Songklanakarin J. Sci. Technol.
43 (1), 144-152, Jan. - Feb. 2021

http://www.sjst.psu.ac.th

Original Article

Predictability by Box-Behnken model for removal of chromium (VI) using *Eclipta prostrata* (Bhringraj) plant powder as an adsorbent

Jayasree P. K.[1], David K. Daniel[1*], Madhu G.[2], and Dipak Kumar Sahoo[2]

[1] *Department of Chemical Engineering, Amal Jyothi College of Engineering,*
Kanjirappally, Kerala, 686518 India

[2] *School of Engineering, Cochin University of Science and Technology,*
Kochi, Kerala, 682022 India

Received: 2 June 2019; Revised: 6 October 2019; Accepted: 28 November 2019

Abstract

The removal of hexavalent chromium ions from aqueous solutions using *Eclipta prostrata* (Bhringraj) plant powder was investigated using the batch adsorption technique. The contact time, pH, initial concentration of chromium (VI) ions and amount of adsorbent were optimized using the Box-Behnken experimental design in response surface methodology to study the effects and interactions of manipulated factors. The experimental data obtained were subjected to analysis of variance and fit with a quadratic model to relate the process parameters to chromium removal. The optimum conditions were found to be pH= 1.78, contact time = 4.31 h, adsorbent dosage = 12.51g/l and initial concentration = 250 mg/l. Confirmatory experiments performed to evaluate the accuracy of the prediction for optimal operating point yielded an adsorption efficiency of 96.69%, which is in a good agreement with the model prediction.

Keywords: *Eclipta prostrata*, biosorption, chromium (VI) ion, Bhringraj, Box-Behnken design, ANOVA, response surface methodology

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1. Introduction

Environmental contamination due to discharge of improperly treated effluents and wastes poses a major threat to communities. Most of these discharged effluents contain non-degradable and toxic heavy metals, the presence and accumulation of which affects living organisms (Aksu & Akpinar, 2001; Venkateswarlu, Ratnam, Rao & Rao, 2007). The presence of chromium in this context is of considerable concern, as it is widely used in metal finishing, leather tanning, electroplating, nuclear power plants, textile industries, and chromate preparation industries (Hadjmohammadi, Salar & Biparva, 2011). Substantial research attention has been paid towards reducing or removing chromium from wastewater using techniques like chemical reduction (Parames wari, Lakshmanan & Thilagavathi, 2009), electroplating (Chen, Cheng, Li, Chai & Chang, 2007), bioaccumulation (Preetha & Viruthagiri, 2007), ion exchange (Cavaco, Fernan des, Quina & Ferreira, 2007), activated carbons (Mohan, Singh & Singh, 2005; Imran, 2010), immobilized whole cells (Vaishnavi & David, 2018), and fly ash (Vasanthy, Sangeetha & Kalaiselvi, 2004); but these techniques lead to incomplete chromium removal and involve excessive monitoring and equipment costs, and are energy intensive and expensive. Hence, there is a need to develop effective and economical process for the removal of chromium with high selectivity. Biosorption in this regard has emerged as a promising alternative to conventional chromium treatment technologies (Oboh, Laluyor & Audu, 2009). Various biosorbents (Chakresh, Davendra & Anuj, 2016; Kumar & Krithika, 2009; Mishra, Dubey & Shinghal, 2015), with reasonable adsorption capacity, and which are relatively inexpensive, include agricultural materials that have been investigated in the past, such as untreated coffee husks

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*Corresponding author
Email address davidkdaniel@amaljyothi.ac.in

(Oliveira, Santos, Saldahna & Salum, 2008), coconut fiber (Manju & Anirudhan, 1997), eucalyptus bark (Sarin & Pant, 2006), sawdust and charcoal from sugarcane bagasse (Dhungana & Yadav, 2009), tamarind fruit shell and hull (Verma, Chakraborty & Basu, 2006; Popuri, Jammala, Reddy & Abburi, 2007), treated sawdust (Baral, Das & Rath, 2006), maple saw dust (Yu, Shukla, Dorris, Shukla & Margrave, 2003), potato peel waste (Devi & Mohammed, 2009), wheat bran (Nameni, Alavi & Arami, 2008), activated neem leaves (Babu & Gupta, 2008), neem saw dust (Vinodhini & Nilanjana, 2009), rice husk (Bansal, Garg, Singh & Garg, 2009; Hasan, Singh, Prakash, Talat & Ho, 2008), oil palm fiber (Isa *et al.*, 2008), sunflower stem waste (Jain, Garg & Kadirvelu, 2009), banana peel (Suphakit & Guntharee, 2019), and walnut, hazelnut and almond shell (Farooq, Kozinski, Khan & Athar, 2010; Pehlivan & Altun, 2008;). Although various materials have been used to extract contaminants from wastewater, information on contaminant removal by a proper whole plant is scarce. In this context, *Eclipta prostrata* (Bhringraj) plants are widespread in India and able to grow in a broad diversity of environments. They offer a remarkable potential as biosorbent. The present work was carried out to evaluate the potential of this plant as whole plant biomass, as a low cost adsorbent for the removal of chromium (VI) ions from aqueous solutions. In the present work, therefore an attempt has been made to study the effects of factors influencing the chromium adsorption efficiency in aqueous effluents by assessing effects of operating parameters, to obtain the optimum conditions using Box-Behnken design (Box & Behneken, 1960) and Response Surface Methodology (Montgomery, 1997).

2. Materials and Methods

2.1 Materials

Potassium dichromate, diphenyl carbazide and all other chemicals were of analytical grade and procured from standard sources. 1000 mg/l of standard stock solution equivalent to 1.0 g of chromium (VI) was prepared with distilled water and diluted to obtain a series of standard solutions having different concentrations, used to prepare a calibration plot. *Eclipta prostrata* (Bhringraj) plants were collected locally, washed with water and then dried at 60ºC in an oven. The dried material was then ground and sieved to get particles of different sizes (100-200 mesh) that were stored in air-tight glass containers.

2.2 Batch adsorption experiments

A series of standard chromium test solutions were prepared by appropriately diluting the chromium stock solution. Batch experiments were performed on a temperature controlled orbital shaker at 150 rpm in 250 ml Erlenmeyer flasks containing 100 ml of the test solution and a known amount of the adsorbent. The suspensions were filtered and the concentration of the metal ions in the filtrate was analyzed using UV-visible spectrophotometer (Shimadzu, UV 1800, Japan). Chromium (VI) ions were analyzed after the formation of colored complexes with diphenyl carbazide and the absorbance of this colored complex was measured at 540 nm as per standard procedures (APHA, 2005). All the measurements were done after samples were left to stand for 5-10 min, to allow for color development. The metal uptake by the adsorbent was determined as the adsorption efficiency using the following relation.

$$\text{Adsorption efficiency} = \left[\frac{(C_i - C_e)}{C_i}\right] \times 100 \qquad (1)$$

where,
C_i = initial concentration of metal ions in the solution (mg/l)
C_e = final (equilibrium) concentration of metal ions in the solution (mg/l)

2.3 Box-Behnken experimental design

Based on our preliminary studies (Madhu, Jayasree & Jahana, 2014) and literature on single-factor experiments, contact time, pH, initial concentration and adsorbent dosage were selected as the four significant independent variables. A 4-factor, 3-level and 27-run Box-Behnken experimental design *(*Abd *et al.*, 2018***)*** was applied to provide data for quadratic polynomial fits modeling effects of these significant process variables. In the experimental design the variables were coded as x_i according to the following relationship.

$$x_i = \frac{(X_i - X_0)}{\Delta X_i} \qquad (2)$$

where X_i is the value of the variable, X_0 is the actual value on the centre point and ΔX_i is the step interval. The following response model for adsorption efficiency was used in the response surface analysis.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} {X_i}^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad (3)$$

where Y is the predicted response, β_0 is a constant, β_i are linear coefficients; β_{ii} are quadratic coefficients; β_{ij} are cross term coefficients. X_i and X_j are independent factors.

The data were analyzed using Minitab trial version program by analysis of variance to find out about the interactions between factors and response. The quality of fit by the regression model was assessed from the coefficient of determination (R^2) using the same program.

3. Results and Discussion

3.1 Statistical analysis and model development

The Box-Behnken design is a useful experimental design for response surface methodology, based on three level factorial designs (Biswas, Kumari, Adhikari & Dutta, 2017; Vahid & Seyyed, 2017; Then *et al.*, 2016). Contact time, pH, initial concentration and adsorbent dosage, identified as influencing factors from our earlier work (Madhu, Jayasree & Jahana, 2014), were chosen for the Box- Behnken design, and their coded and uncoded values are shown in Table 1. Table 2 depicts the full experimental plan involving the levels of these factors together with the response values and predicted results. An analysis of variance (ANOVA) was further applied to evaluate the significance and adequacy of the model (Table 3).

Table 1. Variables and their levels tested (coded and actual values)

Factor	Variable	Unit	Levels of coded variables		
			-1 (Low)	0 (Mean)	+1 (High)
X_1	Contact time	h	3	4	5
X_2	pH	-	1	2	3
X_3	Initial chromium concentration	mg/l	250	275	300
X_4	Adsorbent dosage	g/l	11	12	13

Table 2. Experimental Box-Behnken design matrix and adsorption responses by *Eclipta prostrata*

Run No.	Contact Time (h)	pH	Initial chromium concentration (mg/l)	Adsorbent dosage (g/l)	Adsorption efficiency (%) Observed	Adsorption efficiency (%) Predicted
1	4	3	300	12	89.87	89.75
2	4	2	275	12	94.00	94.14
3	5	1	275	12	93.00	92.90
4	4	2	250	11	96.00	95.91
5	5	3	275	12	90.00	89.91
6	3	2	275	13	93.60	93.47
7	4	3	250	12	93.00	92.93
8	4	3	275	11	90.00	89.87
9	5	2	300	12	94.00	93.87
10	4	2	275	12	94.56	94.14
11	4	1	300	12	93.00	92.91
12	4	3	275	13	90.00	89.94
13	5	2	275	13	94.00	93.93
14	3	3	275	12	90.00	89.95
15	4	1	250	12	94.80	94.76
16	4	1	275	12	92.00	92.77
17	4	2	300	11	93.20	93.19
18	5	2	275	11	93.40	93.37
19	3	2	275	11	93.00	92.91
20	4	2	275	12	94.10	94.14
21	3	2	300	12	93.40	93.31
22	4	1	275	13	93.00	92.93
23	3	2	250	12	96.00	95.93
24	4	2	250	13	96.40	96.27
25	3	1	275	12	92.00	91.94
26	4	2	300	13	94.00	93.95
27	5	2	250	12	96.40	96.29

Table 3. ANOVA for quadratic response surface model of chromium adsorption by *Eclipta prostrata*

Source	Sum of Squares	df	Mean Squares	F-value	Prob > F
Model	99.069	14	7.0764	409.19	< 0.0001
X_1	0.7008	1	0.7008	40.53	< 0.0001
X_2	18.5754	1	18.5754	1074.11	< 0.0001
X_3	19.3294	1	19.3294	1117.71	< 0.0001
X_4	0.9633	1	0.9633	55.70	< 0.0001
$X_1 X_2$	0.2500	1	0.2500	14.46	0.003
$X_1 X_3$	0.0225	1	0.0225	1.3	0.276
$X_1 X_4$	0.0000	1	0.0000	0.00	1.000
$X_2 X_3$	0.4422	1	0.4422	25.57	0.000
$X_2 X_4$	0.2500	1	0.2500	14.46	0.003
$X_3 X_4$	0.0400	1	0.0400	2.31	0.154
X_1^2	0.6706	1	0.6706	38.77	< 0.0001
X_2^2	36.2848	1	36.2848	2098.15	< 0.0001
X_3^2	5.9268	1	5.9268	342.71	< 0.0001
X_4^2	0.7187	1	0.7187	41.56	< 0.0001
Residual	0.2075	12	0.0173		
Lack of fit	0.0291	10	0.0029	0.03	1.000
Pure error	0.1784	2	0.0892		
Total	99.2765	26			

As seen in Table 3, the F-value obtained, 409.19 is greater than the F value 2.61 for 95% significance from the standard distribution table, confirming the adequacy of model fit. The significance of each term is listed in Table 3, and the p-values (Prob > F) showed the factors to be significant, implying that increasing these terms beyond the design boundaries decreased the adsorption efficiency. The P value limit 0.05 was used to determine whether a factor has a significant effect on the response. A probability of $p < 0.05$ indicates that the model term is significant at 95% probability. Table 3 shows the regression results and the significance levels of each factor. A value of $p \ll 0.05$ was found for most of the variables, interaction terms, and quadratic terms, implying that these factors and interactions are significant in affecting the chromium removal within the experimental range. The lack of fit F-value of 0.03 was not significant as the p-value is greater than 0.05. The non-significant lack of fit therefore shows that the model is valid for the present work. The quadratic model was selected for response, and the final empirical regression model in terms of coded factors is shown in equation (4).

$$\begin{aligned} Y = {} & 166.1 + 2.75X_1 + 16.85X_2 - 1.0118X_3 \\ & + 8.49X_4 - 0.3546{X_1}^2 - 2.6083{X_2}^2 \\ & + 0.0017{X_3}^2 - 0.3671{X_4}^2 - 0.25X_1X_2 \\ & + 0.003X_1X_3 - 0.0133X_2X_3 - 0.25X_2X_4 \\ & + 0.004X_3X_4 \end{aligned} \tag{4}$$

From Equation (4) it can be seen that the contact time, pH, initial concentration and adsorbent dose affect the chromium adsorption. In order to evaluate and ensure the adequacy of the proposed model, a plot between experimental (actual) and model predicted values of the adsorption efficiency was prepared (Figure 1). As evidenced by the distribution of points close to the diagonal line, it was concluded that the experimental values for the chromium adsorption were in a good agreement with the fitted model. The adjusted determination coefficient (R^2) value for the model (Equation (3)) was 0.9979. The closeness of R^2 value to 1 indicates high reliability for the developed regression model in explaining the variations in the experimental data. The high R^2 value, significant F-value and insignificant lack of fit p-value of the model indicate high precision in predicting the chromium adsorption efficiency, and therefore this model was used in further analysis. Three-dimensional (3D) and contour (2D) plots were also based on the second order polynomial model to analyze the responses. Figures 2-7 show the surface and contour plots for each interacting variable pair, with two variables kept constant while the other two are varying within the experimental ranges.

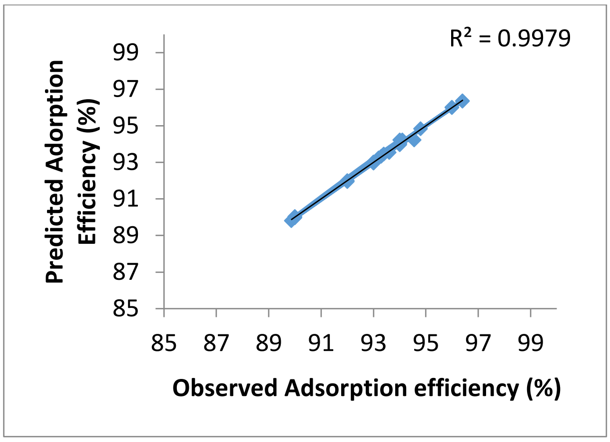

Figure 1. Predicted vs. Experimental values of chromium adsorption by *Eclipta prostrata*

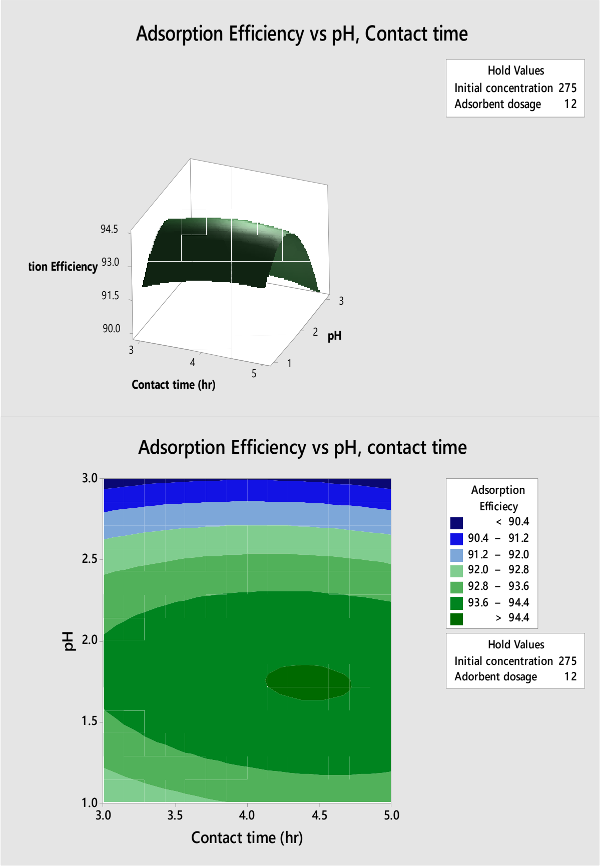

Figure 2. 3-D response surface (left) and contour plot (right) showing the interactions between pH and contact time for chromium adsorption by *Eclipta prostrata* (at initial concentration 275 mg/l; adsorbent dose 12 g/l).

3.2 Effects of pH and contact time

pH is an important controlling parameter in the adsorption, due to its influence on the surface properties of the adsorbent and the electrostatic interactions with the metal ions in the solution (Mahajan & Sud, 2011). The pH of the solution can considerably impact the adsorption efficiency. The pH was varied using 0.1 N HCl solution. The combined effects of contact time and pH on the adsorption efficiency are shown in Figure 2. The adsorption efficiency was found to be maximum at the fourth hour and at pH 2, beyond which it remained constant. However, as the pH increased, adsorption efficiency decreased gradually. This decrease in adsorption efficiency at a higher pH was due to the weakening of electrostatic attraction between the oppositely charged adsorbate and adsorbent, because at a high pH, the adsorbent surface became negatively charged due to abundance of negatively charged hydroxyl ions.

3.3 Effects of initial chromium concenteration and contact time

Figure 3 shows the interaction between initial concentration and contact time at constant pH 2 and 12 g/l adsorbent dose. As illustrated in Figure. 3, the adsorption of Cr (VI) ions decreased with increase in contact time but the adsorption efficiency was maximum at an initial concentration of 250 ppm, after which it was found to decrease. This is due to the fact that at a low chromium concentration the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions interact with the adsorbent, thereby enhancing their removal from solution. However, the amount of metal ions adsorbed per unit weight of adsorbent (adsorption capacity) was found to be higher at a higher chromium concentration.

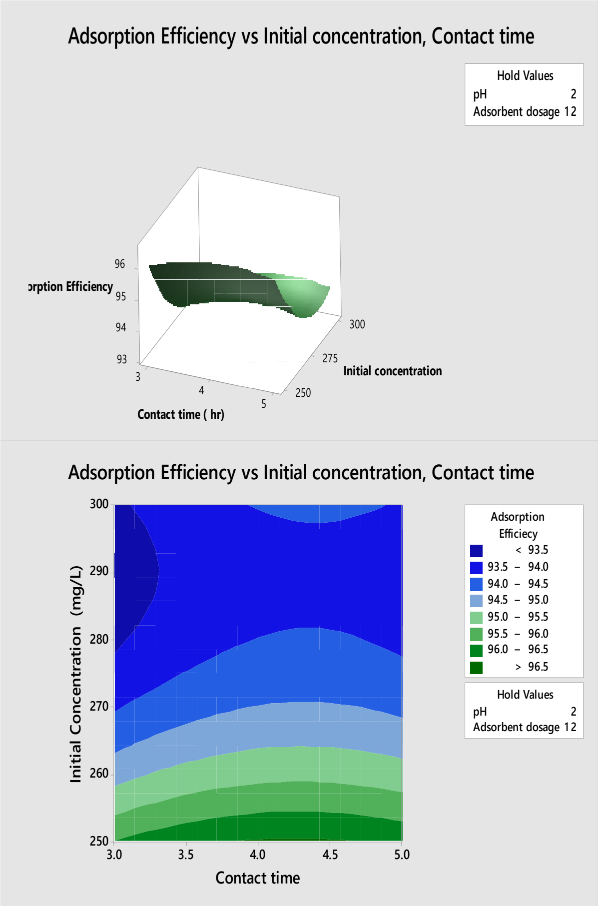

Figure 3. 3-D response surface (left) and contour plot (right) showing the interaction between initial concentration and contact time for chromium adsorption by *Eclipta prostrata* (at pH 2; adsorbent dose 12 g/l)

3.4 Effects of adsorbent dosage and contact time

Figure 4 shows the three-dimensional response surface for the interaction effect of adsorbent dose and contact time, on the adsorption efficiency at a constant pH 2 and 275 ppm initial concentration. Increasing the adsorbent dose from 11 g/l to 13 g/l improved adsorption efficiency. This may be due to the increase in the number of binding sites on the adsorbent. A maximum adsorption efficiency of 94.14% was observed at 4 h with an adsorbent dose of 12 g/l. There was clearly a lower adsorption efficiency at the lower adsorption dose (11 g/l) and shorter contact time (3 h).

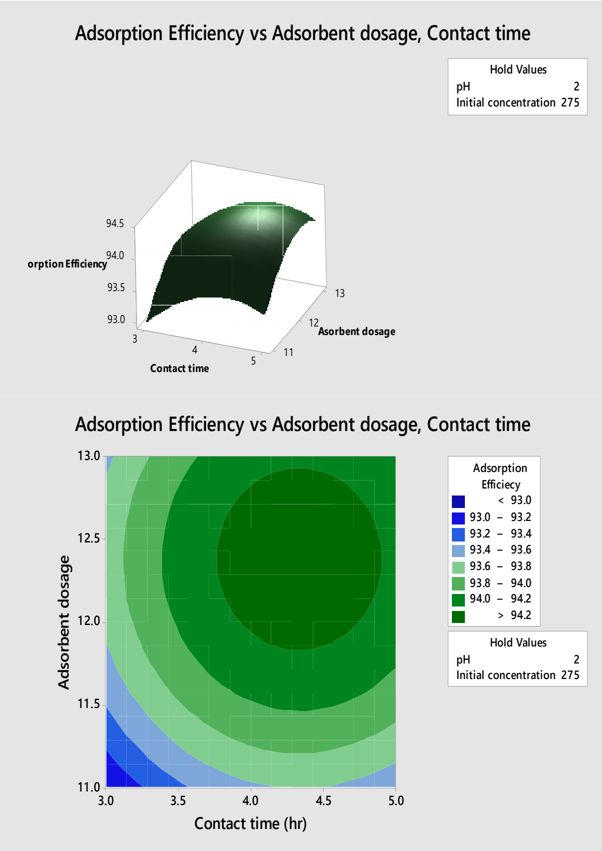

Figure 4. 3-D response surface (left) and contour plot (right) showing the interaction between adsorbent dose and contact time for chromium adsorption by *Eclipta prostrata* (at pH 2; initial concentration 275 mg/l)

3.5 Effects of pH and initial concentration

The interaction between pH and initial concentration is shown in Figure 5. When the pH was maximum and initial concentration at its minimum, the adsorption efficiency was 92.93% with an adsorbent dose of 12 g/l and contact time 4 h. The adsorption efficiency increased with initial concentration up to 275 ppm and then decreased at 300 ppm. This may be due to the higher Cr (VI) ion adsorption per unit mass of adsorbent with increase in the hexavalent chromium ion concentration in the adsorbate solution. However, because the ratio of the surface active sites to the total metal ions in the solution was low at high concentrations, the interaction of the metal ions with the adsorbent was lesser, leading to decreased adsorption efficiency.

3.6 Effects of pH and adsorbent dosage

The pH and adsorbent dose are the most important process parameters determining the removal capacity of an

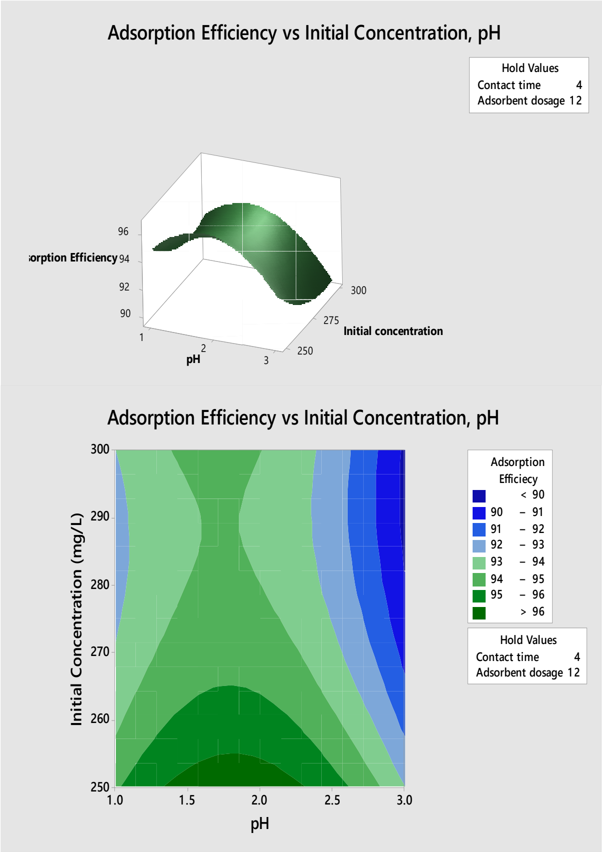

Figure 5. 3-D response surface (left) and contour plot (right) showing the interaction between initial concentration and pH for chromium adsorption by *Eclipta prostrata* (at contact time 4h; adsorbent dose 12 g/l)

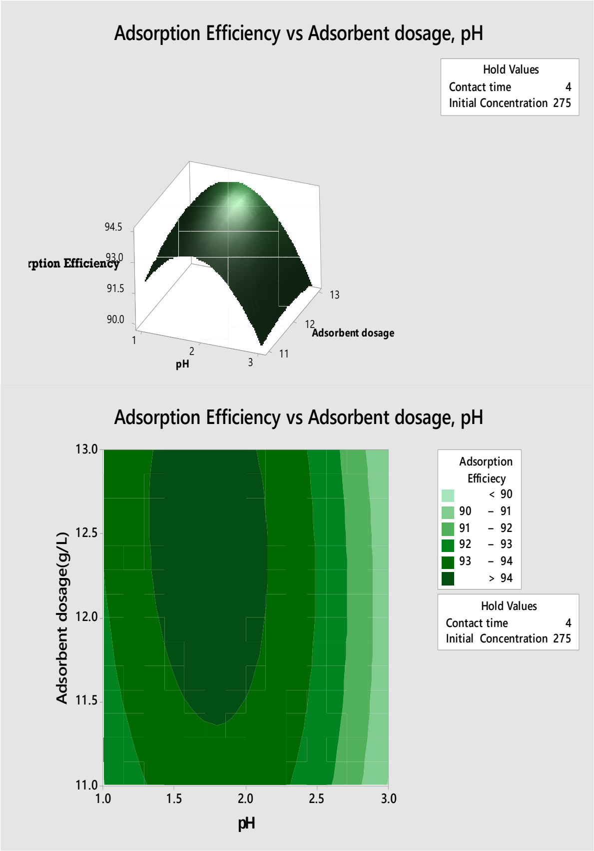

Figure 6. 3-D response surface (left) and contour plot (right) showing the interaction between adsorption dose and pH for chromium adsorption by *Eclipta prostrata* (at contact time 4h; initial concentration 275 mg/l)

adsorbent (Dakiky, Khamis & Manasara, 2002). Adsorption experiments were carried out as per the selected model with selected range of pH and adsorbent dosage. The results clearly indicate increasing adsorption with adsorbent dose from 11 g/l to 12 g/l. The maximum adsorption of chromium (VI) metal ions observed was 94.14% (Figure 6). This trend in the removal was probably because the optimum amount of adsorbent in the experimental solutions caused stronger aggregation of the adsorbent and a reduced contact area for surface binding. These results match earlier studies (Naga, Krishna & Ravindhranath, 2016; Pehlivan & Tutar, 2012).

3.7 Effects of initial concentration and adsorbent dosage

The effects of adsorbent dose and concentration of chromium at constant pH 2 and 4 h contact time are shown in Figure 7. The adsorption efficiency was found to decrease with initial chromium concentration and was maximum at 250 ppm. It is observed that the percentage of chromium removed increased with adsorbent dose up to 12 g/l and then decreased. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of active binding sites on the surface of the adsorbent, which again agrees well with similar observations reported earlier (Kavitha & Arunadevi, 2018; Mishra, Dubey & Shinghal, 2015).

In the present work, the input factors were given specific ranges and the maximal response was sought. The model based maximum adsorption efficiency was 96.69% at a contact time of 4.31 h, pH 1.78, initial chromium concentration of 250 mg/l, and adsorbent dose of 12.31 g/l. Verification experiments were performed at the predicted optimal conditions, showing an adsorption efficiency of 94.65% , which is only slightly lower than the model predicted adsorption efficiency of 96.69%. This indicates the suitability and accuracy of the model of chromium (VI) removal by adsorption. While the use of agricultural wastes as adsorbents has been assessed earlier, the adsorbent capacity of *Eclipta prostrata* (Bhringraj) plant in the present study was found to be 19.3 mg/g, which is quite significant when compared to earlier reported literature (Candice, Martha, Marta & Habauka, 2017; Christine & Astha, 2016; Dessalew, 2017; Moniruzzaman, Rahman, Aktar & Khan, 2017; Naga, Krishna, & Ravindhranath, 2016; Pushpendra, Sohail & Chandra, 2016). Since *Eclipta prostrata* (Bhringraj) plant is extensively used in the Indian hair oil formulation industry, the disposal and utilization of large quantities of this spent plant material is necessary. Hence, through this work the potential of this low-cost adsorbent as a suitable alternative to conventional adsorbents has been established. The findings of this work imply that the approach to optimize the removal of hexavalent chromium using *Eclipta prostrata* (Bhringraj) plant powder and to obtain

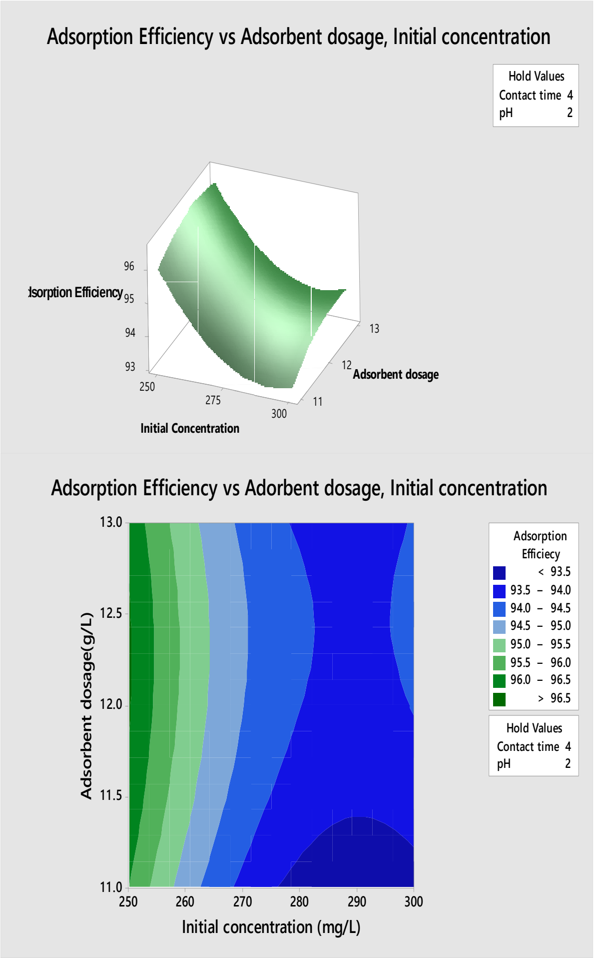

Figure 7. 3-D response surface (left) and contour plot (right) showing the interaction between adsorbent dose and initial concentration for chromium adsorption by *Eclipta prostrata* (at contact time 4 h; pH 2)

the maximal adsorption efficiency by Box-Behnken experimental design was successful.

4. Conclusions

The main objective of the present study was to seek the optimum process variables for the adsorption of chromium using biomass obtained from *Eclipta prostrata* (Bhringraj) plant, by using quadratic model fits to experimental data. The chromium adsorption was successfully achieved with the optimized key factors showing the maximum chromium uptake capacity. A Box-Behnken experimental design with second order polynomial regression fits in response surface analysis proved suitable for determining the effects of the process variables. A maximum removal of 96.69% was obtained at pH of 1.78, contact time of 4.31 h, adsorbent dose of 12.51 g/l and initial concentration of 250 mg/l. Based on the analysis of variance (ANOVA), it was concluded that the quadratic model adequately described the relation between the adsorption efficiency and input parameters, namely the contact time, pH, initial concentration and adsorbent dose. The experimental values and the predicted values of response were in good agreement with R^2 value of 0.9979. The optimized results revealed that *Eclipta prostrata* (Bhringraj) plant powder appears to be an effective and economically feasible biosorbent for the removal of Chromium (VI).

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