was also proposed. In the experimental stages, the input variables were translated into the analysis output response [19]. CCD, on the other hand, is highly preferred for assigning process individual variables, which are subjected to a series of evaluations through a rationalized number of design points along with a reliable curvature estimate to provide an acceptable amount of information to test for lack of fit [20].

Today, among the toxicity monitoring methods, bioassay with *Daphnia* stands out as one of the most common methods due to its unique properties, especially in recent years [21]. The toxicity parameter is one of the basic parameters in environmental water quality monitoring. However, monitoring the toxicity parameter can be evaluated by using organisms such as *Daphnia magna* to evaluate the quality of life in the aquatic environments in which they live. *D. magna* mortality studies are one of the most useful methods to have an idea about the toxicity assessment of wastewater without the immediate intervention of living things [22]. The reason why *D. magna* was chosen as the standard test species is that it has several advantageous properties. *D. magna* are small and easy to culture in the laboratory. Their ability to grow parthenogenetic under stress-free conditions also allows testing of clones, which increases the reproducibility and reproducibility of test results. In addition, the organism is relatively more sensitive to chemicals than other freshwater invertebrates [23].

The aim of this study was to optimize the biosorption of Co(II) from aqueous solutions by using *Homalothecium sericeum* as a biosorbent and to evaluate the toxicity of the medium after biosorption using *D. magna* as a model organism.

2. Material and methods

2.1. Collecting H. sericeum (Hedw.) Schimp

It is a plant belonging to the Bryophyta division, Bryopsida class, Hypnales order, Brachytheciaceae family. It is one of the 5 taxa of the genus Homalothecium in the world [24,25]. *H. sericeum* is a taxon that prefers basic and arid environments and open areas, spreading epiphytically on tree trunks and epilithic environments such as stone, wall and rock surfaces [26,27]. *H. sericeum* samples were taken from the Abant Mountains, Erelti plateu of Bolu, at an altitude of 1,323 m, at the coordinates of N 40° 38′ 30. 9″ E 31° 19′ 33. 1″ (Fig. 1). These samples were then taken to the Munzur University Environmental Engineering Department Laboratory. These samples were first dried and ground at

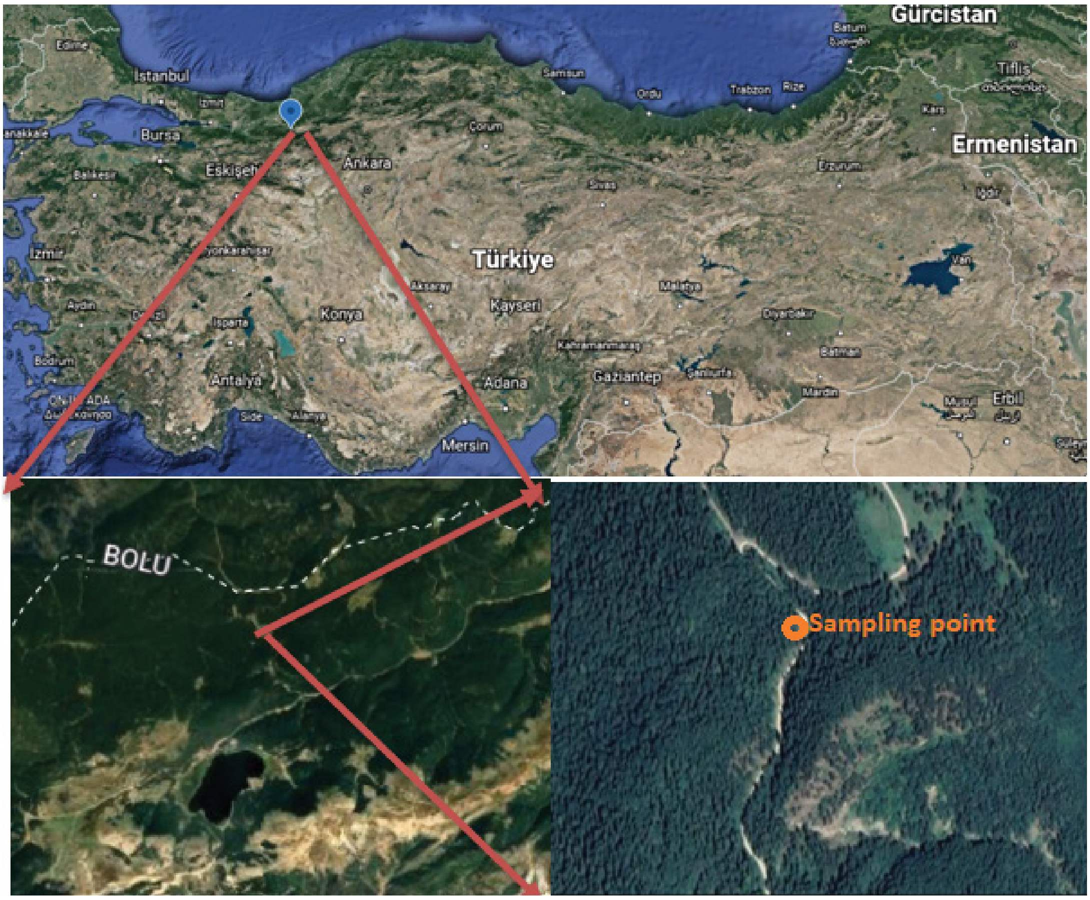

Fig. 1. Sampling point.

room conditions and then passed through a 250 μm sieve. *H. sericeum* can also seen in Europe, Faroe Islands, Iceland, Cyprus, The Middle East, Kashmir, China, Macaronesia, North America, and North Africa.

2.2. *D. magna* bioassay

D. magna individuals were used from stock available in our laboratory. *D. magna* was fed once a day using suitable foods and the aquariums was constantly oxygenated. Periodic water changes were made. Three groups were designed for the mortality bioassay (pre-adsorption, post-adsorption, and natural living water). For this purpose, 20 first-stage juvenile water fleas were added to the 250 mL mediums as the application amount and the experiment was started under optimum conditions. During the experiment, the animals were not fed. The number of dead test organisms in each well was counted after 24, 48 and 72 h. At the end of the application period, the number of dead individuals was determined, and mortality rates were calculated.

2.3. Batch biosorption procedure

The batch system was used to comprehend the sorption performance of *H. sericeum* for removal of the Co(II) ions. The cobalt solutions were prepared using 1,000 mg/L cobalt standard solution. All biosorption experiments were carried out in 250 mL Erlenmeyer flasks including 50 mL Co(II) ions solution in an incubator shaker (at a speed of 250 rpm) at 25°C and natural pH. The initial Co(II) concentration, *H. sericeum* amount, and process time were adjusted according to proposed design by RSM-CCD. Before the analysis, the samples were filtered by using 0.2-μm filter for the separation of adsorbent. The Co(II) concentrations in the solutions was determined by using atomic absorption spectrometer (PerkinElmer Analyst 800). The Co(II) removal efficiency (*R*, %) was determined via the following equation:

$$\text{Co}(\text{II})\,\text{removal efficiency}\,(R,\%) = \frac{(C_0 - C_t)}{C_t} \times 100 \tag{1}$$

where C_0 and C_t are the concentration of Co(II) in solution at $t = 0$ and $t = t$, respectively (mg/L).

2.4. Experimental design by CCD

The optimal conditions of the biosorption process based on Co(II) removal efficiency were investigated using RSM with the CCD. In this work, the biosorption experiments were carried out at an initial Co(II) concentration between 2 and 10 mg/L, a *H. sericeum* amount between 0.05 and 0.50 g/50 mL and a process time between 5 and 60 min.

Table 1
Independent factors and their levels for central composite design experiments

Factor	Symbol	–α	–1	0	+1	+α
Initial Co(II) concentration (mg/L)	X_1	2	3.62	6	8.38	10
Homalothecium sericeum amount (g/50 mL)	X_2	0.05	0.14	0.275	0.41	0.50
Process time (min)	X_3	5	16.15	32.50	48.85	60

The factors studied, the levels for each variable, and their symbols are shown in Table 1.

A second-order polynomial model was considered to explain the functional numerical relationship between the process factors and the response as follows [28];

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y is the predicted answer (Co(II) removal, %), β_0 is the constant coefficient, β_i is the linear regression coefficient, β_{ij} is the interaction regression coefficient, β_{ii} is the quadratic regression coefficient, x_i is the independent variable, x_i^2 is the square effects of variables, $x_i x_j$ is the variable interaction effects and ε is the random error of regression.

Design–Expert (trial version 7.0, USA) software was used for CCD design, process optimization and analysis of variance (ANOVA) analysis.

3. Results and discussion

3.1. Statistical analysis and model development

The effects of independent factors such as initial Co(II) concentration (X_1), *H. sericeum* amount (X_2) and process time (X_3) on the biosorption performance were investigated and optimized in a batch system. 20 sets of experiments were performed for Co(II) biosorption and removal values (%) for each run are presented in Table 2.

The model equation for response according to coded factors was showed by the following second-order polynomial model:

$$\begin{aligned} Y\left(\text{Co}\left(\text{II}\right)\text{removal,\%}\right) &= +73.31 - 13.67X_1 + 19.11X_2 \\ &+ 1.01X_3 + 6.55X_1X_2 - 0.36X_1X_3 + 0.079X_2X_3 \\ &- 1.55X_1^2 - 8.43X_2^2 - 0.63X_3^2 \end{aligned} \quad (3)$$

The equation given above explain the impact of independent factors on the biosorption of Co(II) by *H. sericeum*. The positive sign of the coefficients in Eq. (1) indicates a synergistic effect, while the negative sign of the coefficients indicates an antagonistic.

The significance and adequacy of the model were determined by analysis of variance (ANOVA) and the results are summarized in Table 3. From Table 3, the predictability of the model has a confidence level of 99.9%, showing that the predicted response corresponds to the experimentally obtained response. From Table 3, it can be obtained that the regression [Eq. (3)] is statistically significant at F-value of 140.05 for Co(II) biosorption with extremely low probability value (p-value <0.0001).

Table 2
Design of experiments for the biosorption of Co(II) by *Homalothecium sericeum*

Run	Factors			% Co(II) removal
	X_1	X_2	X_3	
1	6.00	0.28	32.50	73.33
2	6.00	0.28	32.50	73.33
3	3.62	0.14	16.15	65.19
4	10.00	0.28	32.50	46.6
5	2.00	0.28	32.50	90.5
6	6.00	0.28	32.50	73.33
7	8.38	0.14	48.85	24.94
8	8.38	0.41	48.85	73.26
9	6.00	0.28	32.50	73.33
10	6.00	0.28	32.50	73.33
11	6.00	0.28	32.50	73.33
12	8.38	0.14	16.15	25.05
13	6.00	0.50	32.50	85.5
14	3.62	0.41	16.15	87.01
15	6.00	0.28	60.00	73.83
16	3.62	0.14	48.85	67.4
17	8.38	0.41	16.15	72.19
18	3.62	0.41	48.85	88.67
19	6.00	0.28	5.00	68.5
20	6.00	0.05	32.50	12.67

As indicated, this regression was deemed statistically significant at an F-value of 140.05 and a p-value greater than > F < 0.0001. This F-value demonstrated a 0.0001 probability of being obtained through the noise.

The R^2 value of the proposed model for *H. sericeum* biosorbent was 0.9921 which demonstrated the perfect of the model in the estimate of the response that are so near to actual values. In addition to, the predicted R^2 (0.9401) was in reasonable agreement with the adjusted R^2 (0.9850) confirming that the model fit the measured values very well [29]. Acceptable precision measures the "signal-to-noise ratio" and confirms the statistical strength and significance of the proposed model and is desirable to be greater than 4 [30]. The ratio of 39.630 obtained in this study indicates an adequate signal and indicates that the model can be used to navigate the design space. Besides, a low value of the coefficient of variance (C.V. %) (4.03%) shows the reproducibility and reliability of the model. According to ANOVA data, X_1, X_2, X_1 X_2, and X_2^2 were found to as significant model terms (p-value <0.0001), whereas other terms were insignificant.

Table 3
Analysis of variance for the biosorption of Co(II) by *Homalothecium sericeum*

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value Prob. > *F*
Model	8,931.75	9	992.42	140.05	<0.0001
x_1	2,551.26	1	2,551.26	360.03	<0.0001
x_2	4,989.38	1	4,989.38	704.09	<0.0001
x_3	13.93	1	13.93	1.97	0.1911
x_1x_2	342.83	1	342.83	48.38	<0.0001
x_1x_3	1.06	1	1.06	0.15	0.7072
x_2x_3	0.050	1	0.050	7.001E-003	0.9350
x_1^2	34.64	1	34.64	4.89	0.0515
x_2^2	1,024.72	1	1,024.72	144.61	<0.0001
x_3^2	5.65	1	5.65	0.80	0.3930
Model statistics					
Std. Dev	2.66				
Mean	66.06				
C.V. %	4.03				
R^2	0.9921				
Adjusted R^2	0.9850				
Predicted R^2	0.9401				
Adequate precision	39.630				

The linear correlation between the experimental and predicted values is given in Fig. 2. There is good agreement between the estimated and experimental Co(II) removal efficiency (%).

3.2. Effect of independent factors on Co(II) biosorption

Effects of the independent factors obtained from CCD experiments were illustrated by three-dimensional (3-D) plots as shown in Fig. 3.

Fig. 3a shows the interaction effect of the initial Co(II) concentration and the amount of *H. sericeum*. As the initial concentration of Co(II) increased, the Co(II) biosorption efficiency of *H. sericeum* decreased. As the initial concentration of Co(II) metal ions increases, it produces a significant driving force to overcome the mass transfer resistance due to the increased collision between Co(II) and adsorbents. This case may increase the biosorption of Co(II) ions by *H. sericeum*, but the removal efficiency is reduced due to the reduction of available active sites of the biosorbent with increasing initial concentration [31]. Fig. 3b shows the interaction effect of the initial Co(II) concentration and the process time. It was found that the biosorption efficiency decreased with increasing initial concentration and increased with increasing contact time [32].

Fig. 3c shows the interaction effect of the *H. sericeum* amount and the process time. As seen in Fig. 3c, as the amount of *H. sericeum* increased initially, the removal efficiency of Co(II) ions by the biosorbent increased. The increase in biosorption efficiency may be due to the higher specific surface area of biosorbent at higher amounts and the higher number of biosorption sites on the biosorbent. In addition, competition between Co(II) ions for active sites of the biosorbent probably decreased as the amount of biosorbent increased. Then, at higher biosorbent amounts, it was observed that the removal efficiency was relatively lower due to the lower accessibility of Co(II) ions to the biosorbent due to the aggregation caused by the overlapping of the biosorbent particles [33].

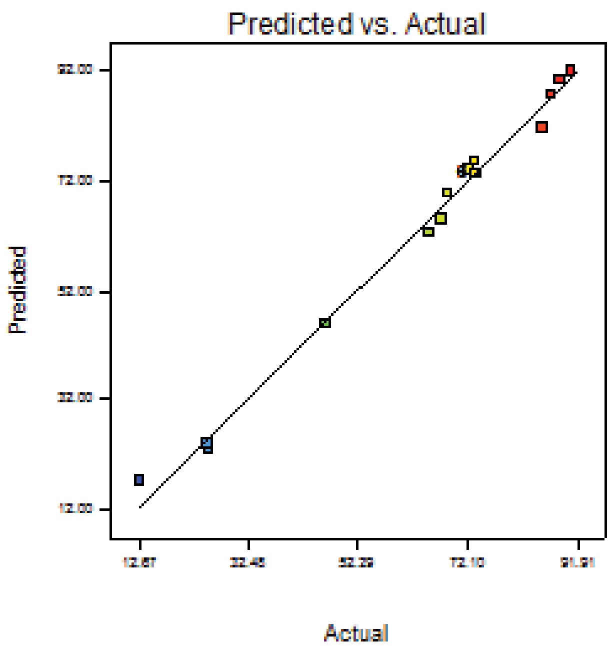

Fig. 2. Scatter plot of predicted vs. actual for the biosorption of Co(II) by *Homalothecium sericeum*.

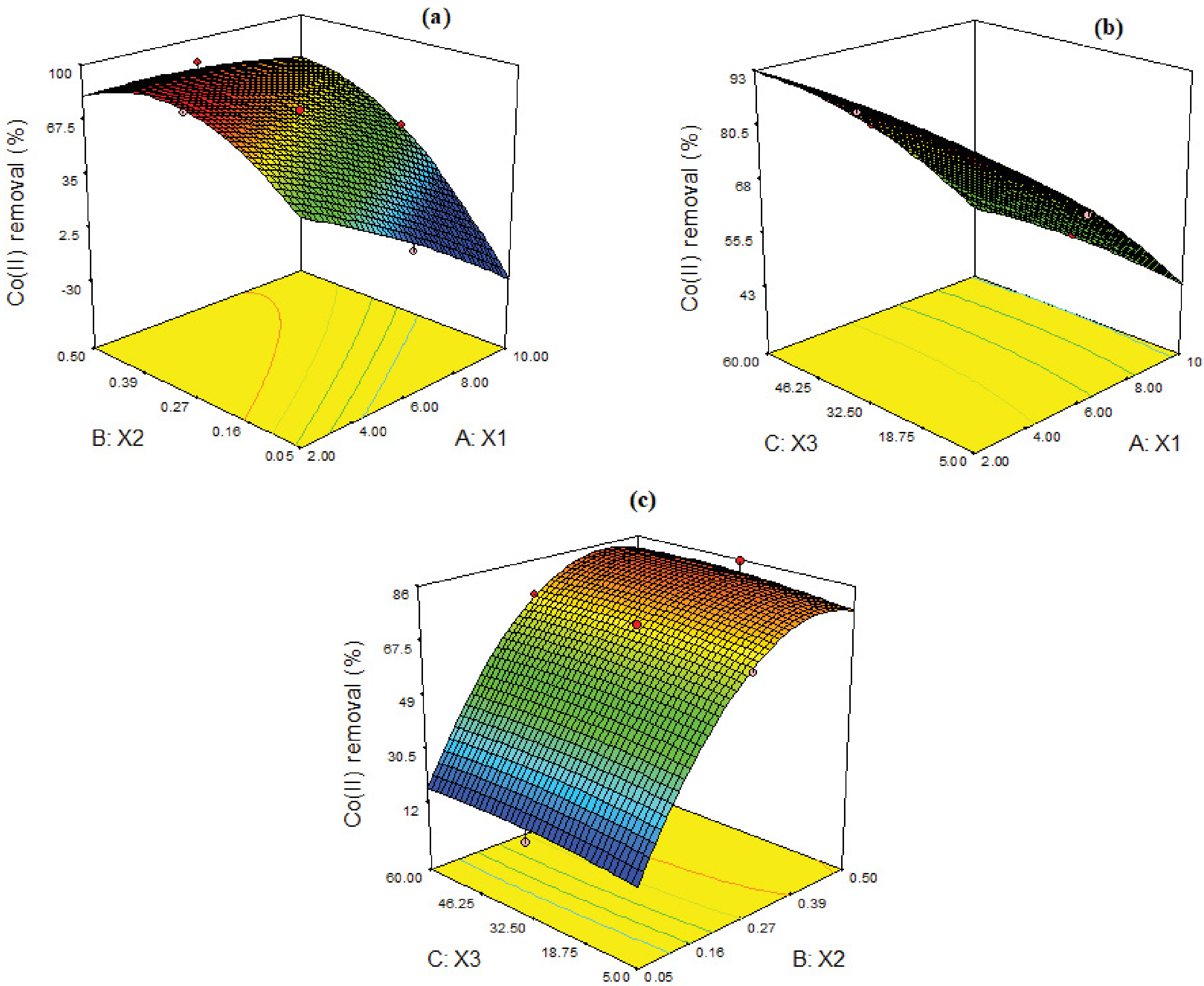

Fig. 3. 3-D response surface plots for the biosorption of Co(II) by *Homalothecium sericeum* (X_1: initial Co(II) concentration (mg/L); X_2: *Homalothecium sericeum* amount (g/50 mL); X_3: process time (min)).

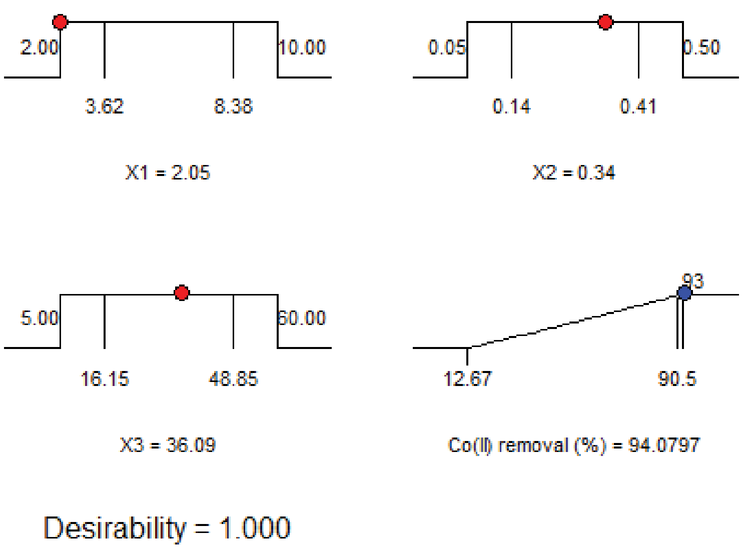

Fig. 4. Desirability ramp for optimization of the Co(II) biosorption by *Homalothecium sericeum*.

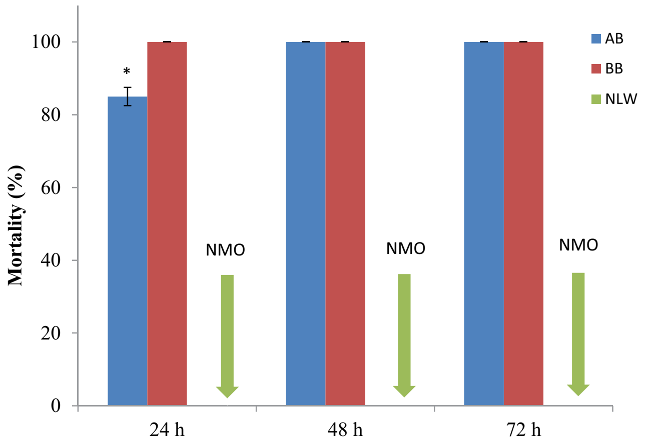

Fig. 5. The mortality rates of *Daphnia magna*, AB: after biosorption (94.07% removal), BB: before biosorption (2.05 mg/L Co(II)), NLW: natural living water, NMO: not mortality observed. The asterix (*) on the bar indicate the statistically differences between groups at the same periods according to independent *t*-test. $n = 20$, mean ± SE

3.3. Optimization process for biosorption of Co(II)

By utilizing numerical optimization, a desired value can be chosen for each input factor and response. Possible input optimizations to select from here include: minimum, range, maximum, target, none (for responses), and set to generate an output value optimized for a given set of condition [34]. In present study, the response is designed to reach a maximum while the input variables are given certain ranged values. Utilizing these conditions, the maximum Co(II) removal efficiency achieved is 94.07% at an initial Co(II) concentration of 2.05 mg/L, a *H. sericeum* amount of 0.34 g/50 mL, and a process time of 36.09 min (Fig. 4). To control the 94.07% Co(II) removal efficiency achieved by the model, a Co(II) removal efficiency of 93.02% was obtained by confirmatory experiment performed under optimal conditions. This demonstrates the accuracy and fit of the model.

3.4. D. magna bioassay

It was observed that all individuals used in the experiment died after 24 h of application before biosorption. Based on this situation, no living individuals remained until the 48th and 72nd hour, which are the continuation of the application. The mortality rate at the 24th hour after biosorption was 85%. In the continuation of the experiment, this rate reached 100% and no living individuals remained. The absence of death in the natural living water during the experimental period showed that the normal biology of the model organisms used was healthy. (Fig. 5).

As can be seen from Fig. 5 although the removal rates are at high levels, these rates are insufficient for the reduction of mortality. Similarly, Stubblefield et al. [35] reported that the cobalt even at very low concentrations have high toxicity on invertebrates. Also, In the study of Edwin et al. [36] the LC_{50} value they found was similar to the concentration of the medium after biosorption in our study. This shows us that the toxic effects of cobalt are still high. In order for this effect to disappear or mortality rates to be seen at lower levels, it is thought that there is more removal efficiency or different application times.

4. Conclusion

In our study, the maximum Co(II) removal efficiency achieved is 94.07% at an initial Co(II) concentration of 2.05 mg/L, a *H. sericeum* amount of 0.34 g/50 mL, and a process time of 36.09 min. Also, the toxicity of the medium after biosorption carried out under optimized conditions was also tested with the *D. magna* bioassay. Although a high removal efficiency of 94.07% was obtained in our study, this situation was not reflected in the mortality results due to the very high toxicity of Co(II). At the same time, it has been shown that wastewater containing Co(II) still carries an ecotoxicological risk, even though it has been improved with a high removal rate.

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