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Process optimization of adsorption of Cr(VI) on activated carbons prepared from plant precursors by a two-level full factorial design

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ABSTRACT

Commercial activated carbon (CAC) prepared from coconut shell and activated carbon (AC) prepared from bael fruit (*Aegle marmelos*) shell (BFS) were used as adsorbents for the adsorption studies of hexavalent chromium in aqueous solution. The main and interactive effects of four different experimentally controlled environmental factors like pH, initial concentration of Cr(VI) (C_i), adsorbent dose (m) and temperature (T) are investigated through the model equations designed by a two-level full factorial design (FFD) in a shake-flask system. Activated carbon prepared from BFS has more removal capacity of Cr(VI) than CAC under tested conditions. The results predicted using factorial regression model showed high values of regression coefficients ($R^2_{\text{CAC}} = 0.952$ and $R^2_{\text{BFS AC}} = 0.995$) indicating good agreement with experimental data. Main and interacting effects of different process parameters on the response (% removal of Cr) were found. Optimization of the process was carried out by using desirability (D) function by targeting the factors to desired levels for maximum removal of Cr(VI).

1. Introduction

Waste water discharges from chromate mining activities and electroplating industries are often contaminated with high concentrations of hexavalent chromium which has negative effect on the water environment. Hexavalent chromium compounds are toxic, carcinogenic, and mutagenic and even cause lung cancer [1,2]. Chromium compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile and steel fabrication industries. Effluents from these industries contain large quantities of hexavalent chromium. The undesirable effects of Cr(VI) can be avoided by treating the effluents prior to discharge into water streams. Various techniques have been employed for the removal of heavy metals including precipitation, adsorption, ion-exchange, membrane separation and reverse osmosis [3].

The process of adsorption is most often involved in the product purification and treatment of industrial discharges [4]. Activated carbon widely used in the adsorption process can be made from several materials among which coal [5], wood [6] and coconut shells [7] are popular due to the high porosity and large surface area.

Various studies reported the removal of Cr(VI) using a variety of adsorbents such as activated carbon [8–10], rice husk ash [11], waste tyres [12] sugar cane pulp residue [13] and fungus *Rhizopus nigricans* [14]. Activated carbons because of their high surface area, microporous character and the chemical nature of their surface have been considered as potential adsorbents for the removal of heavy metals from industrial effluents [15]. The adsorption efficiency of activated carbon depends on surface area and pore volume and these principle characteristics made activated carbon ideal for adsorption. However, for the removal of dissolved metal ions, the surface properties also play an important role [16]. Carbon adsorption is not as effective at removing metals as it is in removing organic compounds. Therefore surface modification techniques by activation (physical or chemical) were used to boost up the adsorption capacity and to add selectivity to adsorbent. The characteristics of the adsorbent greatly influence the removal efficiency of activated carbon. In general, the properties of the activated carbon vary depending on the nature of the raw material, activating agent and the conditions of activation process.

In the search of cost-effective adsorbents for Cr(VI) removal from the mine water discharges, microporous activated carbon from bael fruit shell (BFS) has been prepared by H_3PO_4 impregnation. The objective of present investigation was to introduce a new precursor for preparing high surface area and microporous activated carbon which is efficient for Cr(VI) metal removal and to establish the interactions of pH, initial concentration of Cr(VI), adsorbent dose and temperature to achieve maximum removal of Cr(VI). Factorial design technique was used to reduce the number of experiments, time, overall process cost and to obtain better response and many authors applied factorial designs for the development of adsorption process in various applications [17–20]. In

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the present investigation, optimization of the process parameters affecting the adsorption process was made by a two-level, four-factor, full factorial experimental design with Design Expert 7.1 software.

2. Material and methods

2.1. Materials

Commercial activated carbon (CAC) samples prepared from coconut shell were obtained from Kalpaka Chemicals, Tuticorin, India. Bael fruit shell (BFS) used as a raw material in this study was collected in the NIT campus, Rourkela, India. Prior to use, sample was air dried, grounded in high speed rotary cutting mill and then screened to get 1.0–1.8 mm particle size.

2.2. Preparation of activated carbon

In this investigation, the impregnation of raw material in H_3PO_4 was varied from 10% to 50% (BFS AC10 – BFS AC50). Raw material of about 40 g was impregnated for 12 h with 150 ml of different concentrations of H_3PO_4 solution and stirred to ensure a complete reaction between H_3PO_4 and BFS particles. The mixtures were then filtered and dried at 110 °C for about 12 h.

Carbonization of the impregnated sample was carried out in a tubular furnace (Bysakh & Co.) with tube dimensions of 104 mm length and 70 mm diameter to attain maximum surface area and porosity. Carbonization was done at various temperatures starting from 400 °C to 700 °C at heating rate of 4 °C/min. About 10 g of the sample was placed in furnace under N_2 gas flow (100 cm^3/min) and held for 1 h at the final carbonization temperature. The resulting solids were rinsed by warm distilled water several times and then dried at 110 °C for 12 h.

2.3. Characterization of adsorbent

The surface area and pore volume of the CAC and BFS ACs were determined by N_2 adsorption isotherms at 77 K using an automatic adsorption unit (Autosorb-1, Quantachrome). For gas adsorption measurements, the samples were degassed for 2 h at 200 °C in vacuum. The surface area was determined by the application of Brunauer–Emmett–Teller (BET) and the total pore volumes (V_t) were estimated by the volume of N_2 adsorbed at high relative pressure near unity (≈0.99) [21]. The DR-method was applied for determination of micropore volume (V_{mi}) and micropore surface area (S_{mi}). The mesopore volume (V_{me}) and mesopore surface area (S_{me}) were obtained by deducting the micropore volume and micropore surface area from total pore volume and BET surface area respectively.

Proximate and elemental analyses of BFS AC-30 carried out by thermogravimetric analyzer (Shimadzu, DTG-60H) [22] and CHNS analyzer (Elementar Vario EL CUBE), respectively. The adsorbents used in this work were characterized by SEM (scanning electron microscope) to observe the network of pores.

2.4. Batch adsorption experiments

Batch adsorption experiments were carried out in 250 ml of Erlenmeyer flasks by taking 50 ml of aqueous Cr(VI) solution. Chromium stock solution (10 mg/l) was prepared by dissolving 2.83 g of potassium dichromate ($K_2Cr_2O_7$) in 1 l distilled water. The pH of the solutions was measured (Microcontroller benchtop – Systronics, 9101 ATC) and adjusted to desired point by using 0.1 N HCl and 0.1 N NaOH solutions. The flasks were gently agitated in Environmental Orbital Shaker Incubator (DENEB Instruments) at 120 rpm for a period of 120 min to attain equilibrium. The contact time was fixed because the adsorption of Cr(VI) attains equilibrium with in 120 min [23]. The content of adsorbent was separated by filtration and the filtrate was analyzed for remaining Cr(VI) concentration. 1,5-Diphenylcarbazide reagent was used to determine the remaining concentrations of Cr(VI) spectrophotometrically (JASCO UV/Vis 550) at a wavelength of 540 nm. The analysis was carried out according to the procedure given by Gilcreas et al. [24]. The percentage removal of Cr(VI) was calculated by using following equation:

$$\%R = \left(\frac{c_i - c_t}{c_i}\right) \times 100 \tag{1}$$

where c_i and c_t are the Cr(VI) concentrations in milligrams per liter initially and at a given time t respectively. The adsorption capacities of adsorbents used in this study were determined by using the equation:

$$q_e = \frac{(c_i - c_e)V}{W} \tag{2}$$

where V is the volume of the solution (l), C_i is the initial concentration (mg/l), C_e is the equilibrium concentration (mg/l), and W is the weight of the adsorbent (g).

3. Modeling by full factorial design

In order to develop an adsorption process, a number of factors influencing the process such as pH, Cr(VI) concentration, adsorbent dose and temperature are to be studied. But the studying of the each and every factor is quite tedious and time consuming. Thus, a factorial design can minimize the above difficulties by optimizing all the affecting parameters collectively at a time [25]. Factorial design is employed to reduce the total number of experiments in order to achieve the best overall optimization of the process [26–28]. The design determines the effect of each factor on response as well as how the effect of each factor varies with the change in level of the other factors [29]. Interaction effects of different factors could be attained using design of experiments only [26,28]. Factorial design comprises the greater precision in estimating the overall main factor effects and interactions of different factors. In full factorial design every setting of every factor appears with every setting of every other factor. Factorial designs are strong candidates in examining treatment variations. Instead of conducting a series of independent studies we can combine these studies into one. A common experimental design is one with all input factors set at two-levels each. These levels are called ‘high’ and ‘low’ or ‘+1’ and ‘−1’ respectively. If there are k factors each at two-levels, a full factorial design has 2^k runs.

In the present study, four-factor two-level full factorial design (2^4 runs) was used for the modeling of adsorption process.

4. Results and discussion

Surface characteristics of CAC and the prepared activated carbons such as surface area, total pore volume and micropore volume were presented in Table 1. Surface area, total pore volume and micropore volume of the prepared activated carbon increased with the increase of H_3PO_4 concentration till 40% and then suddenly declined. BFS AC30 was used for further batch adsorption experiments because of steep increase in the surface areas (S_{BET}, S_{mi}) and pore volume parameters (V_t, V_{mi}) from 20% to 30% impregnation. SEM micrographs of the adsorbents were presented in Fig. 1(a) and (b). These figures show that the two adsorbents have an irregular and porous surface which indicates high surface area and pore volume.

Proximate and ultimate analysis results of BFS AC were tabulated (Table 2) comparing with CAC [30,31].

Table 1
Surface area and pore volume parameters of the CAC and BFS AC (T_{carb} = 400 °C and H_3PO_4 impregnation 10–50%).

Sl. no.	Parameter	Sample					
		CAC	BFS AC-10	BFS AC-20	BFS AC-30	BFS AC-40	BFS AC-50
1	S_{BET} (m^2/g)	957.46	109.03	320.21	1011.75	1041.41	421.52
2	S_{mi} (m^2/g)	940.00	98.35	302.63	988.18	1013.28	36.87
3	S_{me} (m^2/g)	17.46	10.68	17.58	23.57	28.13	384.65
4	V_t (cm^3/g)	0.4957	0.071	0.192	0.584	0.6073	0.22
5	V_{mi} (cm^3/g)	0.4867	0.067	0.185	0.57	0.5909	0.008
6	V_{me} (cm^3/g)	0.009	0.004	0.007	0.014	0.164	0.21

S_{BET}, BET surface area; S_{mi}, micropore surface area; S_{me}, mesopore surface area; V_t, total pore volume; V_{mi}, micropore volume; V_{me}, mesopore volume.

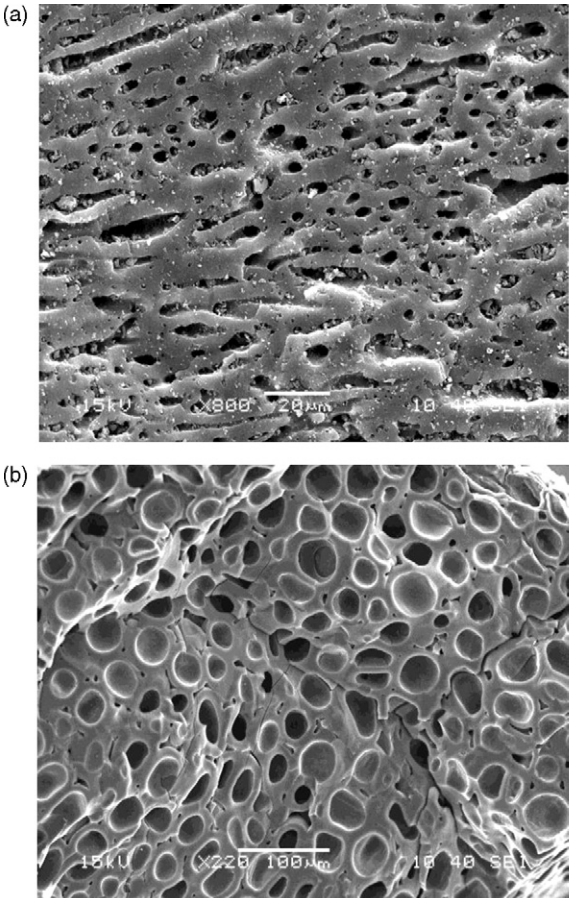

Fig. 1. Scanning electron microscopic images of adsorbents (a) CAC and (b) BFS AC.

Table 2
Proximate and elemental analysis of commercial (CAC) and prepared (BFS AC) activated carbons.

Sl. no.	Parameter	CAC [17]	BFS AC
	Proximate analysis		
1	Moisture	6.11	9.34
2	Volatile matter	72.29	61.08
3	Fixed carbon	21.02	28.73
4	Ash	0.58	0.85
Sl. no.	Parameter	CAC [18]	BFS AC
	Elemental analysis		
1	Carbon	88	58.68
2	Hydrogen	0.4	4.05
3	Sulphur	–	0.00
4	Nitrogen	2.1	0.43
5	Oxygen[a]	9.5	36.84

[a] By difference.

Table 3
Experimental ranges and levels of the factors used in the factorial design.

Independent variable	Coded symbol	Range and level	
		−1	+1
pH	*A*	2	7
Initial metal ion concentration (mg/l)	*B*	2	10
Adsorbent dose (g/l)	*C*	1	5
Temperature (°C)	*D*	20	40

4.1. Design of experiments by FFD

The levels and ranges of the studied process parameters (A – pH, B – initial concentration of Cr(VI) (C_i), C – adsorbent dose (m) and D – temperature (T)) affecting chromium removal employed in the experiment are given in Table 3. The observed and predicted percentages of Cr(VI) removal by both CAC and BFS AC are presented in Table 4. The effect of a factor is defined as the change in response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest in the experiment [22]. Process pH has an adverse effect on the response for CAC where as initial Cr(VI) concentration plays an important role in the case of BFS AC. Other parameters like adsorbent dose and temperature affected the process of adsorption significantly. The results were analyzed using the software Design Expert 7.1 and along with the main effects the interactions of different factors were determined. The coded mathematical model for 2^4 factorial designs can be given as:

$$\begin{aligned}\%R &= X_0 + X_1A + X_2B + X_3C + X_4D + X_5AB + X_6AC + X_7AD + X_8BC \\ &\quad + X_9BD + X_{10}CD + X_{11}ABC + X_{12}ABD + X_{13}ACD + X_{14}BCD \\ &\quad + X_{15}ABCD \end{aligned} \tag{3}$$

where R (%) is the percentage removal of Cr(VI), X_0 is the global mean, X_i represents the other regression coefficients and A, B, C, D stands for pH, initial concentration of Cr(VI), amount of adsorbent and temperature, respectively. By substituting the coefficients X_i in Eq. (2) by their values we get:

$$\begin{aligned}\%R_{CAC} &= 60.50 - 28.34A - 5.38B + 5.08C - 4.90D - 3.39AB \\ &\quad - 1.44AC - 6.44AD + 2.74BC + 2.93BD - 2.17CD \\ &\quad - 2.20ABC + 0.67ABD - 0.576ACD - 0.36BCD + 1.77ABCD \end{aligned} \tag{4}$$

$$\begin{aligned}\%R_{BFS\,AC} &= 79.61 - 3.29A + 14.47B + 0.36C + 0.85D + 1.70AB \\ &\quad - 0.11AC - 0.068AD - 0.44BC - 0.23BD - 0.016CD \\ &\quad + 0.15ABC - 0.16ABD - 0.32ACD + 0.26BCD + 0.73ABCD \end{aligned} \tag{5}$$

Table 4
Factorial design matrix of four variables along with experimental and predicted responses for Cr(VI) removal by CAC and BFS AC.

Run no.	Coded values of independent variables				Cr(VI) removal (%)					
	A	*B*	*C*	*D*	CAC			BFS AC		
					Observed	Predicted	Residual	Observed	Predicted	Residual
1	−1	−1	−1	−1	90.48	91.68	−1.20	68.86	69.13	−0.27
2	+1	−1	−1	−1	48.64	46.73	1.91	57.11	57.34	−0.23
3	−1	+1	−1	−1	67.85	68.42	−0.57	94.78	94.91	−0.12
4	+1	+1	−1	−1	25.65	25.80	−0.14	92.81	92.25	0.56
5	−1	−1	+1	−1	92.59	92.73	−0.14	69.44	69.45	−0.01
6	+1	−1	+1	−1	63.10	63.67	−0.57	60.84	61.26	−0.42
7	−1	+1	+1	−1	98.25	96.34	1.91	94.90	94.77	0.13
8	+1	+1	+1	−1	36.63	37.82	−1.20	91.41	91.04	0.36
9	−1	−1	−1	+1	88.03	89.71	−1.68	69.30	69.25	0.04
10	+1	−1	−1	+1	27.03	26.07	0.97	62.10	61.65	0.45
11	−1	+1	−1	+1	82.94	85.25	−2.31	96.80	96.90	−0.10
12	+1	+1	−1	+1	12.78	9.76	3.02	92.26	92.59	−0.33
13	−1	−1	+1	+1	92.20	89.18	3.02	72.94	72.71	0.24
14	+1	−1	+1	+1	24.94	27.25	−2.31	60.53	60.33	0.20
15	−1	+1	+1	+1	98.37	97.41	0.97	96.25	96.16	0.09
16	+1	+1	+1	+1	18.53	20.21	−1.68	93.50	94.09	−0.59

Table 5
Estimated regression coefficients of significant factors (coded units) and their effects for Cr(VI) removal.

Adsorbent	Factor	Effect	Coefficient	Sum of squares	Standard error	*F*-value	*P*-value
CAC	*A*	−56.68	−28.34	12849.10	1.01	796.70	0.0002
	B	−10.75	−5.38	462.29	1.01	28.66	<0.0001
	C	10.15	5.08	412.16	1.01	25.56	0.0033
	D	−9.79	−4.90	383.72	1.01	23.79	0.0041
	AB	−6.78	−3.39	183.89	1.01	11.40	0.0047
	AD	−12.89	−6.44	664.37	1.01	41.19	0.0169
	BC	5.49	2.74	120.53	1.01	7.47	0.0017
	BD	5.86	2.93	137.19	1.01	8.51	0.0332
BFS AC	*A*	−6.59	−3.29	3599.64	0.14	549.00	<0.0001
	B	28.95	14.47	173.60	0.14	10600.21	<0.0001
	C	0.72	0.36	3351.96	0.14	6.61	<0.0001
	D	1.69	0.85	2.09	0.14	36.23	0.0422
	AB	3.40	1.70	11.46	0.14	146.25	0.0009
	BC	−0.87	−0.44	46.25	0.14	9.64	<0.0001
	ACD	−0.63	−0.32	3.05	0.14	5.04	0.0210

4.2. Analysis of variance (ANOVA)

After estimating the main effects, the interacting factors affecting the removal of Cr(VI) were determined by performing the analysis of variance (ANOVA). Sum of squares (SS) of each factor quantifies its importance in the process and as the value of the SS increases the significance of the corresponding factor in the undergoing process also increases (Table 5). The main and interaction effects of each factor having P values <0.05 are considered as potentially significant.

4.3. Main and interaction effects

The effect of each factor was statistically significant at $P < 0.05$ [32]. For CAC, the main effects A, B, C and D and interactions AB, AD, BC and BD are of higher statistical significance, where as for BFS AC, the significant effects are A, B, C, D, AB, BC and ACD. Based on F-ratio and P-value statistically insignificant factors were discarded. Fig. 2(a) and (b) shows the main effects of the process parameters for the CAC and BFS AC, respectively. The sign of the main effect indicates the directions of the effect. It can be seen from Fig. 2 that in case of CAC, the effect of pH was characterized by a greater degree of departure and also had a negative effect on the response, whereas for BFS AC, the concentration of Cr(VI) has a positive effect on the response with greater departure. Contour plots for the significant interactions of CAC and BFS AC were shown in Fig. 3(a) and (b). The interaction plots for CAC and BFS AC showed that interaction of pH and Cr(VI) concentration played major role and also these two factors interacted strongly with other factors indicating predominant influence in removal. In case of BFS AC, interactions of pH and Cr(VI) concentration with temperature were insignificant on the response, whereas for CAC, these interactions were statistically significant. After discarding insignificant terms, the resultant models can be represented as:

$$\%R_{\mathrm{CAC}} = 60.50 - 28.34A - 5.38B + 5.08C - 4.90D - 3.39AB - 6.44AD + 2.74BC + 2.93BD \quad (6)$$

$$\%R_{\mathrm{BFS\,AC}} = 79.61 - 3.29A + 14.47B + 0.36C + 0.85D + 1.70AB - 0.44BC - 0.32ACD \quad (7)$$

The adsorption capacities (q_e) of CAC and BFS AC used in the present study were compared with the various adsorbents for Cr(VI) removal in Table 6. The adsorption capacity of BFS AC obtained in this study was far higher (464.06 mg/g at pH 7; 473.91 mg/g at pH 2) than the other adsorbents previously reported for chromium removal.

4.4. Normal probability plot of residuals

The normality of the data can be checked by plotting a normal probability plot of the residuals. If the data points on the plot fall fairly close to the straight line, then the data are normally dis-

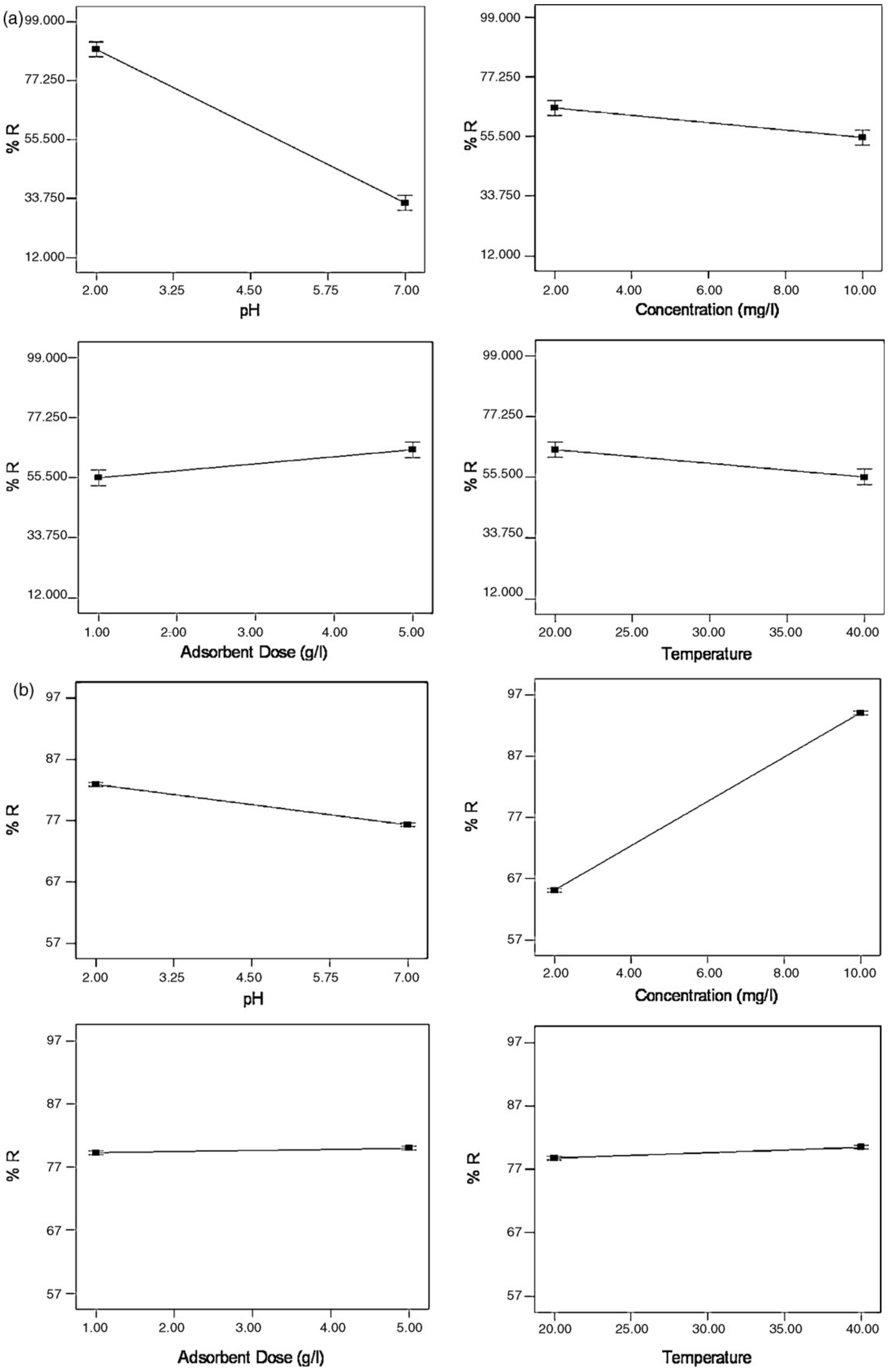

Fig. 2. Main effect plots of (a) CAC and (b) BFS AC.

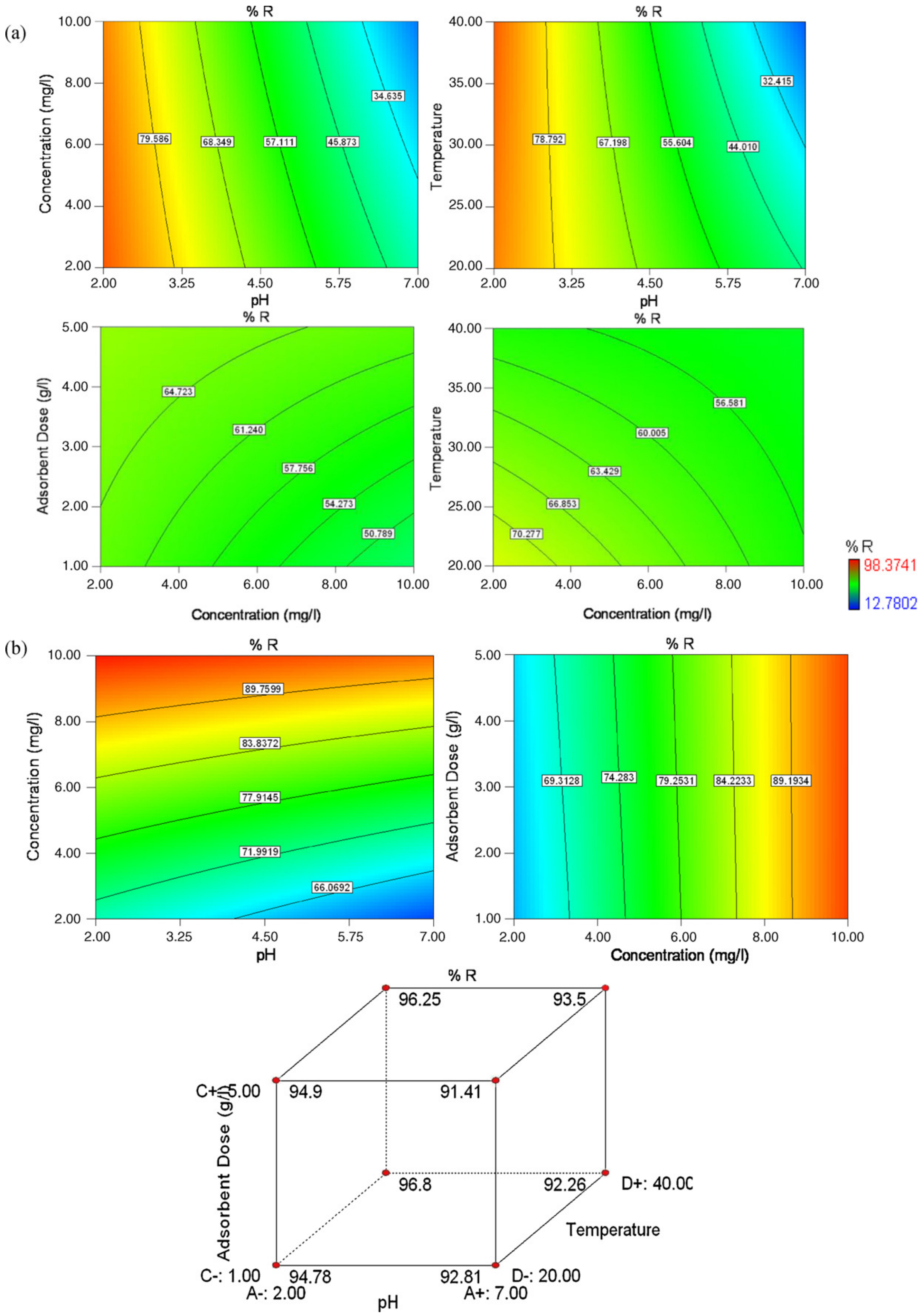

Fig. 3. Contour plots for interaction effects (a) CAC and (b) BFS AC.

Table 6
Comparison of adsorption capacities of various adsorbents used for chromium removal.

Adsorbents	Adsorption capacity (mg/g)	Initial Cr(VI) concentration (mg/l)	pH	Ref.
Leather	459.00	1000	2.0	[33]
Tyres activated carbon	58.50	60	2.0	[10]
Leaf mould	43.10	1000	2.0	[34]
Coconut shell carbon	20.00	–	2.0	[35]
	10.88	25	4.0	[36]
Beech sawdust	16.10	200	1.0	[37]
Rubber wood sawdust activated carbon	44.05	200	2.0	[38]
Tamarind hull activated carbon	85.91	25–75	2.0	[39]
Olive cake	33.44	100	2.0	[40]
Terminalia arjuna nuts activated carbon	28.4	10–30	1.0	[41]
Bael fruit shell activated carbon	17.27	50–125	2.0	[23]
CAC	128.26	10	7	Present study
	339.25	10	2	Present study
BFS AC	464.06	10	7	Present study
	473.91	10	2	Present study

tributed [42]. The normal probability plot of the residuals for CAC and BFS AC was shown in Fig. 4(a) and (b). It can be seen that for both adsorbents, the data points were fairly close to the straight line and it indicates that the experiments come from a normally distributed population.

4.5. Optimization

Optimization of Cr(VI) removal was carried out by a multiple response method called desirability (*D*) function to optimize different combinations of process parameters such as pH, initial concentration (C_i), adsorbent dose (*m*) and temperature (*T*). The goal of optimization was to improve adsorption conditions in batch process, i.e., to minimize the adsorbent dose and to increase the initial concentration of Cr(VI). To achieve maximum desirability, pH and temperature were set to within the range, whereas initial concentration of Cr(VI) and adsorbent dose were set to maximum and minimum levels, respectively. Fig. 5(a) and (b) shows the graphical desirability for CAC and BFS AC generated from 46 optimum points via numerical optimization, respectively.

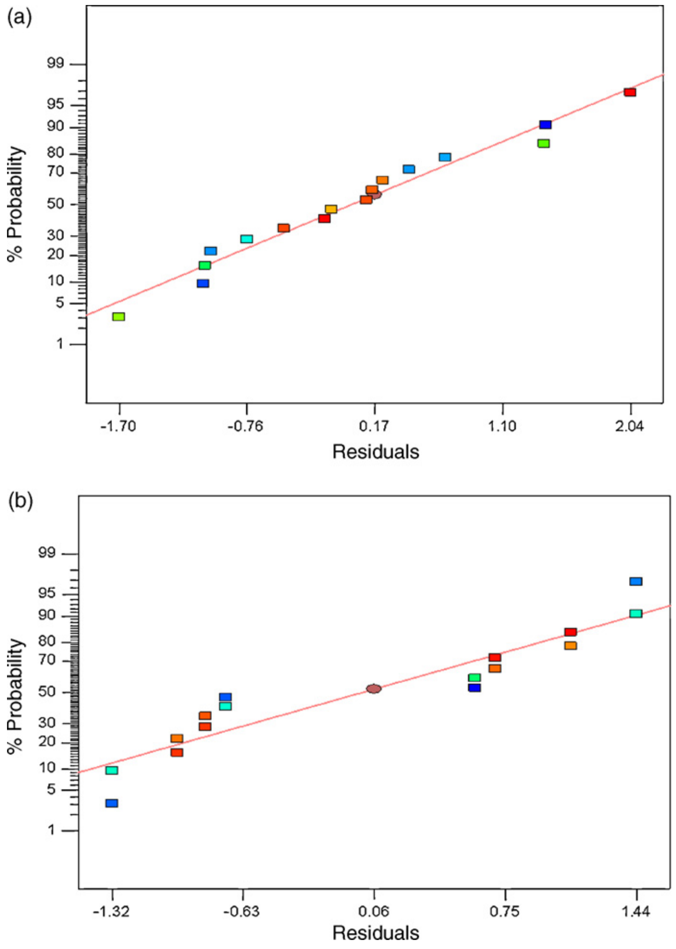

Fig. 4. Normal probability plots of residuals for (a) CAC and (b) BFS AC.

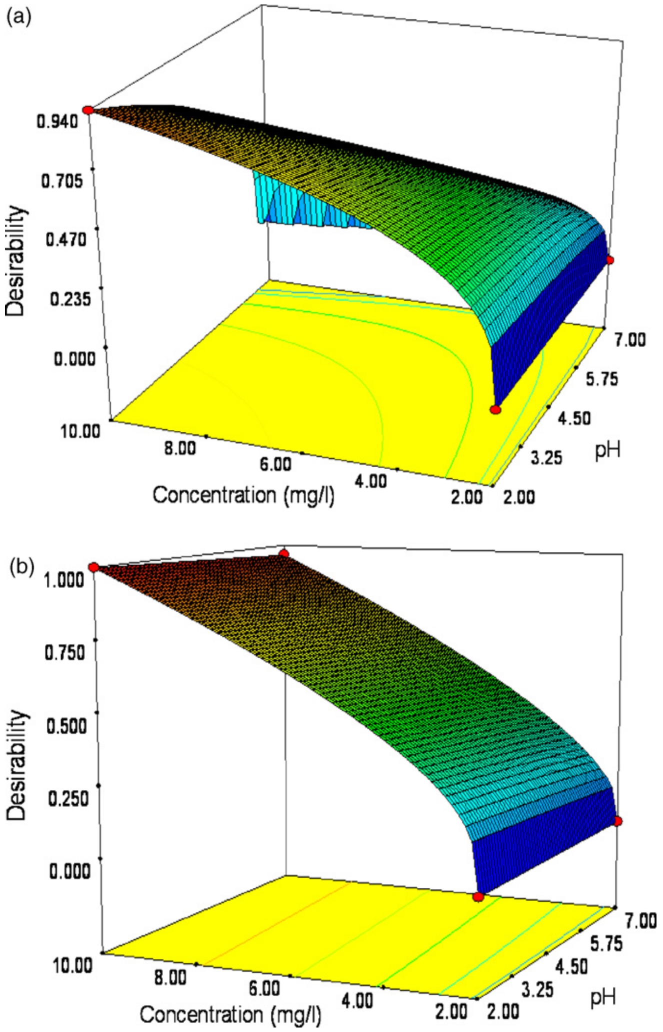

Fig. 5. Desirability fitted 3D surface for Cr(VI) removal by (a) CAC and (b) BFS AC.

Among 46 starting points, for CAC the best local maximum for Cr(VI) removal (89.8%) was found at pH – 5.33, initial concentration of Cr(VI) – 6.68 mg/l, adsorbent dose – 2.56 g/l, and at temperature – 30 °C and the value of desirability obtained was 0.949. For BFS AC, the maximum removal (96.34%) observed at pH – 6.39, initial concentration of Cr(VI) – 7.51 mg/l, adsorbent dose – 2.18 g/l and temperature – 36.38 °C with 0.989 desirability.

5. Conclusion

Activated carbon prepared from bael fruit shell (BFS) was successfully employed for the Cr(VI) removal and removal efficiency was compared with the commercial activated carbon (CAC). Analysis of results carried out by using two-level full factorial design (FFD) to avoid the traditional one-factor-at-a-time experiments and the model developed by FFD resulted in improved response, reduced process variability and closer confirmation of response to targeted requirements. Common statistical tools such as analysis of variance (ANOVA) and *F*-test were used to define the most important process variables affecting the efficiency of Cr(VI) removal. The use of FFD allowed for identification of the most significant parameters under tested conditions. Main effects like pH (*A*), initial concentration of Cr(VI) (*B*), adsorbent dose (*C*), temperature (*D*) played important role and interaction effects like pHC_i (*AB*), $C_i m$ (*BC*) and pHmT (*ACD*) were significant in case of BFS AC.

Effect of process parameters on Cr(VI) removal was investigated. In economic point of view, high concentration of metal removal at neutral pH with minimum amount of adsorbent was appreciable. Under desired conditions (pH – 7, C_i – 10 mg/l, m – 1 g/l, T – 20 °C), BFS AC has better Cr(VI) removal potential (92.81%) than CAC (25.65%). For BFS AC the % removal decreased very slightly with the increase of temperature from 20 °C to 40 °C. Maximum removal of Cr(VI) by using BFS AC was attributed to the large surface area and micropore volume of the prepared activated carbon (Table 1).

Thus, activated carbon prepared from bael fruit shell with H_3PO_4 activation can be applied for the treatment of effluents from different industries and chromate mining areas. BFS AC showed a good potential for Cr(VI) removal and its application is economical than commercial activated carbon.

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