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Response Surface Modeling and Optimization of Chromium (Vi) Removal From Aqueous Solution Using *Borasus Flabellifer* Coir Powder

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Abstract: The potential use of *Borasus flabellifer* coir powder for the removal of chromium (VI) from aqueous solution has been investigated in batch mode experiments. Percentage removal of chromium (VI) is found to be 97.6% at pH 2, amount of adsorbent dosage of 0.5 g in 50 mL solution and temperature of 303 K. Influences of parameters like initial chromium (VI) concentration (5-30 mg/L), pH (1-3), and biomass dosage (10-14 g/L) on chromium (VI) adsorption were examined 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 conditions for maximum removal of chromium (VI) from an aqueous solution of 20 mg/L were as follows: adsorbent dosage (10.1869 g/L), pH 1.9 and initial chromium (VI) concentration (6.3244 mg/L). The high correlation coefficient (R^2 =0.989) between the model and the experimental data showed that the model was able to predict the removal of chromium (VI) from aqueous solution using *B. flabellifer* coir powder efficiently.

Keywords: Box-behnken design (BBD); borasus flabellifer coir powder; chromium (VI); adsorption.

1. Introduction

Water contamination with heavy metals is a very severe problem all over world [1, 2]. The world production of chromite ore is several millions of tons in a year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (the aluminothermic process) or by electrolysis of either CrO_3 or chrome alum solutions. Chromium and its compounds are extensively used in metal finishing, leather tanning, electroplating, textile industries, and chromate preparation [3]. In aqueous phase chromium mostly exists in two oxidation states, namely, trivalent chromium (Cr^{+3} and $Cr(OH)^{2+}$) and hexavalent chromium ($HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$, etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic. For example, it was reported that $Cr_2O_7^{2-}$ can cause lung cancer [4, 5].

Chromium (III) and Chromium (VI) have major environmental significance because of their stability in the natural environment. Cr (VI) is known to have 100 fold more toxicity than Cr (III)

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because of its high water solubility and mobility as well as easy reduction [6]. International agency for research on cancer has determined that Cr (VI) is carcinogenic to humans. The toxicological effect of Cr (VI) originates due to oxidizing nature as well as the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell [8]. Therefore, the World Health Organization (WHO) recommends that the toxic limits of chromium (VI) in waste water at the level of 0.05 mg/L, while total Chromium containing Cr (III), Cr (VI) and other species of chromium is regulated to be discharged below 2 mg/L [7].

Several methods are used to remove chromium from the industrial wastewater. These include reduction followed by chemical precipitation [9], ion exchange [10], reduction [11], electrochemical precipitation [12], solvent extraction [13], membrane separation [14], evaporation [15] and foam separation [16]. Above cited conventional chromium elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. Since this noble approach is effective and cheap many researchers exploring appropriate biomaterials that effectively remove Cr (VI) from aqueous solutions [17, 18]. A variety of adsorbents like tamarind seeds [19], rice husk [20], *Azadirachta indica* [21], maize bran [22], red saw dust [23], wall nut hull [24], groundnut hull [25], and *Limonia acidissima* hull powder [26] were reported in the literature for removal of chromium from aqueous solutions or waste waters in a batch or column reactor system.

In this work, it has been reported the results obtained through the batch experimentations [45] on removal of chromium from aqueous solution by *B. flabellifer* coir powder. The influence of several operating parameters, such as initial chromium concentration, pH, and adsorbent dosage were investigated in batch mode. The conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. The conventional technique for the optimization of a multivariable system usually defines one-factor at a time. Such a technique needs to perform a lot of experiments and could not reveal the alternative effects between components. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable. Recently many statistical experimental design methods have been employed in chemical process optimization. Experimental design technique is a very useful tool for this purpose as it provides statistical models, which helps in understanding the interactions among parameters that have been optimized [27]. These methods involve mathematical models for designing chemical processes and analyzing the process results. Among them, response surface methodology (RSM) is one suitable method utilized in many fields. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [28]. 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)	Cynobacterium	To study the effect of initial concentration, pH and temperature on chromium adsorption	[31]
2.	Cr(VI)	Carbon aerogel	To achieve maximum removal efficiency, pH, initial metal ion concentration and charge were optimized.	[32]
3.	Cr(VI)	Treated *Helianthus annuus*	To study effect of pH, initial concentration and dosage on chromium adsorption.	[33]
4.	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.	[34]
5.	Zn(II)	Magnetic nanoparticle	To optimize three variables pH of solution, amount of extract and amount of nanoparticles for extraction of zinc samples	[35]
6.	Cd(II)	HCl solution	To study the effect of sampling flow rate, reagent concentration, pH and buffer concentration on biosorption of Cd(II)	[36]
7.	Cd(II)	*Synechocystis pevalekii*	To study the optimize pH, biomass and metal concentration for cadmium removal.	[37]
8.	Cd(II)	Carbon aerogel	To study the optimize pH, adsorbent dosage and temperature for cadmium removal.	[38]
9.	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.	[39]
10.	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.	[40]
11.	Hg	Carbon aerogel	To study the influence of three parameters *i.e.* initial concentration, pH and charge on the percentage removal of mercury.	[41]
12.	Cu(II)	*Ascophyllum nodosum*	To evaluate the effects of temperature, pH and initial concentration in the Cu(II) sorption process on the adsorption	[42]
13.	Pb(II)	Carbon aerogel	To study the influence the three parameters, adsorbent concentration, pH and temperature on the percentage removal of Pb(II).	[43]
14.	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.	[44]

In the present investigation, batch experimental studies were carried out for the removal of chromium (VI) from aqueous solution using *B. 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 chromium (VI) are initial chromium (VI) concentration, adsorbent dosage and pH. The process optimization has been carried out using BBD to optimize the input parameters to the process for maximum chromium (VI) removal.

2. Materials and methods

2.1. The diphenylcarbazide method

A 0.25% (w/v) solution of diphenylcarbazide was prepared in 50% acetone. Each sample solutions (15 mL) containing various concentrations of Cr (VI) were pipette out into 25 mL standard flasks. To this 2 mL of 3 M H_2SO_4 was added followed by 1 mL of diphenylcarbazide and total volume was made up to 25 mL using deionised, double distilled water. Chromium (VI) concentrations estimated by the intensity of the red brownish color complex formed, was measured using UV-spectrophotometer at 540 nm. The absorbance was measured indicating adherence to the Beer Lambert's law (0 to 30 mg/L).

2.2. Preparation of the adsorbent

The sorbents used were crushed *B. flabellifer* coir powder. The *B. flabellifer* coir was obtained from local market; materials were 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 in the range of 63 to 125 µm.

2.3. Preparation of chromium stock solution

Potassium dichromate ($K_2Cr_2O_7$) is used as the source for chromium stock solution. All the required solutions are prepared with analytical reagents and double-distilled water. The chromium (VI) stock solution (1000 mg/L) was made by dissolved 2.835 g of 99% $K_2Cr_2O_7$ in 1.0 L distilled water. Synthetic samples of different concentrations of chromium (VI) are prepared from this stock solution by appropriate dilutions. The chromium stock solution (100 mg/L) is prepared by diluting 100 mL of 1000 mg/L chromium stock solution with distilled water in 1000 mL volumetric flask up to the mark. Similarly solutions with different metal concentrations such as (5, 10, 15, 20, 25 and 30 mg/L) are prepared.

$$Cr\ equivalent\ to\ 1\ gm = \frac{Molecular\ weight\ of\ K_2Cr_2O_7 \times 100}{Atomic\ weight\ of\ Cr \times 2 \times purity} \quad (1)$$

2.4. Batch mode adsorption studies [45]

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage, agitation time and pH. The solution containing adsorbate and adsorbent 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).

2.5. Metal analysis

Final residual metal concentration after adsorption was measured by UV-Spectrophotometer after sample was complexed with 1-5 diphenylcarbazide. To estimate the percentage removal of chromium (VI) from aqueous solution, the following equation was used.

$$\text{Percentage removal of Cr (VI)} = \frac{C_0 - C_e}{C_0} \tag{2}$$

where, C_0 and C_e are the concentrations of chromium (VI) at the beginning and at the end of the adsorption process. The metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)v}{1000w} \tag{3}$$

Where q_e (mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, C_0 and C_e are the initial and equilibrium chromium ion concentration (mg/L), v is the volume of aqueous solution (mL), and w is the adsorbent weight (g).

2.6. 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 [28]. A standard RSM design called Box-Behnken Design (BBD) was applied in this work to study the variables for adsorption of chromium from aqueous solution using in a batch process. BBD for three variables (initial chromium (VI) 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 [29]. A total of 15 experiments are needed to be conducted to determine 10 coefficients of second order polynomial equation [30, 31]. In the experimental design model, initial chromium (VI) concentration (5-30 mg/L), pH (1-3) and biomass dosage (10-14 g/L) were taken as input variables. Percentage removal of chromium (VI) was taken as the response of the system. The experimental design matrix derived from BBD is given in Table 3.

Basically this optimization process involves three major steps, which are, performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model.

$$Y = f(X_{1,} X_{2,} X_{3,} X_{4,} .....X_n) \tag{4}$$

Where Y is the response of the system and X_i is the variables of action called factors. The goal is to optimize the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surfaces.

The optimization of Cr (VI) uptake was carried out by three chosen independent process variables using Box-Behnken design with 12 unique runs including 3-replicates at center points. The quadratic equation model for predicting the optimal point was expressed according to Eq (4).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^{\;2} + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta x_i x_j + \varepsilon \tag{5}$$

Three factors were studied and their low and high levels are given in Table 2. Percentage adsorption was studied with a standard RSM design called Box-Behnken Design (BBD). Fifteen experiments were conducted in duplicate according to the scheme mentioned in Table 3. *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 [28].

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)	X_1	15	20	25
pH	X_2	1	2	3
Biomass loading (g/L)	X_3	10	12	14

Table 3. Experimental design & results for the chromium removal & pH after contact time

Run	Coded Values			Actual values			Percentage removal of Cr(VI)		pH after contact time	
	X_1	X_2	X_3	X_1	X_2	X_3	observed	Predicted	observed	Predicted
1	-1	-1	0	15	1	12	91.15	91.4038	1.3	1.29
2	-1	1	0	15	3	12	89.25	89.5088	3.2	3.3
3	1	-1	0	25	1	12	87.75	87.4913	1.21	1.24
4	1	1	0	25	3	12	85.86	85.6063	3.4	3.3
5	-1	0	-1	15	2	10	93.86	93.3500	2.1	2.2
6	-1	0	1	15	2	14	92.47	92.4675	2.2	2.3
7	1	0	-1	25	2	10	90.45	90.4525	2.3	2.28
8	1	0	1	25	2	14	87.04	87.5500	2.1	2.18
9	0	-1	-1	20	1	10	88.18	88.4363	1.21	1.24
10	0	-1	1	20	1	14	86.79	86.5387	1.18	1.21
11	0	1	-1	20	3	10	86.29	86.5413	3.15	3.19
12	0	1	1	20	3	14	84.91	84.6538	3.16	3.18
13	0	0	0	20	2	12	93.43	93.6467	2.1	2.14
14	0	0	0	20	2	12	93.53	93.6467	2.1	2.13
15	0	0	0	20	2	12	93.98	93.6467	2.1	2.15

3. Results and discussions

3.1. Characterization of *B. flabellifer* coir powder

The scanning electron micrographs (SEM) of *B. flabellifer* coir powder before chromium (VI) adsorption and after chromium (VI) adsorption are shown in Figures 1 and 2. The surface morphology revealed that *B. flabellifer* coir powder was found to be irregular and porous and thus would facilitate the adsorption of metal ions on different parts of the *B. flabellifer* coir powder. The SEM micrographs showed that pores with different sizes and different shapes existed on external surface of *B. flabellifer* coir powder. The micrograph of *B. flabellifer* coir powder after chromium (VI) adsorption shows a reduction of number of pores, pore space and surface area available (refer to Figure 2). Hence it is confirmed that there is metal adsorption on the surface of adsorbent. Furthermore, the EDS spectra of selected zone of *B. flabellifer* coir powder before adsorption and after adsorption was carried out to investigate the chemical constituents in the carbon matrix (refer to Figure 3). It has been found from Figure 3(a) that *B. flabellifer* coir powder having the carbon, oxygen on its surface before interaction with Cr (VI) ions, whereas in Figure 3(b), new chromium peak was observed with the surface bearing groups of carbon and oxygen, which confirmed the Cr (VI) adsorption on *B. flabellifer* coir powder.

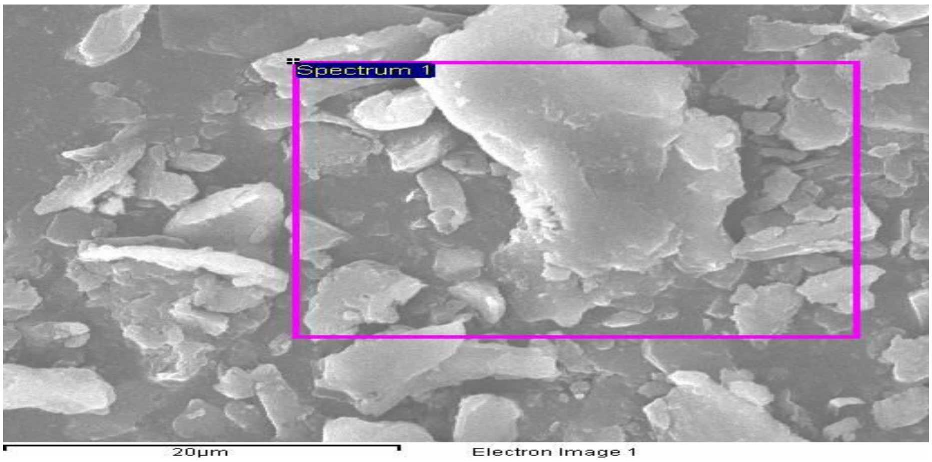

Figure 1. SEM images of *B. flabellifer* coir powder before chromium (VI) adsorption

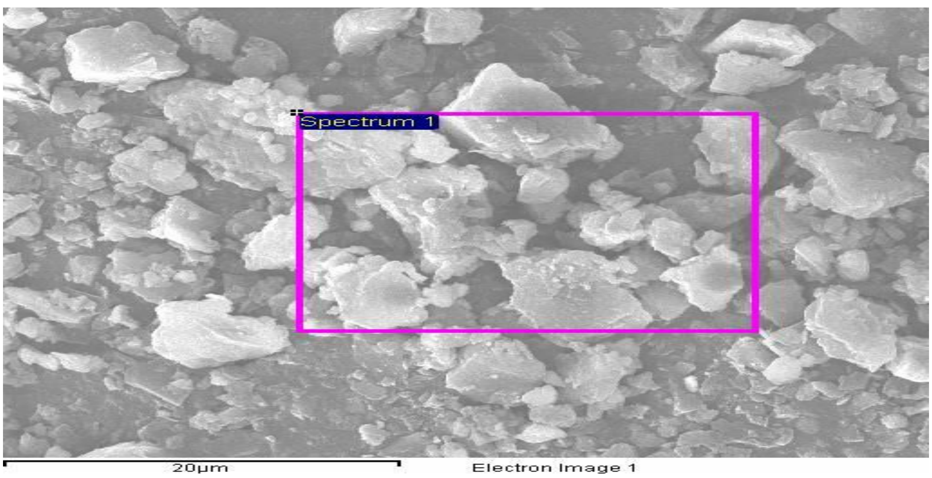

Figure 2. SEM images of *B. flabellifer* coir powder after chromium (VI) adsorption

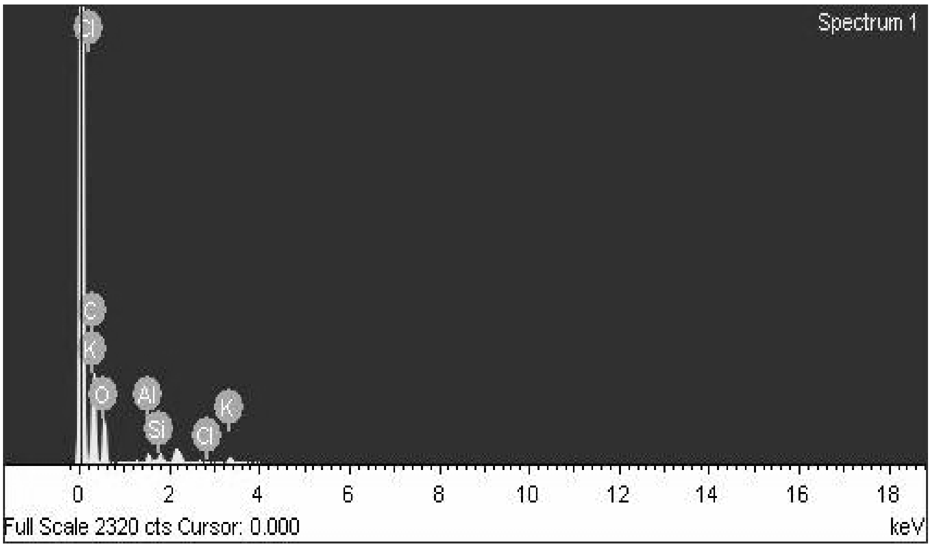

Figure 3. (a) Energy-disperse spectra of *B. flabellifer* coir powder before chromium (VI) adsorption

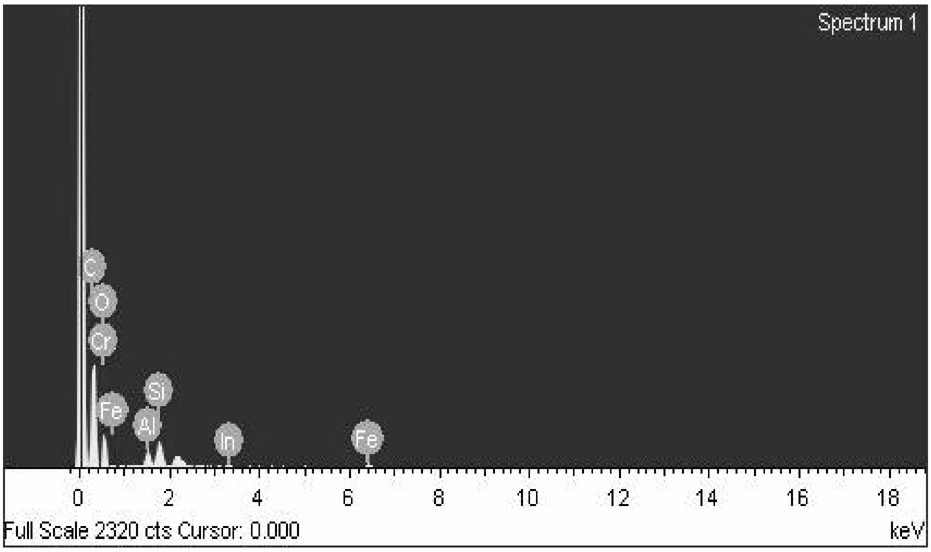

Figure 3. (b) Energy-disperse spectra of *B. flabellifer* coir powder after chromium (VI) adsorption

3.2. 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 adsorption.

$$Y = 93.6467 - 1.9538X_1 - 0.945X_2 - 0.9462X_3 - 0.3658X_1^2 - 4.7783X_2^2 - 2.3258X_3^2 + 0.0025X_1X_2 - 0.505X_1X_3 + 0.0025X_2X_3 \quad (6)$$

where Y is the percentage removal of Chromium (VI).

X_1 is the scaled initial concentration of Cr (VI), X_2 is pH and X_3 is scaled adsorbent dosage.

Regression coefficient of full polynomial model is given in Table 4. Analysis of variance has been calculated to analyze the accessibility of the model. The analysis of variance for the response has been predicted 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 variance contributed by the model is significantly larger than random error. As a general rule, if *p*-value is less than 0.05, model parameter is significant (Table 4). On the basis of analysis of variance, the conclusion is that the selected model adequately represents the data for chromium (VI) removal from aqueous solution by *B. flabellifer* coir powder. The Experimental values and the predicted values are in perfect match with R^2 value of 0.989 (Figure 4). 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 values of input variables from regression equations for the adsorption of chromium (VI) were shown in Table 6. The optimum values of initial concentration of chromium (VI), pH and adsorbent dosage from Box-Behnken design were found to be 6.3244 mg/L, 1.90043 and 10.1869 g/L respectively. The maximum predicted adsorption of chromium (VI) was found to be 98.9961%.

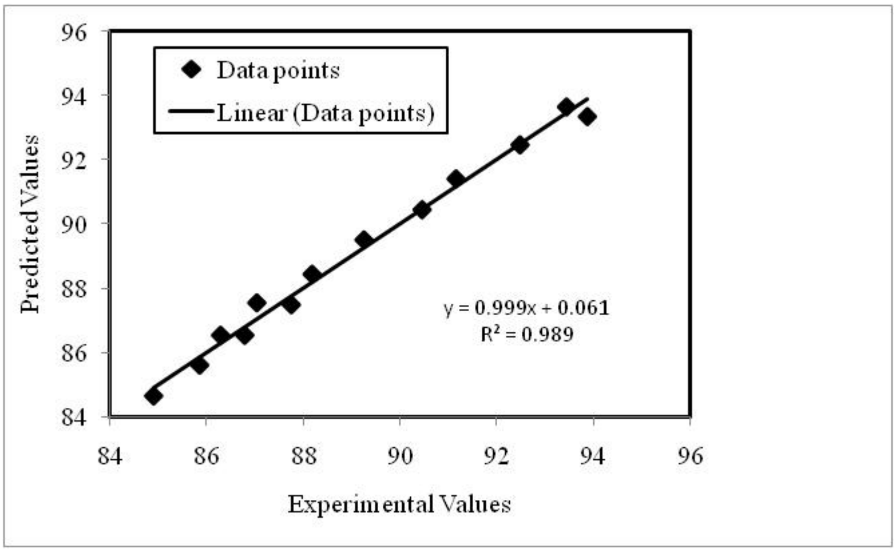

Figure 4. Parity plot showing the distribution of experimental vs predicted values of percentage removal of chromium (VI)

Table 4. Regression coefficient of full polynomial model. (*significant<0.05)

Coefficient	Parameter estimate	*p*-value
β0	93.6467	0.000
β1	-1.9538	0.0001
β2	-0.9450	0.0029
β3	-0.9462	0.0029
β11	-0.3658	0.2127
β22	-4.7783	0.000
β33	-2.3258	0.0003
β12	0.0025	0.9923
β13	-0.505	0.0955
β23	0.0025	0.9923

Table 5. ANOVA test results

Source of variation	Degrees of Freedom	Sum of squares	Mean square	*F*-value	*p*-value
Regression	9.00	144.4876	16.0542	66.2223	0.0001
Residual	5.00	1.2121	0.2424		
Total	14.00	145.6997			

Table 6. Optimum values of variables obtained from regression equations for the removal of chromium

S. No	Parameter	Optimum value	Maximum predicted value
1	Initial concentration	6.3244	98.99
2	pH	1.9	
3	Biomass loading (g/L)	10.1869	

3.2.1. Effect of pH and initial concentration of chromium (VI) on removal of Cr (VI) by *B. flabellifer* coir powder

The percentage adsorption of Cr (VI) with *B. flabellifer* coir powder was studied by pre-selected range of pH and initial concentration of chromium (VI). The results have been depicted in Figure 5. The results indicated that the maximum adsorption has been occurred in the acidic range and at low initial concentration of chromium (VI).

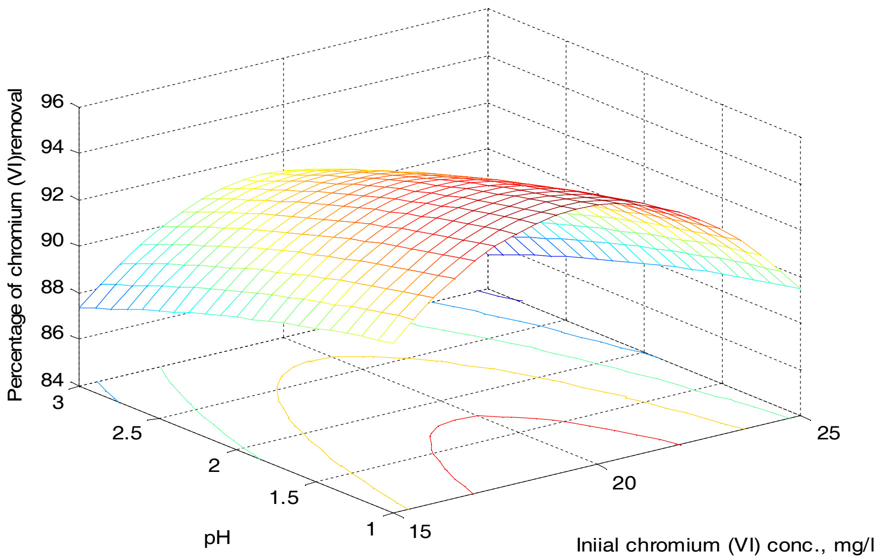

Figure 5. Response surface of 3D plot indicating the effect of interaction between initial concentration and pH on removal of chromium (VI) while holding the biomass loading at 10.1869 g/L

3.2.2. Effect of pH and adsorbent dosage on removal of Cr (VI) by *B. flabellifer* coir powder

The pH and adsorbent dosage are most important process parameters for assessing the removal capacity of an adsorbent. Adsorption experiments were carried out as per the selected model with selected range of pH and adsorbent dosage. The maximum adsorption of chromium (VI) metal ions was 94% for *B. flabellifer* coir powder at pH 1.9 and adsorbent dosage 10.1869 g/L (Figure 6). Thus with *B. flabellifer* coir powder, adsorption takes place mainly in acidic medium.

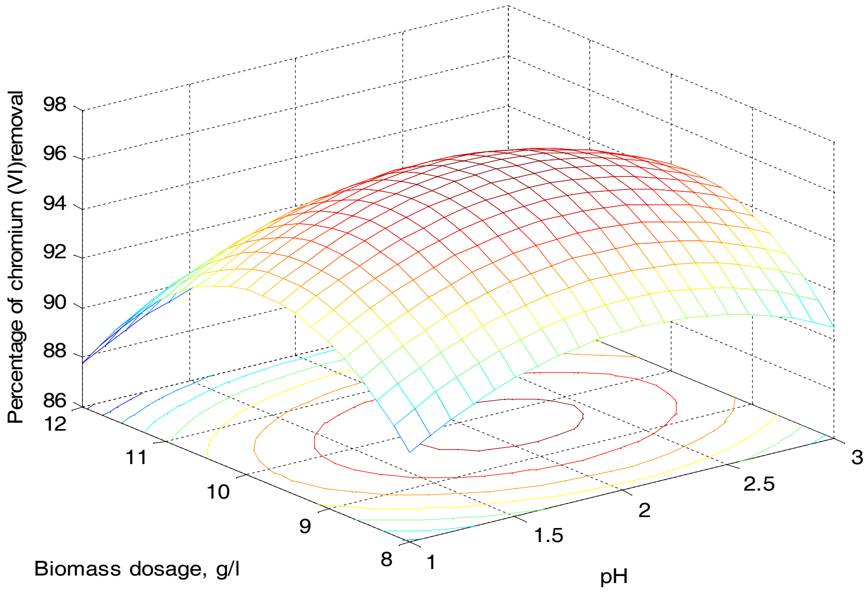

Figure 6. Response surface of 3D plot indicating the effect of interaction between biomass loading and pH on removal of chromium (VI) while holding initial concentration at 6.3244 mg/L

3.2.3. Effect of adsorbent dosage and initial concentration of chromium (VI) on removal of Cr (VI) by *B. flabellifer* coir powder

The combined effect of adsorbent dosage and initial concentration chromium (VI) has been presented in Figure 7. The results show that the maximum adsorption was recorded at the 10.1869 g/L adsorbent dose and lower initial concentration of chromium (VI).

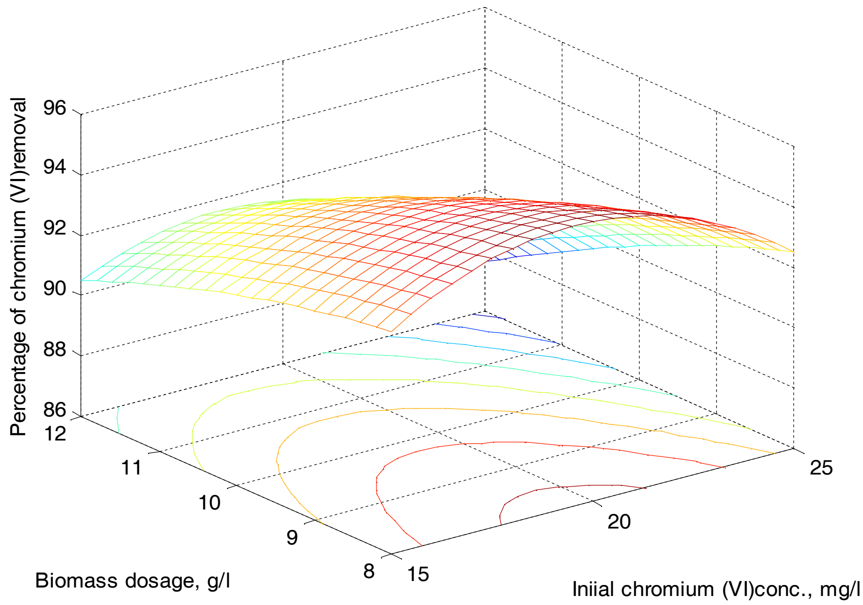

Figure 7. Response surface of 3D plot indicating the effect of interaction between biomass loading and initial concentration of chromium (VI) on removal of Chromium (VI) while holding the pH at 1.9

4. Conclusions

A detailed batch experimental study was carried out for the removal of chromium (VI) from aqueous solution by using *B. flabellifer* coir powder. The objective of the present study was to find out the optimum process conditions, using response surface methodological approach for the removal of chromium (VI) from aqueous solution by *B. flabellifer* coir powder as adsorbent. Response surface methodology using Box-Behnken design 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 0.989. 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 adsorption of chromium (VI) was obtained as initial concentration of chromium (VI), pH and adsorbent dosage and these were found to be 6.3244 mg/L, 1.9 and 10.1869 g/L, respectively, resulting in 98.99% of maximum predicted adsorption of chromium (VI).

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