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Response Surface Modeling and Optimization of Cu (II) Removal from Waste Water Using Borasus Flabellifer Coir Powder

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Abstract: In the present work, Cu (II) removal from waste water was investigated using *Borasus flabellifer* coir powder as adsorbents in batch mode experiments. The effect of such parameters as initial Cu (II) concentration (20-60 mg/L), pH (5-7), and biomass dosage (10-14 g/l) on Cu (II) removal have been investigated using response surface methodology. The Box-Behnken experimental design in response surface methodology was used for designing the experiments as well as for full response surface estimation and 15 trials as per the model were run. The optimum input parameters for maximum removal of Cu (II) from an aqueous solution of 20 mg/L were as follows: biomass dosage (12.3646 g/L), pH (6.30642) and initial Cu (II) concentration (25.0414 mg/L). The high correlation coefficient (R^2=0.977) between the model and the experimental data showed that the model was able to predict the removal of Cu (II) from waste water using *Borasus flabellifer* coir powder efficiently.

Keywords: Response surface methodology; box-behnken design (BBD); borasus flabellifer coir powder; Cu (II) removal.

1. Introduction

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment [1]. Primarily some anthropogenic activities such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals [2, 3]. Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity [4, 5]. Among these heavy metals, copper is considered as one of the most toxic one. The potential source of copper in industrial effluents includes paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and painting bath etc. The excessive intake of copper may cause renal and hepatic damage, severe mucosal, irritation, wide spread capillary damage, gastrointestinal irritation and possibly necrotic changes in kidney and liver. World health organization (WHO) recommends that toxic limits of Cu (II) concentration in drinking water at the level of 1.5 mg/L [6]. Consequently, it is essential that the potable water should be given some treatment before domestic supply.

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Conventional methods for the removal of copper from the industrial wastewater include reduction followed by chemical precipitation [7], ion exchange [8], reduction [9], electrochemical precipitation [10], solvent extraction [11], membrane separation [12], evaporation [13] and foam separation [14]. Above cited processes are costly or ineffective at small concentrations. Therefore, biosorption of copper using non-conventional biosorbents is opted as one of the economical methods for recovering small concentrations of copper from waste water. A lot of research was focused on biosorbent materials which can efficiently remove heavy metals from aqueous bodies.

In this work, it has been reported the results obtained through the batch experimentations on removal of Cu (II) from waste water by *Borasus flabellifer* coir powder. The influence of several operating parameters such as initial Cu (II) concentration, pH, and biomass dosage were investigated in batch mode. The conventional technique for the optimization of a multivariable system usually defines one-factor at a time, does not depict the combined effect of all the factors involved and also requires a lot of experiments, time consuming and could not reveal the alternative effects between components [15]. Statistical technique in response surface methodology (RSM) takes in to account the interactions between the process parameters and reduces the number of experiments to be conducted. Otherwise it is very difficult to obtain the interactions between the process parameters even after conducting numerous experiments [16]. By using this technique, the optimum operational condition of the process can also be determined. Table 1 gives the applications of Box-Behnken design for the removal of heavy metals by different biosorbents in separation technology.

Table 1. Some applications of box-behnken design in separation technology

S.No.	Metal	Adsorbent	Objective of the study	References
1.	Cr (VI)	*Mixed culture of pseudomonas aeruginosa & bacillus subtillis*	To evaluate the effects and interactions of the process variables, biomass concentration, pH, temperature and contact time.	[17]
2.	Cr (VI)	*Borasus flabellifer* coir powder	To study the influence the three parameters, initial concentration, pH and biomass dosage for the maximum removal of Cr (IV)from aqueous solution	[18]
3.	Cadmium (II)	Cynobacterium *synechocystis pevalekii*	To study the optimize pH, biomass and metal concentration for cadmium removal.	[19]
4.	Cadmium (II)	*Carbon aerogel*	To study the optimize pH, biomass dosage and temperature for cadmium removal.	[20]
5.	Cr (VI) Ni (II) Zn (II)	*Bacillus brevis Sp.*	To evaluate the interactive effects of three most important parameters pH, temperature and metal ion concentration.	[21]
6.	Pb (II) Cd (II) Cu (II)	Trichoderma viride	To optimize the various environmental conditions for biosorption of Pb (II), Cd (II) and Cu (II) by investigating as a function of initial metal ion concentration, temperature, biosorbent loading and pH.	[22]

7.	Cu (II)	*Ascophyllum nodosum*	To evaluate the effects of temperature, pH and initial concentration in the Cu (II) sorption process on the adsorption	[23]
8.	Pb (II)	*Carbon aerogel*	To study the influence the three parameters, adsorbent concentration, pH and temperature on the percentage removal of Pb (II).	[24]
9.	Pb (II)	*Pistacia vera L*	To study the influence the three parameters, initial concentration, pH and contact time for the maximum removal of Pb (II)from aqueous solution.	[25]
10.	Cr (VI)	*Limonia acidissima hull* powder	To study the influence the three parameters, initial concentration, pH and biomass dosage for the maximum removal of Cr (IV)from aqueous solution	[29]
11.	Cr (VI)	Treated *helianthus annuus*	To study the effect of pH, initial concentration and dosage on chromium adsorption.	[30]

In the present investigation, batch experimental studies were carried out for the removal of Cu (II) from waste water using *Borasus flabellifer* coir powder. The experimental data points were used to obtain experimental model from Box-Behnken design. The input parameters for the percentage removal of Cu (II) are initial Cu (II) concentration, biomass dosage and pH. The process optimization has been carried out using BBD to optimize the input parameters to the process for maximum Cu (II) removal.

2. Materials and methods

2.1. Chemicals

Copper (II) sulfate, $CuSO_4.5H_2O$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck. Stock solution of Copper (II) sulfate having concentration of about 1 g/L was prepared by using double distilled water. Various concentrations of test solution of Cu (II) ranging from 20-100 mg/L were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 6, using a pH meter. Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

2.2. Preparation of the adsorbent

The *Borasus flabellifer* coir was obtained from local market; washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained at the range of 100 µm.

2.3. Batch mode adsorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration (20-100 mg/L), biomass dosage (0.1-0.7 gm in 50 mL solution), agitation time (0-150 min), pH (2-10) and biosorbent size (100 μm). The solution containing adsorbate and biosorbent was taken in 250 mL capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

2.4. Metal analysis

Final residual metal concentration after adsorption was measured by Atomic absorption Spectrophotometer.

To estimate the percentage removal of copper from aqueous solution, the following equation was used.

$$\text{Removal of Cu (II)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

Metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)v}{1000w} \tag{2}$$

where q_e (mg/g) is the amount of copper adsorbed per unit weight of biosorbent, C_0 and C_e are the initial and equilibrium metal ion concentration (mg/L), v is the volume of aqueous solution (ml) and w is the biosorbent weight (g).

2.5. Experimental design and procedure

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [16]. A standard RSM design called Box-Behnken Design (BBD) was applied in this work to study the variables for removal of copper from aqueous solution using a batch process. BBD for three variables (initial Cu (II) concentration, pH and biomass dosage), each with two levels (the minimum and maximum), was used as experimental design model. The model has advantage that it permits the use of relatively few combinations of variables for determining the complex response function [26]. A total of 15 experiments are needed to conduct and to determine 10 coefficients of second order polynomial equation [27, 28]. In the experimental design model, initial Cu (II) concentration (20-60 mg/L), pH (5-7) and biomass dosage (10-14 g/L) were taken as input variables. Percentage removal of Cu (II) was taken as the response of the system. Three factors were studied and their low and high levels are given in Table 2. The experimental design matrix derived from BBD is given in Table 3.

Table 2. Coded and actual values of variables of the experimental design

Factor		Coded levels of variables		
		-1.00	0	1.00
Initial concentration (mg/l)	X1	20	40	60
pH	X2	5	6	7
Biomass loading (g/l)	X3	10	12	14

Matlab program was used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The variability in dependent variables was explained by the multiple coefficient of determination, R^2 and the model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range [16].

3. Results and discussions

3.1. Results of BBD experiments

The results of the each experiments performed as per the software are given in Table 3. Empirical relationships between the response and the independent variables have been expressed by the following quadratic model.

$$Y = 94.4767 - 3.0163X_1 + 9.6775X_2 + 0.1437X_3 - 1.7371X_1^2 - 14.2696X_2^2 - 0.8071X_3^2 + 1.365X_1X_2 - 0.0025X_1X_3 + 0.485X_2X_3 \quad (3)$$

where Y is the percentage removal of Cu (II), X_1 is initial concentration of Cu (II), X_2 is pH and X_3 is the biomass dosage.

Table 3. Experimental design and results for the copper removal

Run	Coded Values			Actual values			Cu(II) removal		Relative error	Percentage absolute relative error
	x1	x2	x3	X1	X2	X3	Observed	Predicted		
1	-1	-1	0	20	5	12	73.94	73.1738	0.7662	1.0363
2	-1	1	0	20	7	12	87.05	89.7988	-2.7488	3.1577
3	1	-1	0	60	5	12	67.16	64.4113	2.7487	4.0927
4	1	1	0	60	7	12	85.73	86.4963	-0.7663	0.8938
5	-1	0	-1	20	6	10	96.05	94.8025	1.2475	1.2988
6	-1	0	1	20	6	14	95.83	95.095	0.735	0.7669
7	1	0	-1	60	6	10	88.04	88.775	-0.735	0.8348
8	1	0	1	60	6	14	87.81	89.057	-1.2475	1.4207
9	0	-1	-1	40	5	10	68.05	70.064	-2.0138	2.9593
10	0	-1	1	40	5	14	67.88	69.3812	-1.5012	2.2115
11	0	1	-1	40	7	10	89.95	88.449	1.5012	1.6689
12	0	1	1	40	7	14	91.72	89.706	2.0137	2.1955
13	0	0	0	40	6	12	93.93	94.477	-0.5467	0.5821
14	0	0	0	40	6	12	94.593	94.477	0.0533	0.0563

15	0	0	0	40	6	12	94.97	94.477	0.4933	0.5194

Regression coefficients of full polynomial model were given in Table 4. Analysis of variance has been calculated to analyze the accessibility of the model. The analysis of variance for the response was in Table 5. To evaluate the goodness of the model, the coefficient of variation (the ratio of the standard error of estimate to the mean value expressed as a percentage) and *F*-value tests has also been performed. The *F* distribution is a probability distribution used to compare variances by examining their ratio. If they are equal then *F* value would equal to one. The *F* value in the ANOVA table is the ratio of model mean square (MS) to the appropriate error mean square. The larger the ratio, the larger the *F* value and the more likely that the mean square contributed by the model is significantly larger than error mean square. As a general rule, if *p*-value is less than 0.05, model parameter is significant (refer to Table 4). On the basis of analysis of variance, the conclusion is that the selected model adequately represents the data for Cu (II) removal from aqueous solution by *Borasus flabellifer* coir powder. The experimental values and the predicted values are in closely match with R^2 value of 0.977 (refer to Figure 1). So, The high correlation coefficient (R^2=0.977) between the model and the experimental data showed that the model was able to predict the removal of Cu (II) from waste water using *Borasus flabellifer* coir powder efficiently. This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in biosorption. The optimum values of initial concentration of Cu (II), pH and biomass dosage from BBD were found to be 25.0414 mg/l, 6.30642 and 12.3646g/L respectively. The maximum predicted removal of Cu (II) was found to be 99.7242%.

Table 4. Regression coefficient of full polynomial model (*significant, if $p<0.05$)

Coefficient	Parameter estimate	p-Value
β0	94.4767	0.0000*
β1	-3.0163	0.0217*
β2	9.6775	0.0001*
β3	0.1437	0.8816
β11	-1.7371	0.2545
β22	-14.2696	0.0001*
β33	-0.8071	0.5760
β12	1.365	0.3408
β13	-0.0025	0.9985
β23	0.4850	0.7238

Table 5. ANOVA test results

Source of variation	Degrees of freedom	Sum of squares	Mean square	F-Value	p-Value
Regression	9	1584.345	176.0384	26.1639	0.0011
Residual	5	33.6414	6.7283		
Total	14	1617.9869			

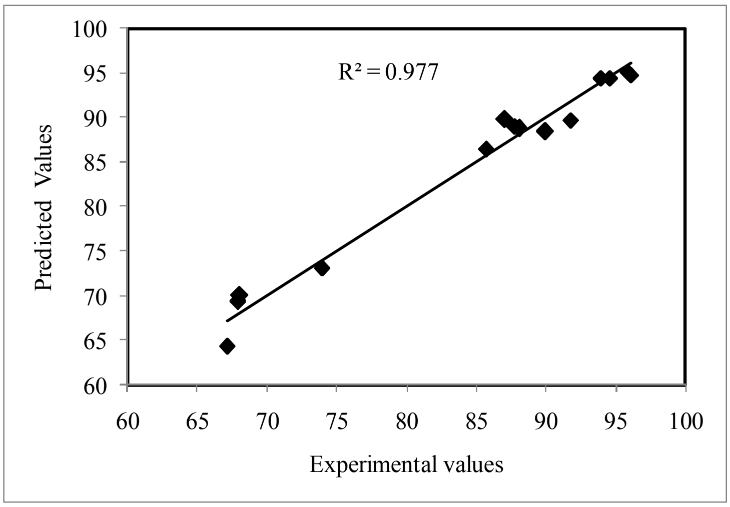

Figure 1. Parity plot showing the distribution of experimental vs predicted values of percentage removal of Cu (II)

3.1.1. Effect of pH and initial concentration of Cu (II) on removal of Cu (II) by borasus flabellifer coir powder

The percentage removal of Cu (II) with *Borasus flabellifer* coir powder was studied by pre-selected range of pH and initial concentration of Cu (II). The results have been depicted in Figure 2. The results indicated that the maximum removal has been occurred in the acidic range and at low initial concentration of Cu (II). Further, the 3D graph obtained from the software, it is clear that the removal of Cu (II) increased at low pH values, after words decreased and decreased with increased initial concentration of Cu (II).

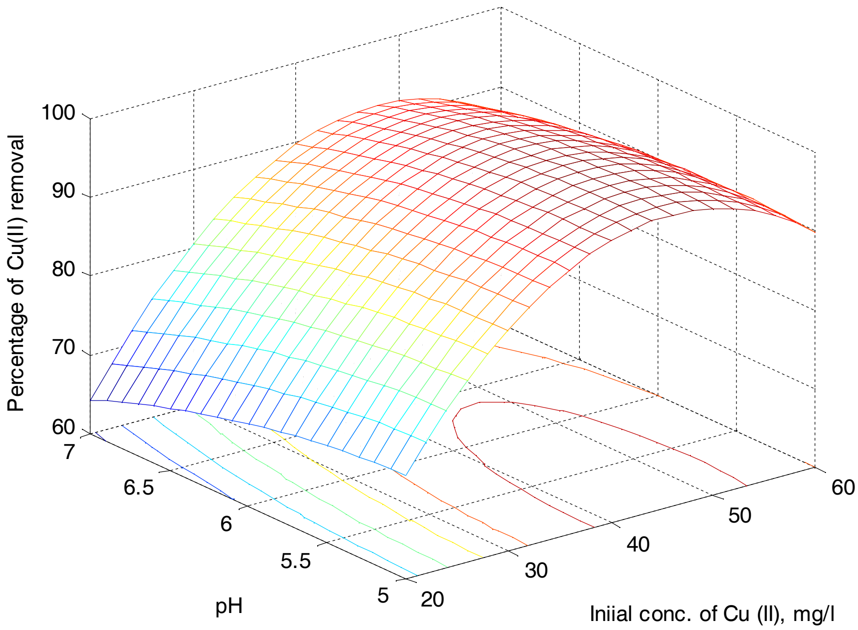

Figure 2. Response surface of 3D plot indicating the effect of interaction between initial concentration and pH on removal of Cu (II) while holding the biomass loading at 12.3646 g/L

3.1.2. Effect of pH and biosorbent dosage on removal of Cu (II) by *borasus flabellifer* coir powder

pH and biomass dosage are most important process parameters for assessing the removal capacity of an biosorbent. Adsorption experiments were carried out as per the selected model with selected range of pH and biomass dosage. The maximum removal of Cu (II) metal ions was 99.7242% for *Borasus flabellifer* coir powder at pH 6.30642 and biomass dosage 12.3646 g/l (Figure 3). Thus with *Borasus flabellifer* coir powder, adsorption takes place mainly in acidic medium. Further, the 3D graph obtained from the software, it is clear that the removal of Cu (II) increased at low pH values, after words decreased and increased with increased biomass dosage.

3.1.3. Effect of biosorbent dosage and initial concentration of Cu (II) on removal of Cu (II) by borasus flabellifer coir powder

The combined effect of biomass dosage and initial concentration Cu (II) has been presented in Figure 4. The results show that the maximum removal was recorded at the 12.3646 g/l biomass dosage and lower initial concentration of Cu (II). Further, the 3D graph obtained from the software, it is clear that the removal of Cu (II) increased with increased biomass dosage and decreased with increased initial concentration of Cu (II)

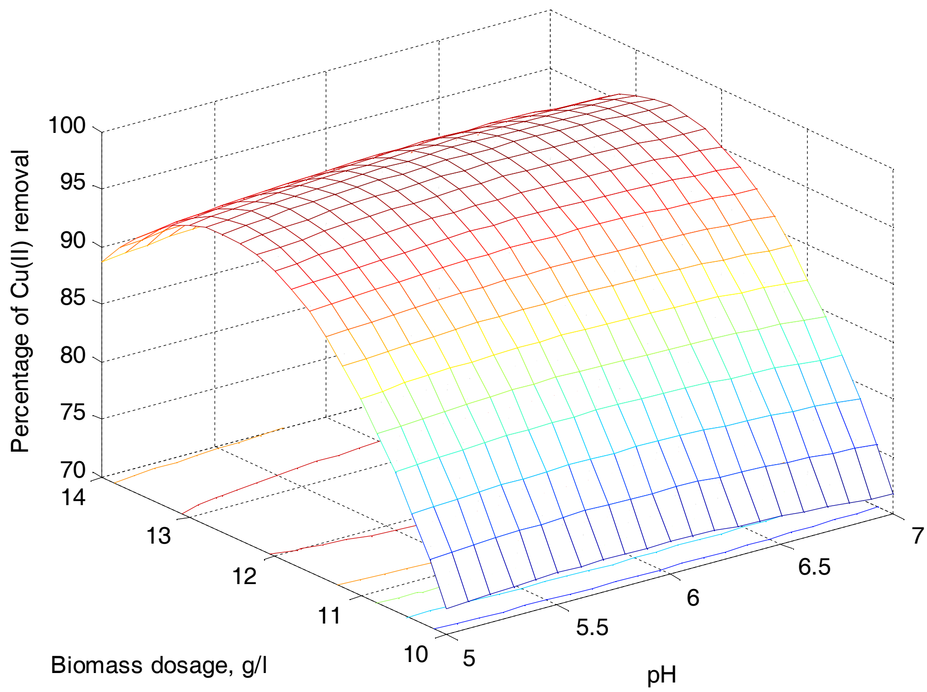

Figure 3. Response surface of 3D plot indicating the effect of interaction between biomass loading and pH on removal of Cu (II) while holding initial concentration at 25.0414 mg/L

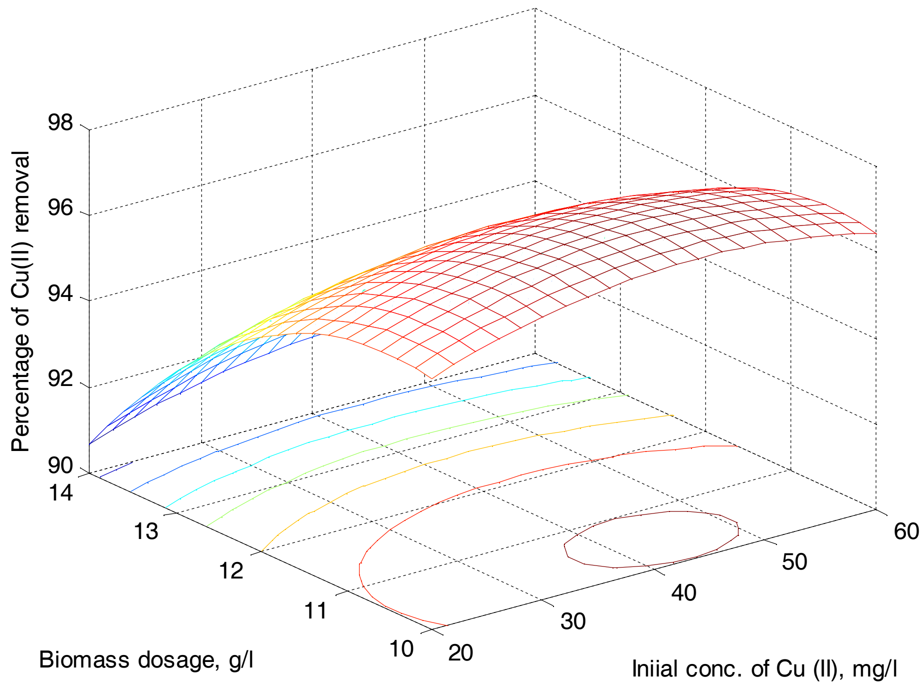

Figure 4. Response surface of 3D plot indicating the effect of interaction between biomass loading and initial concentration of Cu (II) on removal of Cu (II) while holding the pH at 6.30642 g/L

4. Conclusions

A detailed batch experimental study was carried out for the removal of Cu (II) from waste water by using *Borasus flabellifer* coir powder. The objective of the present study was to find out the optimum process conditions, using response surface methodology for the removal of Cu (II) from waste water by *Borasus flabellifer* coir powder as biosorbent. Response surface methodology using BBD proved very effective and time saving model for studying the influence of process parameters on response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions. The Experimental values and the predicted values are in perfect match with R^2 value of 0.977. This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in biosorption. The optimal removal of Cu (II) was obtained as initial concentration of Cu (II), pH and biomass dosage and these were found to be 25.0414 mg/L, 6.30642 and 12.3646 g/L respectively, resulting in 99.7242% of maximum predicted removal of Cu (II). Eigen values of the model are -14.311, -1.7008 and -0.80258. Negative eigen values represent that the system is stable. If one of the eigen value is positive, the system is unstable.

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