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Application of response surface methodology for optimization of Cr(III) and Cr(VI) adsorption on commercial activated carbons

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Abstract

Response surface methodology (RSM) involving D–optimal design was used to optimize the adsorption process of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) from aqueous solutions by commercial activated carbons. Influence of various process parameters such as initial metal concentration, pH, adsorbent dose, contact time, and type of adsorbent on adsorption process was investigated. From the analysis of variance (ANOVA) results, the significance of various factors and their influence on the response were identified. The regression coefficients (R^2) of the models developed and the results of validation experiments conducted at optimum conditions for the removal of both Cr(III) and Cr(VI) indicate that the predicted values are in good agreement with the experimental results. Contour and response surface plots were used to determine the interaction effects of main factors and optimum conditions of process, respectively for the simultaneous removal of Cr(III) and Cr(VI).

Keywords: Activated carbon, response surface methodology, Cr(III), Cr(VI), optimization.

Introduction

Out of several heavy metal pollutants, chromium compounds are very toxic. The toxicity of the chromium in aqueous phase changes with the oxidation state. It is well known that chromium mainly exists in trivalent (Cr(III)) and hexavalent (Cr(VI)) states in the solution phase[1,2]. Trivalent chromium is less toxic compared to the hexavalent chromium, but in higher amounts it is toxic and mutagenic[3]. Chromium poses a great threat to human health and environment and also it confirmed as a carcinogen in hexavalent state[4-6]. Moreover, Cr(III) can be oxidized to Cr(VI) in the presence of certain oxidants such as manganese oxides which commonly found in water environments[7]. Hence, the simultaneous removal of trivalent and hexavalent chromium ions is focused in this study.

Adsorption is commonly used technique for the removal of metal ions from various industrial effluents[8,9]. Among many types of adsorbents, activated carbons are most widely used for chromium removal from aqueous solutions because of their novel porous characteristics, high adsorptive capacity and low cost[10-13]. Many investigators have studied the feasibility of activated carbons prepared from various materials for the removal of chromium from aqueous solutions through conventional adsorption methods[14-17].

Conventional methods of studying a process by maintaining other factors involved at unspecified constant levels does not depict the combined effect of all the factors. This method is time consuming and incapable. This calls for a research effort for developing, improving and optimizing the adsorption process and to evaluate the significance of all the factors involved even in the presence of complex interactions. Recently many statistical experimental design methods have been employed in chemical process optimization[18,19].

Design of experiments is a very useful tool as it provides statistical models, which help in understanding the interactions among the parameters that have been optimized[20]. Response surface methodology (RSM) is one of the experimental designing methods which can surmount the limitations of conventional methods collectively[19]. RSM is a combination of mathematical and statistical techniques used to determine the optimum operational conditions of the process or to determine a region that satisfies the operating specifications[20]. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions[23,24].

In this study, the simultaneous adsorption of Cr(III) and Cr(VI) by commercial activated carbons (CACs) was optimized by studying the effect of various factors like metal concentration, pH, adsorbent dose, contact time, and type of adsorbent. D–optimal design in RSM by Design Expert Version 7.1.6 (Stat Ease, USA) was used to optimize adsorption process.

Material and Methods

Materials: Commercial activated carbons (CACs) with different iodine numbers (950 (ACI) and 1050 (ACII)) were obtained from Kalpaka Chemicals, Tuticorin, India. Cr(III) and Cr(VI) stock solutions of 10 mg/l were prepared by

using chromium chloride ($CrCl_3$) and potassium dichromate ($K_2Cr_2O_7$) procured from Merck.

Experimental methods: The adsorbents used in this study were characterized by N_2 adsorption isotherms to determine porous characteristics like surface area (S), pore volume (V_o), and type of pores (micro, meso and macropores) that take major part in porosity of adsorbent. Imaging of adsorbents was done by Scanning Electron Microscope (SEM - JEOL, JSM 6480 LV). Adsorption experiments were carried out in shake flask system. The stock solutions were diluted as required to obtain standard solutions of concentration ranging between 2 and 10 mg/l. Batch adsorption studies were performed in Erlenmeyer flasks of 250 ml by contacting the selected activated carbon of different doses (0.5 – 2 g/l) with 50 ml of solution containing different metal concentrations (2 – 10 mg/l) at solution pH (2 – 11) and for different contact times (1 – 4 h). All the flasks were maintained at room temperature and provided continuous shaking of 110 rpm by Environmental Orbital Shaker Incubator (DENEB Instruments). Concentration of Cr(III) and Cr(VI) species in the aqueous solutions were determined by standard procedure[25] using UV/VIS spectrophotometer (Jasco, V-530). The percentage removal of Cr(III) and Cr(VI) were calculated according to

$$\text{Adsorption } (\%) = \frac{(C_o - C_f)}{C_o} \text{ X } 100 \qquad (1)$$

where, C_o is the initial concentration and C_f is the final concentration of the metal ions. All the experiments were carried out in duplicate and the mean values are reported.

Selection of factors for experimental design: Modeling of adsorption process of Cr(III) and Cr(VI) on activated carbons was carried out by optimizing four numerical factors such as initial metal concentration (A), pH (B), adsorbent dose (C), and contact time (D) and one categorical factor i.e. type of adsorbent (E). A standard RSM design called D–optimal design was used to determine the main and interaction effects of all the process parameters.

The low and high levels and ranges of all the factors studied were given in table 1. The actual values of the process variables and their ranges were selected based on the preliminary experiments. Twenty four experiments for removal of each metal ion (Cr(III) and Cr(VI)) were conducted. The optimum values of all the variables were obtained by solving the regression equations and by analyzing the contour and 3D surface plots.

Results and Discussion

Characterization of adsorbents: The porous characteristics of CACs analyzed by N_2 adsorption isotherms were shown in table 2. Figure 1 shows that the isotherms obtained by N_2 gas adsorption experiments are of type-I that means the adsorbents mostly contain micropores[26]. Calculation procedure for porous characteristics of adsorbents was cited elsewhere[27]. The pore structure network of the adsorbents was characterized by scanning electron microscope (SEM). A fully developed pore structure similar to honeycomb voids can be observed for both the adsorbents shown in figures 2a and 2b. By N_2 adsorption isotherms, the pores observed by SEM analysis are assumed to be the channels to the network of micropores.

Table-1
Experimental range and levels of independent variables

Factors	Coded symbol	Range and level		
		- 1	**0**	**+ 1**
Initial metal concentration	A	2.0	6.0	10.0
pH	B	2.0	6.5	11.0
Adsorbent dose	C	0.5	1.25	2.0
Contact time	D	1.0	2.5	4.0
Adsorbent type (categorical factor)	E	ACI	–	ACII

Table-2
Porous characteristics of adsorbents (CACs)

Adsorbent	Iodine no	Surface Area (m^2/g)				Pore Volume (cc/g)		
		S_{lang}	S_{mi}	S_{me}	S_{ex}	V_{tot}	V_{mi}	V_{me}
ACI	950	1402	1370	32	29.34	0.50	0.46	0.04
ACII	1050	2058	2010	48	31.13	0.73	0.68	0.05

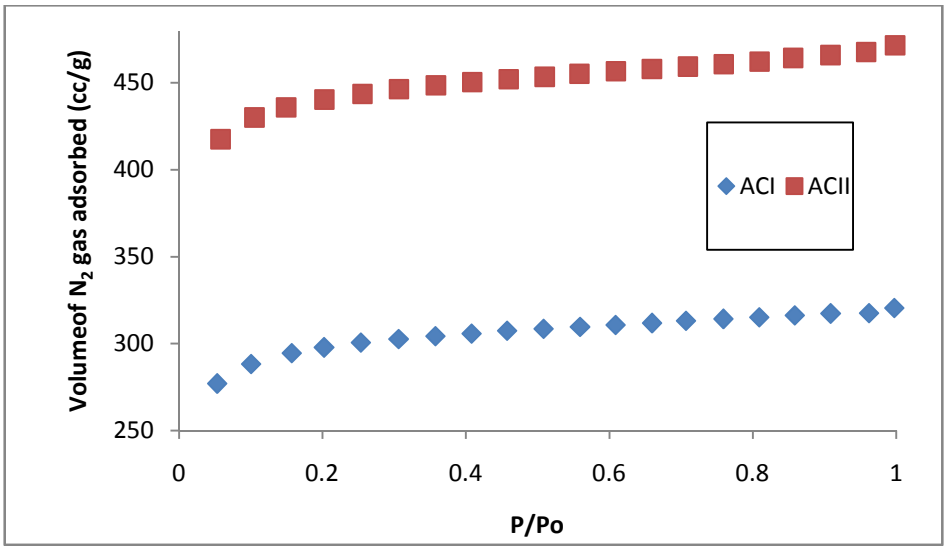
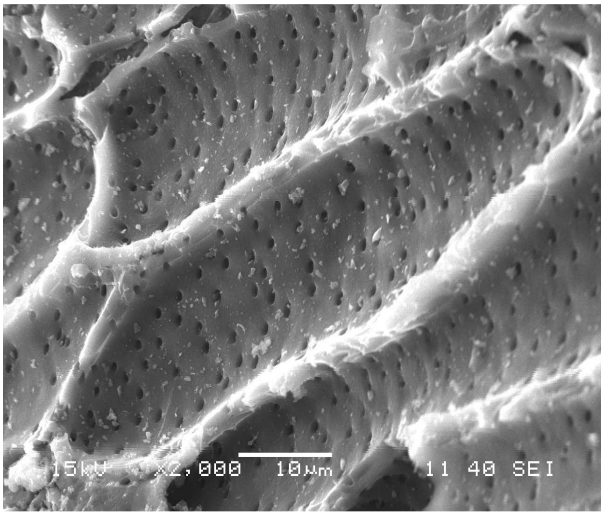
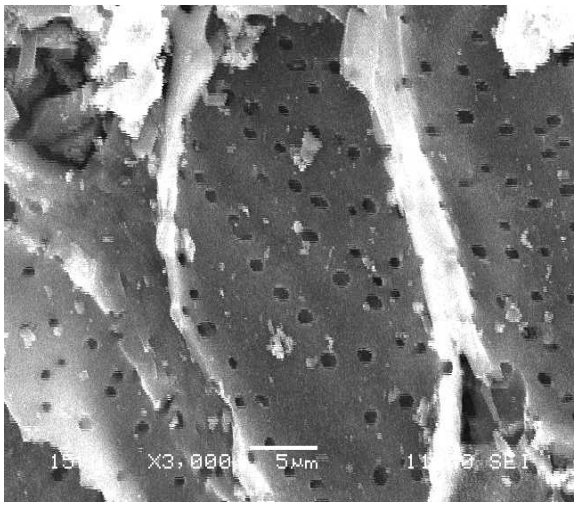


Figure-1
N_2 adsorption isotherms of adsorbents



(a)



(b)

Figure-2
SEM images of adsorbents (a) ACI and (b) ACII

Response surface methodological approach: Experimental design and development of regression model equations: The scheme of experiments carried out in this study was presented in table 3. Regression analysis was performed to fit the response functions, i.e. percentage adsorption of Cr(III) and Cr(VI). The regression models developed represent responses as functions of initial metal concentration (A), pH (B), adsorbent dose (C), contact time (D), and adsorbent type (E). An empirical relationship between the response and input variables expressed by the following response surface reduced cubic model equations (in coded terms):

$$\%\ R_{Cr(III)} = 72.98 + 5.118\ \text{X}\ 10^{-3}A + 35.8B - 3.38C - 1.47D + 17.97E - 5.17AB + 1.61AC + 21.31AD + 20.41BC + 0.83BD - 5.66BE - 0.86CD - 24.98CE - 48.58DE + 2.52A^2 - 23.49B^2 - 29.85C^2 + 3.34D^2 - 47.9ABC - 28.43ABD \quad (2)$$

$$\%\ R_{Cr(VI)} = 8.31 + 2.76A - 31.84B + 6.24C + 4.02D + 2.69E - 2.8AB + 4.08AC - 0.1AD - 7.48AE - 2.47BC - 1.11BD - 2.09BE - 4.74CD - 4.54CE - 5.44DE - 8.16A^2 + 28.44B^2 + 12.21D^2 - 9.88ABC - 8.9ABD \quad (3)$$

where, $R_{Cr(III)}$ and $R_{Cr(VI)}$ are the removal percentages of Cr(III) and Cr(VI), respectively. Insignificant terms which are not included in the models are aliased as suggested by the software.

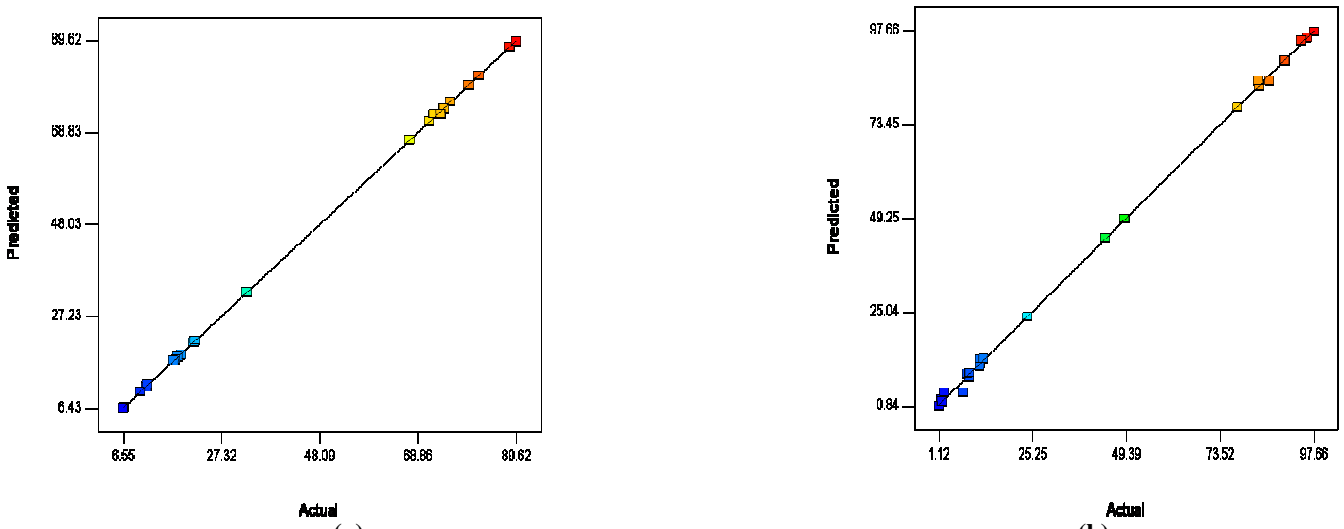
Statistical analysis: The significance of model terms included in the regression equations (eqs. 2 and 3) were evaluated by the F–test for analysis of variance (ANOVA). The ANOVA analysis for both the responses, % $R_{Cr(III)}$ and % $R_{Cr(VI)}$, was shown in table 4. Prob > F value for the models is less than 0.05 indicates that the model terms are statistically significant. The non significant values of lack of fit for both the models showed that developed models are valid[28]. The actual and predicted values of responses for Cr(III) and Cr(VI) were shown in figures 3a and 3b, respectively. Actual values are the measured values for a particular experiment, whereas predicted values are generated by using the approximating functions. The values of R^2 and adjusted R^2 have advocated a high correlation between actual and predicted values.

Table-3
Experimental design matrix with responses

Run	Factors					Response	
	(A) Metal conc.(mg/l)	(B) pH	(C) Adsorbent dose (g/l)	(D) Contact time (h)	(E) Adsorbent type	% $R_{Cr(III)}$	% $R_{Cr(VI)}$
1	+1	+1	-1	-1	-1	6.55	8.79
2	+1	-1	+1	+1	+1	17.13	97.66
3	+1	-1	-1	+1	-1	17.55	78.01
4	+1	+1	+1	-1	+1	71.27	11.86
5	0	0	-1	0	+1	89.62	8.98
6	-1	+1	-1	-1	+1	81.74	1.12
7	+1	-1	+1	0	-1	18.66	95.80
8	-1	-1	-1	-1	-1	11.69	48.92
9	0	+1	0	0	-1	72.27	7.37
10	+1	+1	+1	+1	-1	79.67	12.63
11	+1	+1	-1	+1	+1	67.06	1.92
12	0	-1	+1	+1	-1	10.12	94.49
13	+1	-1	-1	-1	+1	17.90	43.95
14	-1	+1	+1	-1	-1	88.17	1.81
15	-1	+1	-1	+1	-1	21.70	8.33
16	-1	0	+1	+1	-1	75.81	11.60
17	0	+1	0	0	-1	73.58	2.50
18	0	0	+1	0	+1	32.61	11.84
19	+1	-1	+1	-1	+1	21.35	90.15
20	0	0	0	-1	-1	11.34	8.86
21	-1	-1	-1	+1	+1	6.68	86.28
22	-1	-1	+1	-1	+1	11.48	83.51
23	-1	+1	+1	+1	+1	74.35	23.92
24	-1	-1	-1	+1	+1	6.76	83.31

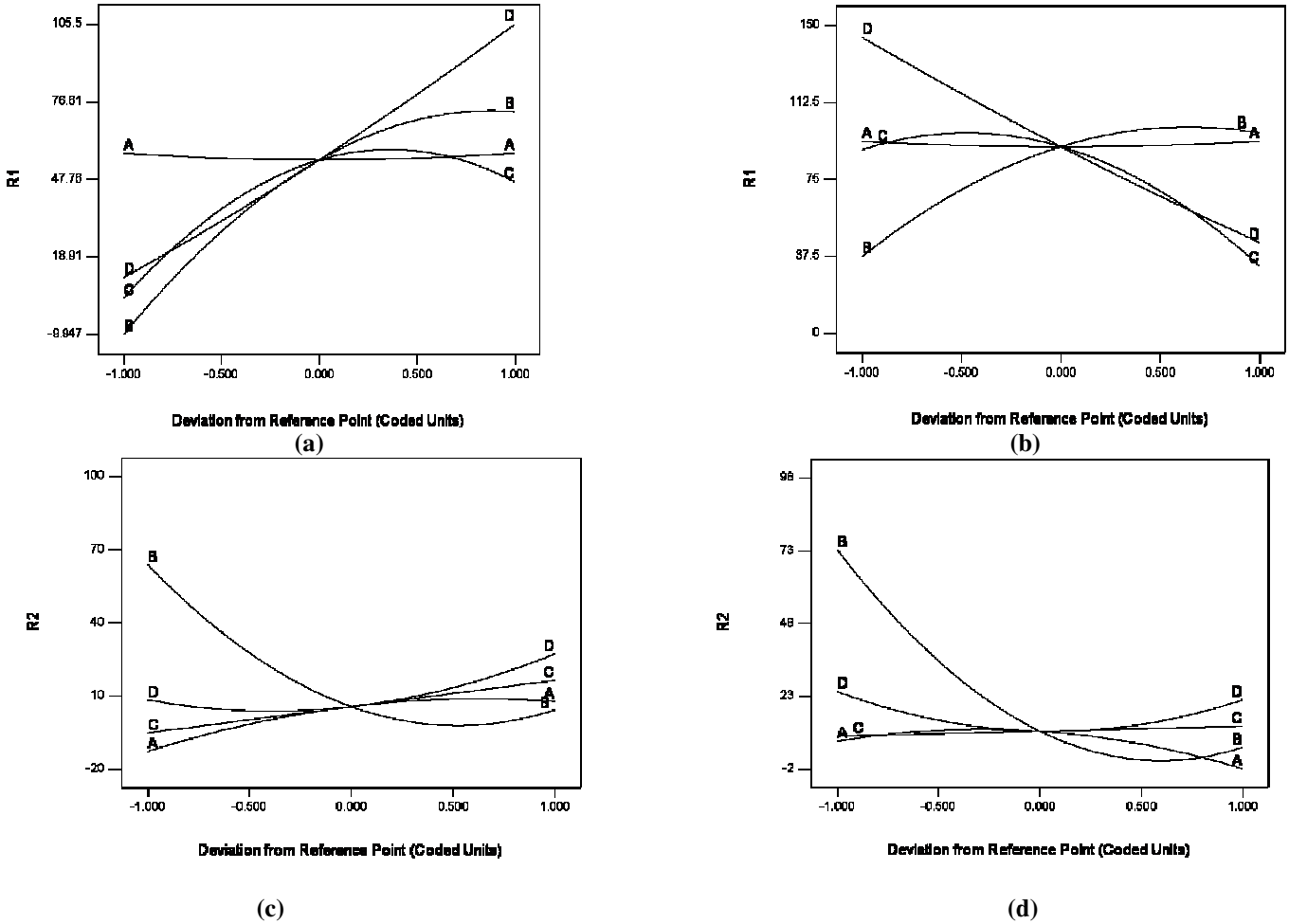
Table-4
ANOVA results

Source	Sum of squares	DF	Mean square	F value	Prob > F
For % $R_{Cr(III)}$					
Model	23785.11	20	1189.26	3034.40	<0.0001
Residual	1.18	3	0.39	–	–
Lack of fit	0.31	1	0.31	0.72	0.4847
Pure error	0.86	2	0.43	–	–
R^2 = 0.9996	–	–	–	–	–
Adeq Precision = 141.79	–	–	–	–	–
For % $R_{Cr(VI)}$					
Model	33495.57	20	1674.78	248.08	0.0004
Residual	20.25	3	6.75	–	–
Lack of fit	3.97	1	3.97	0.49	0.5575
Pure error	16.29	2	8.14	–	–
R^2 = 0.9954	–	–	–	–	–
Adeq Precision = 39.72	–	–	–	–	–



(a) **(b)**

Figure-3
The actual and predicted values of responses (a) % $R_{Cr(III)}$ and (b) % $R_{Cr(VI)}$



(a) **(b)**

(c) **(d)**

Figure-4
Perturbation plots: (a) Cr(III) removal by ACI, (b) Cr(III) removal by ACII, (c) Cr(VI) removal by ACI, and (d) Cr(VI) removal by ACII

Effect of factors and response surface estimation: Response surface methodology was used to estimate the effect of five process variables on the removal of Cr(III) and Cr(VI). Perturbation, contour and 3D surface plots were drawn by using RSM to investigate the effect of all the factors on the responses. The inferences so obtained are discussed below.

Effect of main factors: The individual effect of numerical factors such as metal concentration (A), pH (B), adsorbent dose (C), and contact time (D) was found by perturbation plots for the removal of Cr(III) and Cr(VI) at each level of categorical factor, i.e. adsorbent type (E). Perturbation plots for the removal of Cr(III) and Cr(VI) were shown in figure 4. Perturbation plot does not shows the effect of interactions and it is like one factor at a time experimentation. Perturbation plot helps to compare the effect of all the factors at a particular point in the design space. The response is plotted by changing only one factor over its range while holding of the other factors constant. A steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor[29]. From the figure 4, pH has a great influence on the removal of Cr(III) and Cr(VI) by using both types of activated carbons. Other main factors like adsorbent dose and contact time influence the process significantly whereas, initial metal concentration has less effect on the responses compared to other factors.

Effect of interactions: From the perturbation plots it was clear that for Cr(III) removal, pH (B) and adsorbent dose (C) played important role whereas, for Cr(VI) removal the main influential factors were pH (B) and contact time (D). The interactions of these factors also have a significant effect on the responses (from eqs.2 and 3). The contour plots of the main interactions which effect the responses, i.e. % $R_{Cr(III)}$ and % $R_{Cr(VI)}$, significantly were presented in figure 5. A contour plot is a two dimensional representation of the response for selected factors.

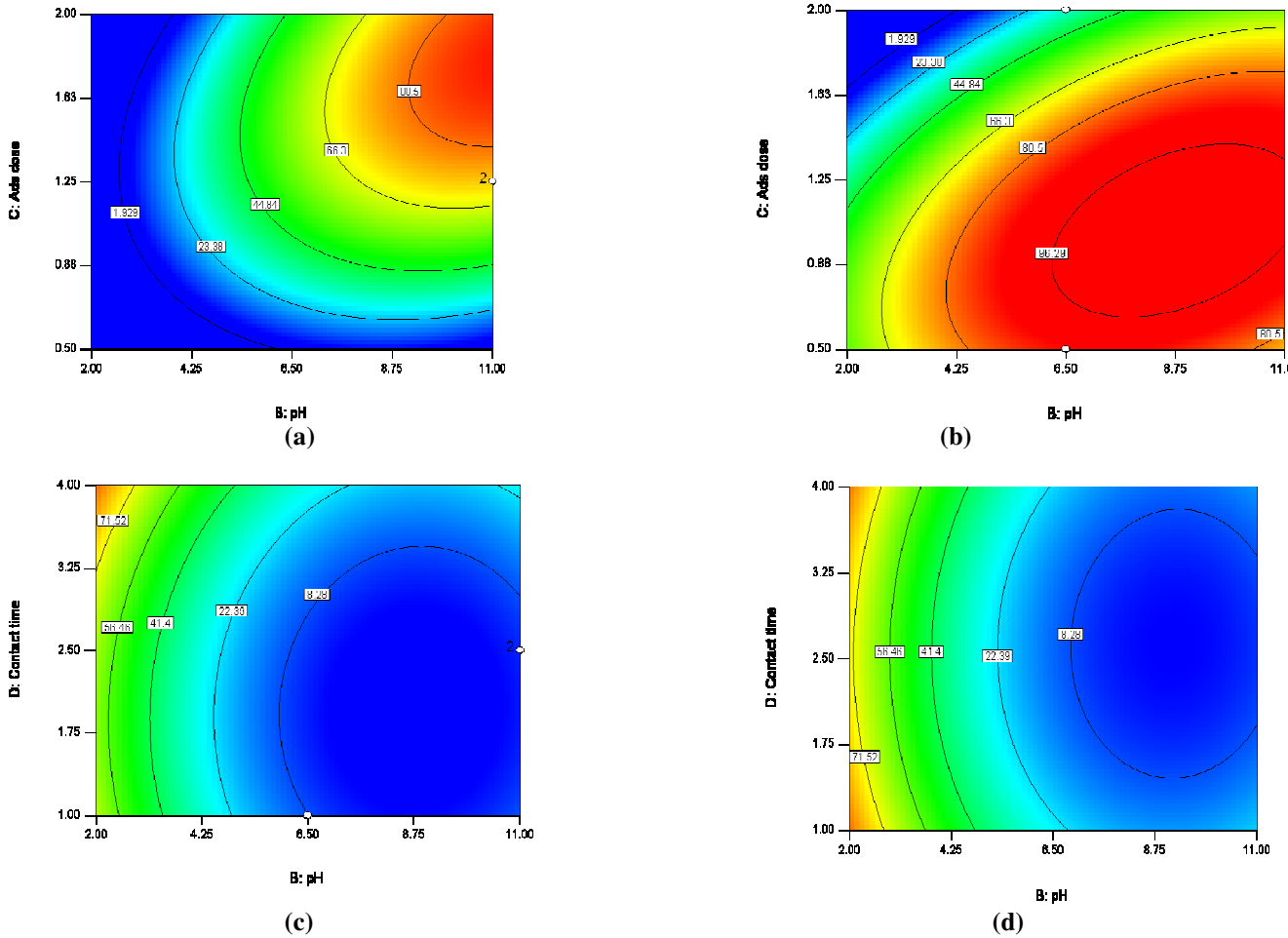
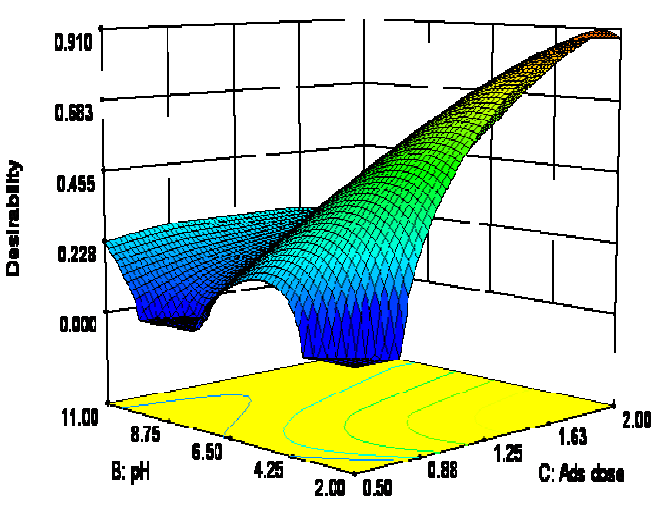
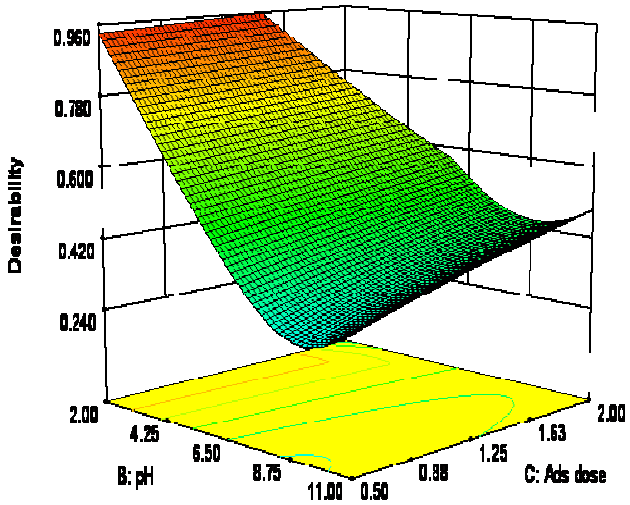


Figure-5
Contour plots for interaction of pH (B) and adsorbent dose (C) for Cr(III) removal by (a) ACI and (b) ACII, and interaction of pH (B) and contact time (D) for Cr(VI) removal by (c) ACI and (d) ACII

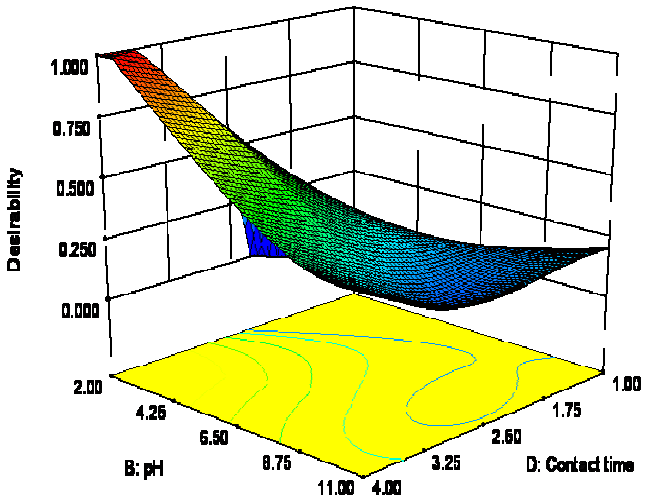
Optimization by response surface modeling: The optimum conditions of all the factors were found for the simultaneous removal of Cr(III) and Cr(VI) by CACs. The efficiency of both the activated carbons was determined individually. In case of ACI, at the optimum conditions (metal concentration – 9.8 mg/l, pH – 2.51, adsorbent dose – 0.58 g/l, and contact time – 3.83 h) the percentage removal of Cr(III) and Cr(VI) were 26.26 and 66.01 %, respectively. For ACII, the removal percentages of Cr(III) and Cr(VI) at optimum conditions (metal concentration – 6.85 mg/l, pH – 2.0, adsorbent dose – 0.5 g/l, and contact time – 1 h) are 89.62 and 71.33 %, respectively. The response surface plots at optimum conditions were shown in figure 6 considering key factors (observed from perturbation plots, figure 4). A multiple response method called desirability (*D*) function was used to find the optimum conditions for the simultaneous removal of Cr(III) and Cr(VI) by targeting the process parameters within the range defined in table 1.



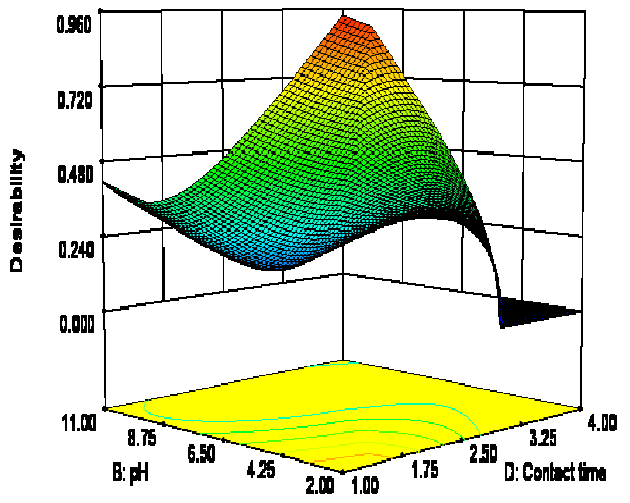
(a)



(b)



(c)



(d)

Figure-6
3D surface plots: Effect of pH (B) and adsorbent dose (C) on Cr(III) removal by (a) ACI and (b) ACII, and effect of pH (B) and contact time (D) on Cr(VI) removal by using (c) ACI and (d) ACII

Table-5
Validation of models

Adsorbent type	Chromium concentration	pH	Adsorbent Dose	Contact time	Responses			
					% $R_{Cr(III)}$		% $R_{Cr(VI)}$	
					Experimental	Predicted	Experimental	Predicted
ACI	9.8	2.51	0.58	3.83	24.53	26.26	63.76	66.01
ACII	6.85	2.0	0.5	1.0	88.85	89.62	72.53	71.33

Experiments for validation of models: The results obtained after optimization were verified by conducting the experiments under the optimized conditions of all the factors. The experimental values closely agreed to the predicted values of developed models with acceptable percentage errors and the details are given in table 5.

Conclusion

The main aim of this study is to find the optimum conditions to remove Cr(III) and Cr(VI) simultaneously from aqueous solutions by studying the effect of various process parameters. Two types of CACs of different adsorption capacities and porous characteristics were successfully tested for chromium (trivalent and hexavalent) metal ions removal. Response surface methodology (RSM) based on five variables D–optimal design was used to estimate the effect of initial metal concentration (2 – 10 mg/l), pH (2 – 11), adsorbent dose (0.5 – 2 g/l), contact time (1 – 4 h), and adsorbent type (ACI and ACII) on the removal of Cr(III) and Cr(VI). Models were developed to correlate variables to the responses by using Design Expert software. Optimization was carried out by RSM and the major findings are: Undoubtedly RSM is a good technique to provide optimum conditions of a process by studying the effect of main factors and their interactions on response with minimum number of experiments. Among the adsorbents used in this study, ACII was found to be more suitable for the simultaneous removal of Cr(III) (89.62 %) and Cr(VI) (71.33 %) and the optimum conditions found were: metal concentration – 6.85 mg/l, pH – 2.0, adsorbent dose – 0.5 g/l, and contact time – 1 h. By conducting the validation experiments at optimum conditions, it was concluded that the developed models could precisely fit to the models developed with acceptable values of percentage errors.

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