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Response Surface Modeling and Optimization of Chromium (VI) Removal from Waste Water using Custard Apple Peel Powder

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Abstract

The potential use of custard apple peel powder for the removal of chromium (VI) from waste water has been investigated in batch mode experiments. Influences of parameters like initial chromium (VI) concentration (5 - 30 mg/l), pH (2 - 4), and biomass dosage (8 - 12 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 per the model were run. The optimum conditions for maximum removal of chromium (VI) from the waste water are as follows: adsorbent dosage (10.3613 g/l), pH (2.78459) and initial chromium (VI) concentration (9.03197 mg/l). The maximum percentage removal of chromium at optimum conditions was 92.82 % (with metal uptake of 2.3045 mg/g). The high correlation coefficient (R^2 = 0.997) between the model and the experimental data showed that the model was able to predict efficiently the percentage removal of chromium (VI) from waste water using custard apple peel powder.

Keywords: Response surface methodology, Box-Behnken design (BBD), custard apple peel powder, chromium (VI), adsorption

Introduction

Water contamination with chromium is a very severe problem as chromium and its compounds are extensively used in metal finishing, leather tanning, electroplating, textile industries, and chromate preparation [1]. Hexavalent chromium is more toxic than trivalent chromium and the World Health Organization (WHO) recommends that the toxic limits of chromium (VI) in waste water at the level of 0.05mg/l [2].

The conventional methods for the removal/ recovery of chromium (VI) include reduction followed by chemical precipitation [3], ion exchange [4], reduction [5], electrochemical precipitation [6], solvent extraction [7], membrane separation [8], evaporation [9] and foam separation [10]. Above cited processes are costly or ineffective at small concentrations. Therefore, adsorption of chromium using non-conventional adsorbents is opted as one of the economical methods for recovering small concentrations of chromium (VI) from waste water. A variety of non-conventional adsorbents like tamarind seeds [11], rice husk [12], *azadirachta indica* [13], maize bran [14], red saw dust [15], wall nut hull [16], groundnut hull [17], *limonia acidissima* hull powder [18] and custard apple peel powder [19] were reported in literature for removal of chromium from aqueous solutions or waste waters in a batch or column reactor system.

The mechanism of adsorption is highly complex and such nonlinear processes can be modeled by using a statistical technique, response surface methodology (RSM). This technique 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. By using this technique, the optimum operational condition of the process can also be determined [25]. For adsorbents cynobacterium [20], carbon aerogel [21] and treated *Helianthus annus* [22], *Borasus flabellifer* coir powder [23] and *Limonia acidissima* hull powder [24], optimum experimental parameters for the removal of chromium (VI) were obtained by using Box-Behnken experimental design technique of response surface methodology (RSM). In the present investigation, batch experimental data points [19] were used to develop model using Box-Behnken design (BBD) and to optimize the input process parameters such as initial chromium (VI) concentration, adsorbent dosage and pH for maximum Cr (VI) removal.

Materials and methods

The diphenylcarbazide method

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

Preparation of the adsorbent

The sorbent used was crushed custard apple peel powder. The custard apple peel was obtained from local market; materials were washed, dried, and crushed in a primary crusher and air dried in the sun for several days until its weight remained constant. After drying, it was crushed in a roll crusher and hammer mill. The material obtained through crushing and grinding was 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 pre-treatment was given to the materials. The particle sizes were maintained in the range of 63 to 125 μm.

Preparation of chromium stock solution

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

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

Batch mode adsorption studies [19]

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage and pH at equilibrium time of 50 min and temperature of 303 K. The solution containing adsorbate and adsorbent was taken in 250 ml capacity conical flasks and agitated at 180 rpm in a mechanical shaker at pre-determined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

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 [25]. 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 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 [26]. A total of 15 experiments is needed to be conducted to determine 10 coefficients of second order polynomial equation [20,27]. In the experimental design model, initial chromium (VI) concentration (5 - 30 mg/l), pH (2 - 4) and biomass dosage (8 - 12 g/l) were taken as input variables. Percentage removal of chromium (VI) was taken as the response of the system. Three factors were studied and their low and high levels are given in **Table 1**. The experimental design matrix derived from BBD is given in **Table 2**. 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 [25].

Results and discussion

Results of BBD experiments

The results of the each experiment performed as per the software are given in **Table 2**. Empirical relationships between the response and the independent variables have been expressed by the following quadratic model.

$$Y = 89.9467 - 1.1238X_1 - 1.2962X_2 + 0.6675X_3 - 0.2558X_1^2 - 3.0308X_2^2 - 1.8333X_3^2$$
$$+ 0.0075X_1X_3 - 0.0525X_2X_3$$

where Y is the percentage removal of chromium (VI), X_1 is initial concentration of Cr (VI), X_2 is pH, and X_3 is the adsorbent dosage.

Analysis of variance has been calculated to analyze the accessibility of the model. The analysis of variance for the response is given in **Table 3**. The regression coefficients of the full polynomial model are given in **Table 4**. 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 the 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, the 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 waste water by custard apple peel powder. The experimental values and the predicted values are in perfect match with R^2 value of 0.997 (**Figure 1**). This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in adsorption. The optimum values of initial concentration of chromium (VI), pH and adsorbent dosage from Box-Behnken design were found to be 9.03197 mg/l, 2.78459 and 10.3613 g/l respectively. The maximum predicted adsorption of chromium (VI) was found to be 92.8115 %.

Table 1 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	2	3	4
Adsorbent dosage (g/l)	X_3	8	10	12

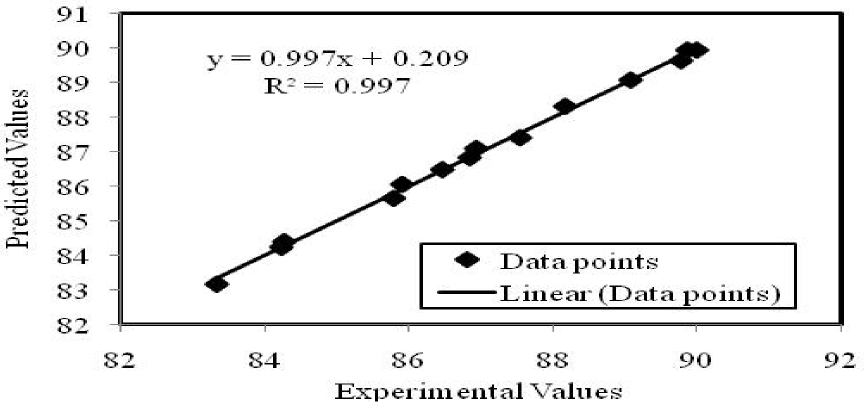

Figure 1 Parity plot showing the distribution of experimental versus predicted values of percentage removal of chromium (VI).

Table 2 Experimental design and results for the chromium removal.

Run	Coded values			Actual values			Cr (VI) removal		pH before and after contact time	
	X_1	X_2	X_3	x_1	x_2	x_3	observed	predicted	before	after
1	−1	−1	0	15	2	10	89.09	89.08	2.21	2.32
2	−1	1	0	15	4	10	86.47	86.488	4.13	4.22
3	1	−1	0	25	2	10	86.85	86.83	2.21	2.31
4	1	1	0	25	4	10	84.23	84.24	4.13	4.23
5	−1	0	−1	15	3	8	88.18	88.321	3.1	3.21
6	−1	0	1	15	3	12	89.79	89.641	3.1	3.22
7	1	0	−1	25	3	8	85.91	86.059	3.14	3.25
8	1	0	1	25	3	12	87.55	87.409	3.16	3.27
9	0	−1	−1	20	2	8	85.79	85.659	2.23	2.34
10	0	−1	1	20	2	12	86.94	87.099	2.12	2.23
11	0	1	−1	20	4	8	83.33	83.171	4.11	4.22
12	0	1	1	20	4	12	84.27	84.401	4.14	4.24
13	0	0	0	20	3	10	90.01	89.947	3.05	3.13
14	0	0	0	20	3	10	89.88	89.947	3.05	3.13
15	0	0	0	20	3	10	89.95	89.947	3.05	3.14

Table 3 ANOVA test results.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F-value	P-value
Regression	9	70.5799	7.8422	219.9264	0.000
Residual	5	0.1783	0.0357		
Total	14	70.7582			

Table 4 Regression coefficients of the full polynomial model. (*significant, if $P < 0.05$).

Coefficient	Parameter estimate	P-value
β_0	89.9467	0.000^*
β_1	−1.1238	0.000^*
β_2	−1.2962	0.000^*
β_3	0.6675	0.0002^*
β_{11}	−0.2558	0.0481^*
β_{22}	−3.0308	0.000^*
β_{33}	−1.8333	0.000^*
β_{12}	−0.0000	1.000
β_{13}	0.0075	0.9398
β_{23}	−0.0525	0.6021

Effect of pH and initial concentration of chromium (VI) on removal of Cr (VI) by custard apple peel powder

The percentage adsorption of Cr (VI) with custard apple peel powder was studied by specified range of pH and initial concentration of chromium (VI). The results have been depicted in **Figure 2**. The results indicated that the maximum adsorption was occurred in the acidic range and at low initial concentration of chromium (VI).

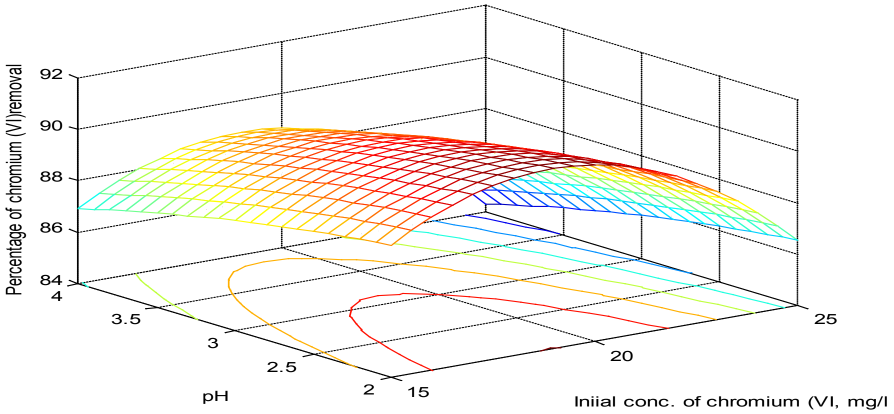

Figure 2 Response surface 3D plot indicating the effect of the interaction between the initial concentration and pH on removal of chromium (VI) while holding the adsorbent dosage at 10.3613 g/l.

Effect of pH and adsorbent dosage on removal of Cr (VI) by custard apple peel powder

Adsorption experiments were carried out as per the selected model with specified range of pH and adsorbent dosage for the fixed value of initial Cr (VI) concentration of 9.03197mg/l. The maximum adsorption of chromium (VI) metal ions was 90.89 % for custard apple peel powder at pH 2.78459 and adsorbent dosage 10.3613 g/l (**Figure 3**). Thus with custard apple peel powder, adsorption occur mainly in acidic medium.

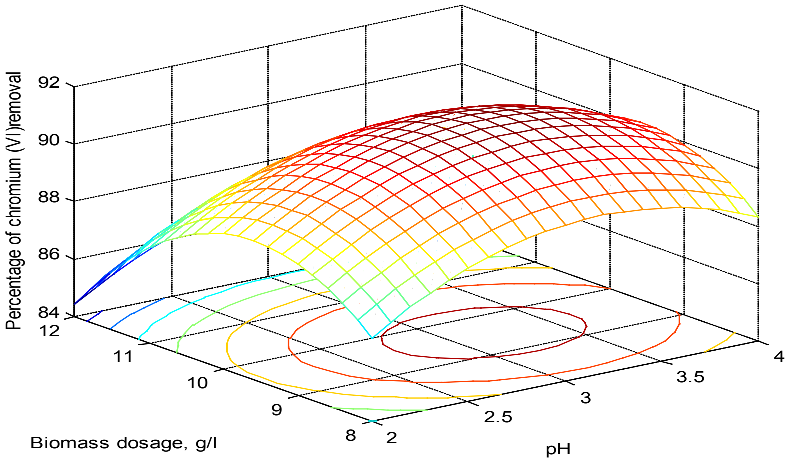

Figure 3 Response surface 3D plot indicating the effect of the interaction between the adsorbent dosage and pH on removal of chromium (VI) while holding the initial concentration at 9.03197 mg/l.

Effect of adsorbent dosage and initial concentration of chromium (VI) on removal of Cr (VI) by custard apple peel powder

The combined effect of adsorbent dosage and initial concentration chromium (VI) has been presented in **Figure 4**. The results indicate that the maximum adsorption was recorded at the adsorbent dosage of 10.3613 g/l adsorbent dose and lower initial concentration of chromium (VI) when pH is fixed at 2.78459.

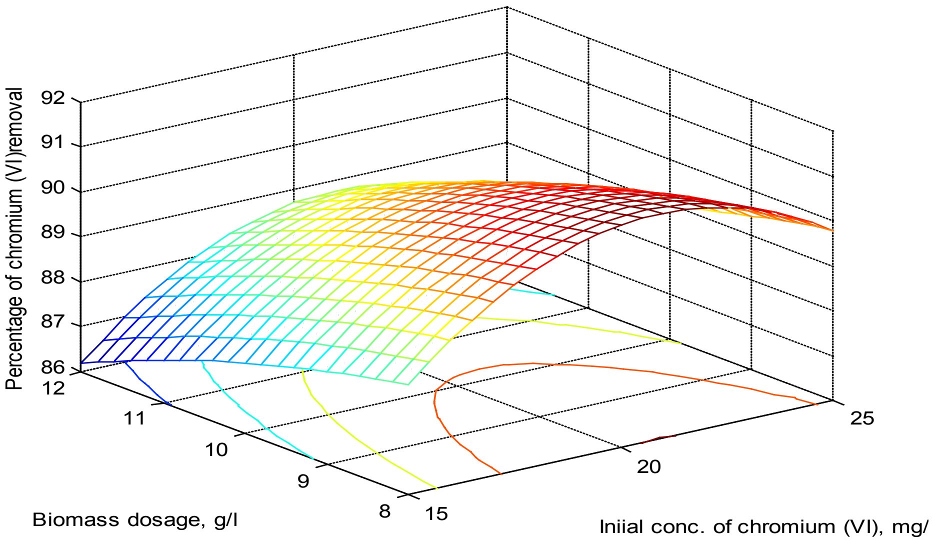

Figure 4 Response surface 3D plot indicating the effect of the interaction between the adsorbent dosage and initial concentration of chromium (VI) on removal of chromium (VI) while holding the pH at 2.78459.

Conclusions

A detailed batch experimental study was carried out for the removal of chromium (VI) from synthetic waste water by using custard apple peel powder. The objective of the present study was to find out the optimum process conditions, using response surface methodology with Box-Behnken design. 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 0.997. This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in adsorption. The optimal adsorption of chromium (VI) (92.82% removal) was obtained with an initial concentration of chromium (VI), pH and adsorbent dosage of 9.03197 mg/l, 2.78459 and 10.3613 g/l, respectively.

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