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Use of Box–Behnken design of experiments for the adsorption of chromium using immobilized macroalgae

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ABSTRACT

Optimization experiments were carried using three-level Box–Behnken design for the adsorption of chromium onto immobilized macroalgae. The influence of independent parameters such as pH (2−8), temperature (303−333 K), and initial chromium concentration (20−100 mg/L) towards chromium ions removal has been performed. Second-order polynomial models were developed for the responses. The significance of the independent parameters and their interactions were investigated using the analysis of variance. The three-dimensional (3-D) response surface plots were used to study the interactive effects of the independent parameters on the chromium removal efficiency. The maximum Cr(VI) removal efficiency of 90.52, 90.86 was observed for *Enteromorpha* sp. immobilized in sodium alginate (ESA), *Enteromorpha* sp. immobilized in polysulfone (EPS), and maximum observed total chromium removal efficiency of 81.14, 79.90 was obtained for ESA, EPS, respectively. The observed value was in good agreement with the predicted values. These results indicated that immobilized macroalgae could be used for the removal of chromium from aqueous solution.

Keywords: Box–Behnken design; Adsorption; Immobilization; Macroalgae; Chromium removal

1. Introduction

The environmental pollution due to the toxic substances discharge from various industrial sectors is of great concern. Major efforts are being made for the removal of the harmful toxic substances from wastewater [1]. The toxic metal ions in the industrial discharges from mine water, tannery, plastic manufacturing, electroplating, fertilizers, metal fabrication, pigments, paints, photography, ceramic, glass industries, fungicides chrome alloy, surface finishing, manufacture of batteries, and metallurgic industries has received wide spread attention throughout the world in recent years [2,3]. Chromium is highly reactive metal ion, which exists in six different oxidation states. The Cr(III) and Cr(VI) are the more stable oxidation states. The hexavalent form of chromium ions is considered more toxic than the trivalent form since the Cr(VI) ions are highly soluble, moves readily through soils and a strong oxidizing agent capable of being absorbed through the skin which can be easily absorbed and accumulated in stomach, kidneys, and

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liver. Owing to the high toxicity effects of Cr(VI), the removal of hexavalent chromium ions before being discharge into the aquatic system is important [4,5]. The maximum permitted level of chromium in wastewater is 5 mg/L for trivalent chromium and 0.05 mg/L in case of hexavalent chromium [6]. Commonly adopted technique for chromium removal from wastewaters includes precipitation, membrane filtration, photocatalysis, ion-exchange, electrolysis, reverse osmosis, chemical oxidation/reduction, and ultra-filtration. These techniques are associated with their technical or economical constrains [7–9]. Biosorption is eco-friendly and cost-effective method, warrant for the sequestration of toxic metal ions from the wastewater [10]. The investigations on low-cost biosorbents towards heavy metal removal have intensified. Materials locally available in bulk quantity such as agricultural waste, natural materials, and industrial byproducts can be utilized as the biosorbents [11,12]. The dead biomass usage in biosorption towards wastewater treatment has increased since the biomass are not affected by the toxic substances, free from nutrients requirements, easy regenerations, and can be used for many recycles [13]. Biomass immobilization on a suitable matrix offers mechanical potency, rigidity, uniform size, and negligible clogging in continuous biosorption system. The important natural and synthetic matrices used in biosorbent immobilization are silica gel, sodium alginate, polysulfone, polyacrylamide, and polyurethane [14,15].

Experiments performed through one variable at time (OVAT) are time-consuming, costlier, and requires large number of experiments. Further OVAT does not include the interactions between the selected parameters [16]. Therefore, in the present study response surface methodology (RSM) a multivariate statistics technique used for the optimization of the biosorption system. To the best of our knowledge, this is the first report which makes use of the *Enteromorpha sp.* immobilized in sodium alginate, polysulfone towards chromium ions removal from aqueous solution. A three-variable Box–Behnken design has been used for the optimization of adsorption process. The variables like pH, temperature, and initial Cr(VI) concentration were optimized, evaluated the single and interactive effects of the variables in the process for the removal of chromium ions from aqueous solution.

2. Materials and methods

2.1. Preparation of metal solution

Stock solution of Cr(VI) was prepared by dissolving potassium dichromate, $K_2Cr_2O_7$ in double-distilled water. The stock solution was then diluted to prepare solutions of the desired concentrations. All solutions, their dilutions and standards were prepared using double-distilled water. The initial pH of each solution was adjusted to the required value using 0.1 M HCl or 0.1 M NaOH.

2.2. Preparation of biomass and its immobilization

Enteromorpha sp. was collected at Kozhikode beach, India. The collected biomass was washed in distilled water to remove dirt and kept on filter paper to reduce water content. The biomass was sun dried for three days and oven dried at 348 K for 40 min. Dried biomass was ground, sieved in the particles size of <0.25 mm and stored until use in an air tight plastic container. A portion of prepared raw biomass was subjected to the immobilization using sodium alginate polymer *Enteromorpha* sp. immobilized in sodium alginate (ESA). About 4.0 g of sodium alginate was dissolved in 100-mL hot (60˚C) double-distilled water. After cooling, 5.0 g of algal biomass was added and the mixture was stirred to obtain a homogenous suspension. The alginate–algal biomass slurry was then added into 0.1-M $CaCl_2$ solution in a dropwise manner using 5-mL syringe. The dry weight of the prepared algal immobilized beads was determined after drying overnight in an oven at 50˚C [17]. The remaining portion of the dried biomass was immobilized in a polysulfone matrix *Enteromorpha* sp. immobilized in polysulfone (EPS). About 10 g of polysulfone was dissolved in 90 ml of N, Ndimethyl formamide using thermostated shaking incubator

Table 1
Coded and real values of the factors (independent variables) for BBD

Process variables	Symbols	Range and levels		
		Low (−1)	Medium (0)	High (+1)
pH	X_1	2	5	8
Temperature (K)	X_2	303	318	333
Initial chromium concentration (mg/L)	X_3	20	60	100

Table 2
Experimental and predicted values of Y for Cr(VI) and total chromium adsorption onto ESA

				Responses			
				Hexavalent chromium		Total chromium	
	Real values of the variables			% Removal (Y_1)		% Removal (Y_2)	
Run order	X_1	X_2	X_3	Observed	Predicted	Observed	Predicted
1	2	318	20	92.47	90.57	21.87	21.26
2	8	318	100	4.15	6.07	72.48	73.10
3	5	303	20	23.86	24.48	40.66	42.75
4	5	318	60	7.22	7.23	38.54	38.55
5	5	318	60	7.22	7.23	38.54	38.55
6	5	333	100	7.12	6.52	33.09	31.00
7	2	318	100	39.90	47.21	3.69	5.66
8	2	333	60	86.63	79.95	13.09	13.27
9	8	303	60	6.73	13.41	77.03	76.86
10	5	303	100	5.34	−3.24	36.12	35.63
11	8	318	20	21.08	13.79	83.09	81.14
12	5	333	20	21.28	29.88	47.03	47.52
13	2	303	60	55.94	57.23	12.48	11.08
14	8	333	60	7.12	5.85	73.39	74.81
15	5	318	60	7.22	7.23	38.54	38.55

Table 3
Experimental and predicted values of Y for Cr(VI) and total chromium adsorption onto EPS

				Responses			
				Hexavalent chromium		Total chromium	
	Real values of the variables			% Removal (Y_3)		% Removal (Y_4)	
Run order	X_1	X_2	X_3	Observed	Predicted	Observed	Predicted
1	5	333	20	57.32	57.31	39.15	37.43
2	5	303	20	50.00	47.35	34.61	37.89
3	5	318	60	30.09	30.10	23.39	23.39
4	2	318	100	49.00	47.20	1.58	3.54
5	5	318	60	30.09	30.10	23.39	23.39
6	5	333	100	29.80	32.45	31.88	28.57
7	2	318	20	90.00	90.86	17.33	17.70
8	5	318	60	30.09	30.10	23.39	23.39
9	5	303	100	15.14	15.17	19.45	21.15
10	8	318	100	6.53	5.66	68.85	68.46
11	2	333	60	81.18	80.35	10.06	11.38
12	8	303	60	9.20	10.05	72.79	71.46
13	8	333	60	36.23	34.47	70.06	73.72
14	2	303	60	75.74	77.53	10.36	6.68
15	8	318	20	17.22	19.04	81.88	79.90

(116736 GB, GeNei). To that suspension 5 g of algal biomass was blended by stirring of mixture using magnetic stirrer, uniform slurry of biomass was formed. Then slurry was added to a glass beaker containing 80% methanol solution in a dropwise manner using a 5-mL syringe. The beads formed were washed in double-distilled water for 1 h on a rotary shaker in order to diffuse out the N, N dimethyl formamide. After curing, the resultant beads were air dried at room temperature for 2–3 d [18].

Table 4
Adequacy of the model tested

Source	Sum of squares	DF	Mean square	*F*-value	*p*-value	Remarks
Sequential model sum of squares for Cr(VI) removal using ESA						
Mean	1,0315.80	1	1,0315.80			
Linear	8,372.44	3	2,790.81	7.80	0.0044	
2FI	551.83	3	183.94	0.43	0.7316	
Quadratic	3,000.38	3	1,000.12	14.09	0.0071	Suggested
Cubic	354.85	3	118.28	63,660,000	<0.0001	Aliased
Residual	0	2	0			
Total	22,595.32	15	1,506.35			
Sequential model sum of squares for total chromium removal using ESA						
Mean	26,434.55	1	2,6434.55			
Linear	8,397.81	3	2,799.27	163.48	<0.0001	
2FI	40.90	3	13.63	0.73	0.5574	
Quadratic	125.78	3	41.92	9.68	0.0159	Suggested
Cubic	21.64	3	7.21	63,660,000	<0.0001	Aliased
Residual	0	2	0			
Total	34,189.71	15	2,279.31			
Sequential model sum of squares for Cr(VI) removal using EPS						
Mean	24,621.80	1	24,621.80			
Linear	8,422.83	3	2,807.61	26.97	<0.0001	
2FI	359.36	3	119.78	1.21	0.3638	
Quadratic	755.88	3	251.96	42.23	0.0006	Suggested
Cubic	29.83	3	9.94	63,660,000	<0.0001	Aliased
Residual	0	2	0			
Total	34,189.71	15	2,279.31			
Sequential model sum of squares for total chromium removal using EPS						
Mean	18,598.12	1	1,8598.12			
Linear	8,432.03	3	2,810.67	34.39	<0.0001	
2FI	18.848	3	6.28	0.05	0.9808	
Quadratic	814.07	3	271.35	20.52	0.0031	Suggested
Cubic	66.09	3	22.03	4,345,338	<0.0001	Aliased
Residual	0	2	0			
Total	27,929.16	15	1,861.94			

2.3. *Experimental setup*

Batch adsorption experiments were conducted in 250-mL Erlenmeyer flasks containing 50 mL of Cr(VI) solution with 0.2 g/L of adsorbent dosage, stirred in thermostated shaking incubator (116736GB, GeNei) and left for 24 h to attain the equilibrium. The adsorption studies were performed by varying the solution pH, initial Cr(VI) concentration, and temperature, respectively. The agitation speed of the stirrer was maintained at 120 rpm. After completion of every set of experiments the solution was separated by filtration through Whatman filter paper no. 42. The analysis of Cr(VI) in the filtrate was carried out using a double-beam UV–visible spectrophotometer (2201, Systronics), by developing a purple-violet color with 1,5-di-phenyl carbazide in acidic solution as a complexing agent [19]. The total chromium concentration was determined with the flame atomic absorption spectrometer (AAS 303, Thermo Fisher Scientific).

The percentage removal of the chromium was calculated using Eq. (1):

$$\text{Removal } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the initial and the equilibrium chromium concentration in the aqueous solution, respectively (mg/L).

Table 5
Adequacy of the model tested

Source	Std. dev.	R^2	Adjusted R^2	Predicted R^2	Press	Remarks
Model summary statistics for Cr(VI) removal using ESA						
Linear	18.8464	0.6818	0.5950	0.4061	7,291.6040	
2FI	20.4793	0.7267	0.5218	−0.0868	13,345.4800	
Quadratic	8.4244	0.9711	0.9190	0.5376	5,677.7080	Suggested
Cubic	0	1	1		+	Aliased
Model summary statistics for total chromium removal using ESA						
Linear	4.1379	0.9780	0.9720	0.9571	368.1991	
2FI	4.2929	0.9828	0.9699	0.9257	637.3480	
Quadratic	2.0807	0.9974	0.9929	0.9596	346.3728	Suggested
Cubic	0	1	1		+	Aliased
Model summary statistics for Cr(VI) removal using EPS						
Linear	10.2028	0.8803	0.8476	0.7774	2,128.8860	
2FI	9.9102	0.9178	0.8562	0.7047	2,824.6190	
Quadratic	2.4425	0.9968	0.9912	0.9501	477.2845	Suggested
Cubic	0	1	1		+	Aliased
Model summary statistics for total chromium removal using EPS						
Linear	9.0403	0.9036	0.8773	0.8382	1,508.9050	
2FI	10.4890	0.9056	0.8349	0.6852	2,936.5680	
Quadratic	3.6357	0.9929	0.9801	0.8866	1,057.4820	Suggested
Cubic	0.0022	1	1		+	Aliased

2.4. Box–Behnken experimental design

The Box–Behnken response surface experimental design (BBD) composed of a set of points lying at the midpoint of each edge and the replicated center point of a multidimensional cube [20]. In the present investigation, BBD with three factors at three levels was used to optimize and investigate the influence of adsorption process variables, such as solution pH, temperature andinitial metal ion concentration on percentage chromiumremoval (%) from an aqueous solution (Table 1). This design was applied using software Design-Expert (Trial Version 7.0.0, Static Made Easy, Minneapolis, Minnesota, USA). In the present study, the number of independent variables is three so for each categorical variable, a 2^3 full factorial BBD consisting of eight factorial points, six axial points, and three replicates at the center points were subjected. The following equation can be used to find the number of experimental runs:

$$N = K^2 + K + x_0 \tag{2}$$

where N is the total number of experiments required, K is the number of variables, and x_0 is the number of central points. Thus, for this design total number of experimental runs (Table 2) will be 15 ($K = 3$, $x_0 = 3$). Independent variables were coded according to the following equation:

$$x_i = \frac{(X_i - X_0)}{\Delta X_i} \tag{3}$$

where x_i and X_i represents the coded and real values of the independent variables, respectively. X_0 and ΔX_i indicates the real value of the independent variables at the center point and step change of X_i, respectively.

The BBD experimental data were analyzed through multiple regression analysis to examinerelevant model (linear, interactive (2FI), and quadraticandcubic) to examine over thechromium adsorptionprocess. The second-order polynomial model generated by this experimental design is as follows:

$$\begin{aligned} Y_i = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 \\ & + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \end{aligned} \tag{4}$$

where Y_i is the predicted response surface (Y_1, Cr(VI) % removal (ESA); Y_2, total chromium % removal

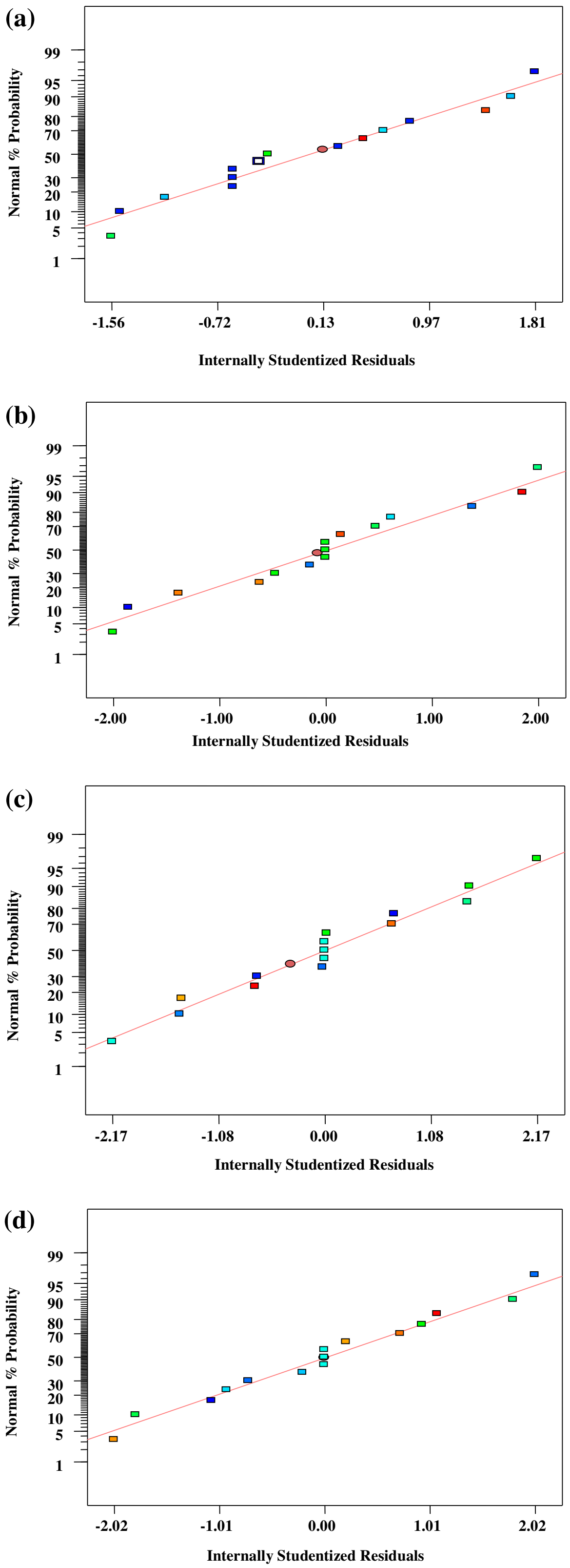

Fig. 1. Normal percentage probability against residual error of (a) Cr(VI) removal, (b) total chromium removal on ESA (c) Cr(VI) removal, and (d) total chromium removal on EPS.

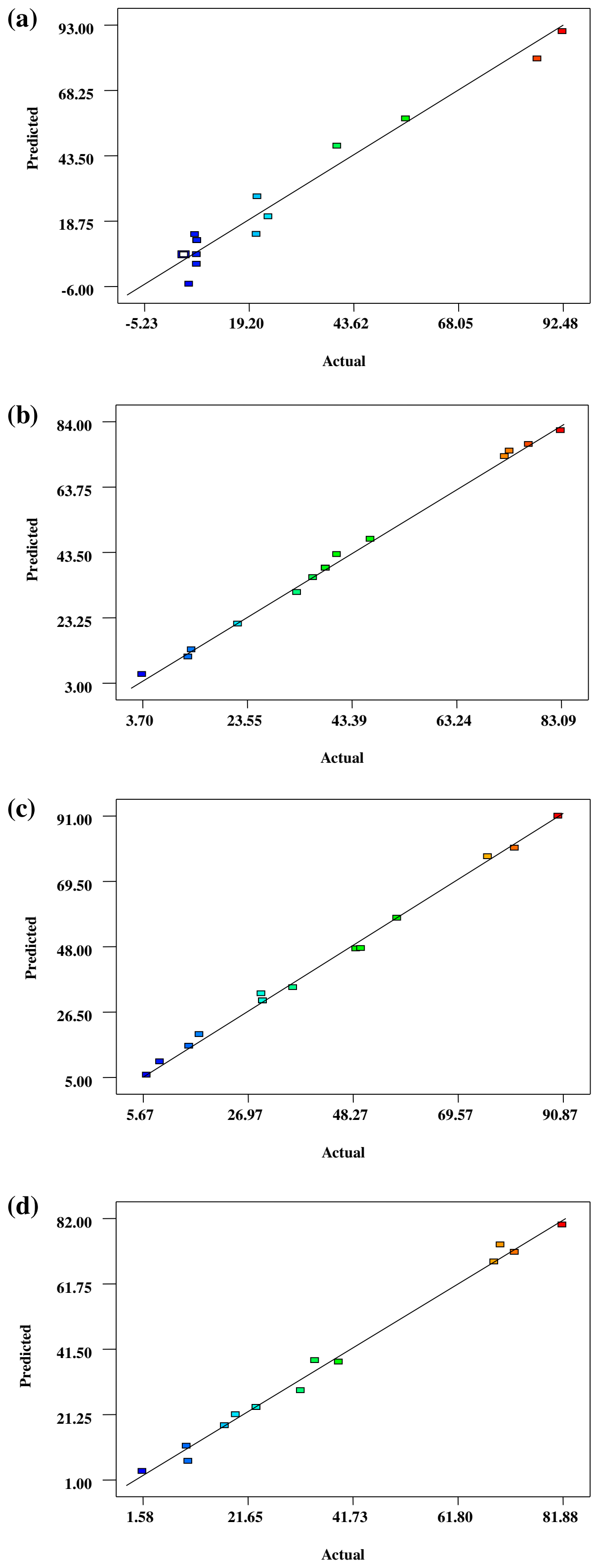

Fig. 2. Predicted response against actual response of (a) Cr (VI) removal, (b) total chromium removal on ESA, (c) Cr (VI) removal, and (d) total chromium removal on EPS.

Table 6
ANOVA for quadratic model for Cr(VI) adsorption using ESA

Source	Sum of squares	DF	Mean square	*F*-value	*p*-value	Remarks
Model	11,831.41	6	1,971.902	35.20393	<0.0001	Significant
X_1	6,952.656	1	6,952.656	124.1242	<0.0001	
X_2	114.739	1	114.739	2.04841	0.1902	
X_3	1,305.05	1	1,305.05	23.29876	0.0013	
X_1X_2	229.4775	1	229.4775	4.096812	0.0776	
X_1X_3	317.6159	1	317.6159	5.670328	0.0445	
X_1^2	2,911.873	1	2,911.873	51.98502	<0.0001	
Residual	448.1095	8	56.01368			
Lack of fit	448.1095	6	74.68491			
Pure error	0	2	0			
Corr. total	12,279.52	14				

Table 7
ANOVA for quadratic model for total chromium adsorption using ESA

Source	Sum of squares	DF	Mean square	*F*-value	*p*-value	Remarks
Model	8,564.516	9	951.6129	219.7893	<0.0001	Significant
X_1	8,118.469	1	8,118.469	1,875.082	<0.0001	
X_2	0.011478	1	0.011478	0.002651	0.9609	
X_3	279.3388	1	279.3388	64.5175	0.0005	
X_1X_2	4.499541	1	4.499541	1.039236	0.3548	
X_1X_3	14.34803	1	14.34803	3.313892	0.1283	
X_2X_3	22.06152	1	22.06152	5.09544	0.0736	
X_1^2	122.3988	1	122.3988	28.26984	0.0031	
X_2^2	0.339055	1	0.339055	0.07831	0.7908	
X_3^2	3.581267	1	3.581267	0.827147	0.4048	
Residual	21.6483	5	4.32966			
Lack of fit	21.6483	3	7.2161			
Pure error	0	2	0			
Corr. total	8,586.165	14				

Table 8
ANOVA for quadratic model for Cr(VI) adsorption using EPS

Source	Sum of squares	DF	Mean square	*F*-value	*p*-value	Remarks
Model	9,538.08	9	1,059.787	177.636	<0.0001	Significant
X_1	6,425.963	1	6,425.963	10,77.087	<0.0001	
X_2	370.674	1	370.674	62.13049	0.0005	
X_3	1,626.194	1	1,626.194	272.5743	<0.0001	
X_1X_2	116.4695	1	116.4695	19.52202	0.0069	
X_1X_3	229.4775	1	229.4775	38.46385	0.0016	
X_2X_3	13.42031	1	13.42031	2.249444	0.1939	
X_1^2	493.3659	1	493.3659	82.69548	0.0003	
X_2^2	294.8149	1	294.8149	49.41538	0.0009	
X_3^2	3.440859	1	3.440859	0.576739	0.4818	
Residual	29.83028	5	5.966057			
Lack of fit	29.83028	3	9.943428			
Pure error	0	2	0			
Corr. total	9,567.91	14				

Table 9
ANOVA for quadratic model for total chromium adsorption using EPS

Source	Sum of squares	DF	Mean square	F-value	p-value	Remarks
Model	9,264.956	9	1,029.44	77.87857	<0.0001	Significant
X_1	8,079.909	1	8,079.909	611.2566	<0.0001	
X_2	24.28836	1	24.28836	1.837449	0.2333	
X_3	327.8354	1	327.8354	24.80122	0.0042	
X_1X_2	1.469308	1	1.469308	0.111155	0.7524	
X_1X_3	1.85946	1	1.85946	0.140671	0.7230	
X_2X_3	15.51927	1	15.51927	1.174055	0.3280	
X_1^2	753.0318	1	753.0318	56.96793	0.0006	
X_2^2	36.51153	1	36.51153	2.76215	0.1574	
X_3^2	82.80055	1	82.80055	6.26398	0.0543	
Residual	66.0926	5	13.21852			
Lack of fit	66.09259	3	22.03086			
Pure error	1.01E-05	2	5.07E-06			
Corr. total	9,331.048	14				

(ESA); Y_3, Cr(VI) % removal (EPS) and Y_4, total chromium % removal (EPS)), b_0 is the model intercept coefficient, b_1–b_{33} are the regression coefficients (linear, interaction, and squared effect), and $X_1 - X_3$ are the coded values of the independent variables.

3. Results and discussion

The Box–Behnken design matrix and corresponding results of RSM experiments were used to determine the effects of variables such as solution pH, temperature, and initial metal ion concentration on the percentage removal of chromium ions using ESA and EPS are represented in Tables 2 and 3. Usually a system with a number of variables is primarily affected by the main effects and low-order interactions. Assuming that the higher order interactions are small in comparison to the low-order interactions, hence in the present study two-way interactions were mainly considered. Models such as linear, interactive, quadratic, and cubic models were analyzed by fitting the experimental data. Two different tests such as sequential model sum of squares and model summary statistics were performed in order to examine the models adequacy among the different models used in the present study. The results of Table 4 indicated that Cubic model was found to be aliased. It was observed from Table 5 that the quadratic model exhibited maximum “Adjusted R^2” and the “Predicted R^2” values, in comparison of all other models [21–23]. Therefore, the quadratic model was chosen to describe the effects of process variables on the removal of chromium ions from aqueous solutions using ESA and EPS.

3.1. Mathematical model development

An empirical relationship between independent variables and response was drawn by a second-order polynomial equations. The following second-order polynomial equations in the coded form were developed in order to explain the removal efficiency of chromium ions.

$$Y_1 = +11.33 - 29.48\ X_1 + 3.79\ X_2 - 12.77\ X_3 - 7.57\ X_1X_2 + 8.91\ X_1X_3 + 27.93\ X_1^2 \tag{5}$$

$$Y_2 = +38.55 + 31.86\ X_1 + 0.038\ X_2 - 5.91\ X_3 - 1.06\ X_1X_2 + 1.89\ X_1X_3 - 2.35\ X_2X_3 + 5.76\ X_1^2 - 30\ X_2^2 + 0.98\ X_3^2 \tag{6}$$

$$Y_3 = +31.10 - 28.34\ X_1 + 6.81\ X_2 - 14.26\ X_3 + 5.40\ X_1X_2 + 7.57\ X_1X_3 + 1.83\ X_2X_3 + 11.56\ X_1^2 + 8.94\ X_2^2 - 0.97\ X_3^2 \tag{7}$$

$$Y_4 = 23.39 + 31.78\ X_1 + 1.74\ X_2 - 6.40\ X_3 - 0.61\ X_1X_2 + 0.68\ X_1X_3 + 1.97\ X_2X_3 + 14.28\ X_1^2 + 3.14\ X_2^2 + 4.74\ X_3^2 \tag{8}$$

where Y_1, Y_2 are the percentage removal of Cr(VI) and total chromium on ESA and Y_3, Y_4 represent the percentage removal of Cr(VI) and total chromium onto EPS. In the above-mentioned four equations, X_1, X_2, and X_3 indicate the independent singular factors,

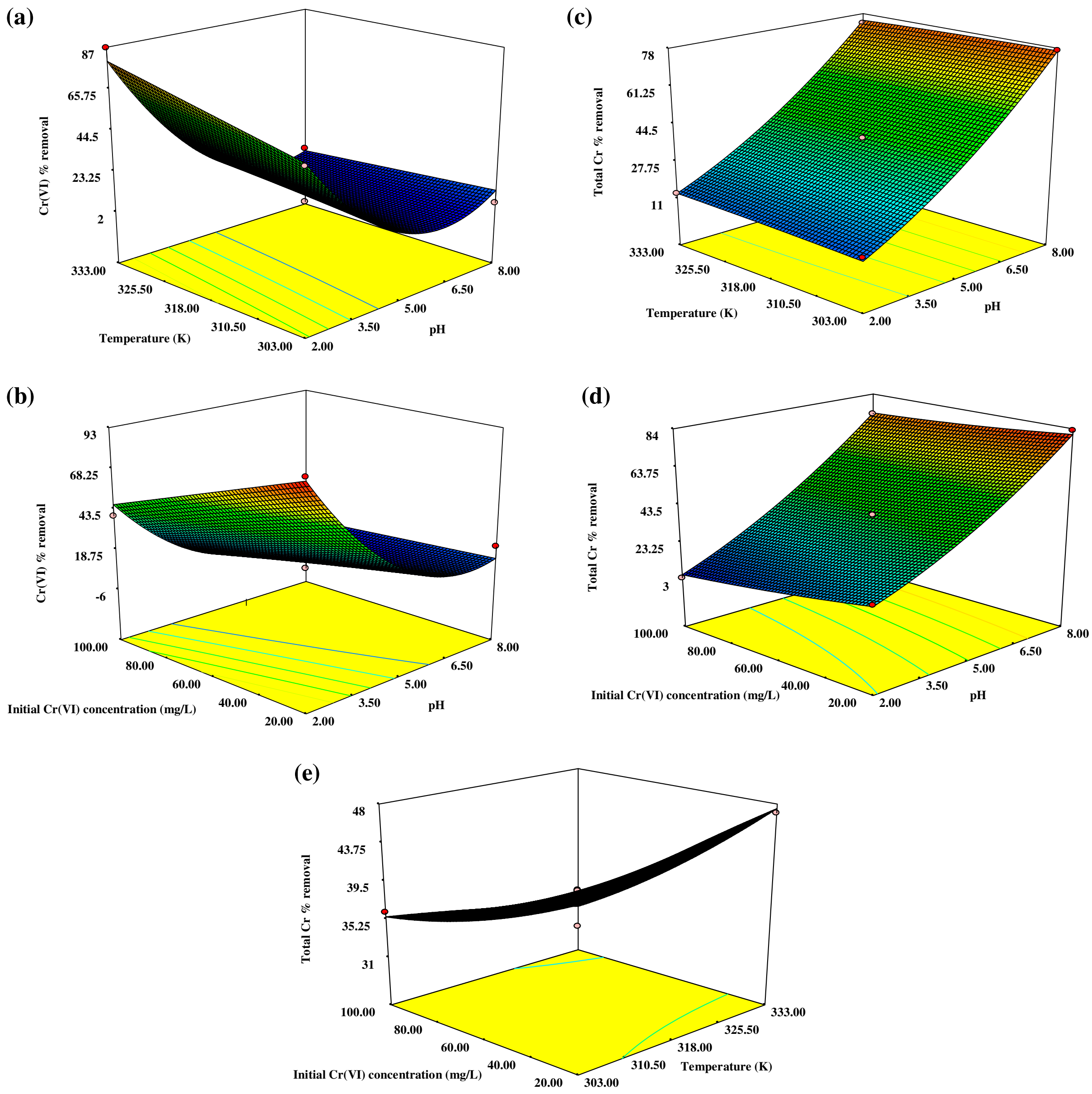

Fig. 3. 3-D response surface plots of interaction effect of two independent variables: (a) temperature and pH, (b) initial Cr (VI) concentration and pH for Cr(VI) removal on ESA, (c) temperature and pH, (d) initial Cr(VI) concentration and pH, and (e) initial Cr(VI) concentration and temperature for total chromium removal on ESA, respectively.

whereas X_1X_2, X_1X_3, and X_2X_3 are interaction factors. The quadratic terms include X_1^2, X_2^2, and X_3^2.

3.2. Adequacy of mathematical models

Data were analyzed in order to verify the normality of the residuals. The analysis of variance (ANOVA) analysis is based on the assumption that the residuals are normally and independently distributed with the same variance at the each factor level. The residuals are the results of the difference between the actual and the predicted values. Residual plots given in Fig. 1 were used to check the assumption. Normal probability plot (Fig. 1) lie reasonably close on a straight line, which confirmed the normal distribution of the observed data. Moreover, the diagnostic plot between the actual and the predicted values (Fig. 2) gives the relationship between those values. As represented in Fig. 2 the data points on diagnostic plot lie very close to the diagonal line, which infer a good

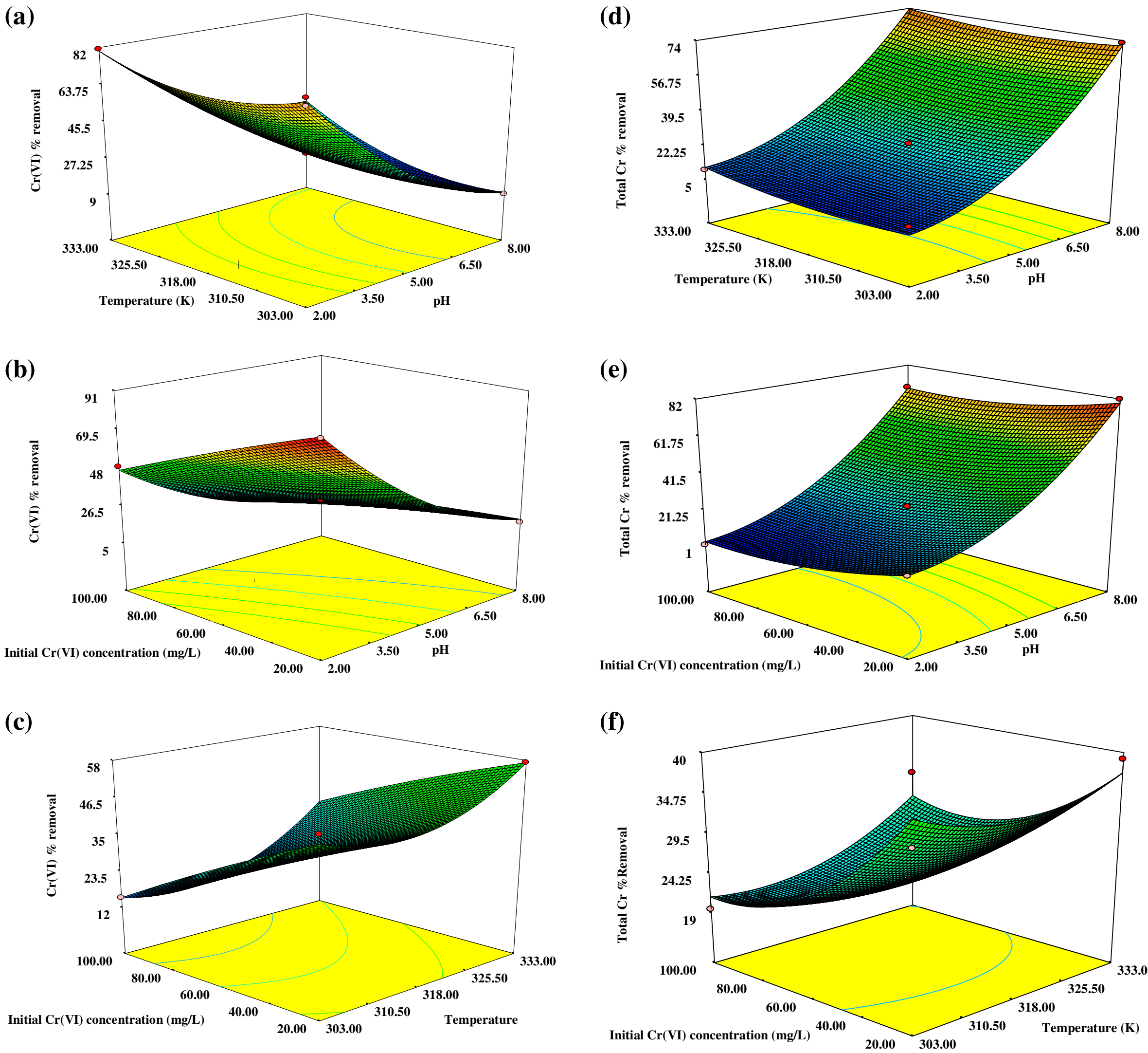

Fig. 4. 3-D response surface plots of interaction effect of two independent variables: (a) temperature and pH, (b) initial Cr (VI) concentration and pH, (c) initial Cr(VI) concentration and temperature for Cr(VI) removal on EPS, (d) temperature and pH, (e) initial Cr(VI) concentration and pH, and (f) initial Cr(VI) concentration and temperature for total chromium removal on EPS, respectively.

correlation between the actual and the predicted values [24,25]. The conclusions also display that the chosen quadratic model was considered to be satisfactory for the prediction of chromium adsorption system.

3.3. Analysis of variance (ANOVA)

The competence of the model was further analyzed using ANOVA. ANOVA is a statistical technique which subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the model parameters [26]. The ANOVA analysis represents the relationship between the variables and response. The *p*-values were used to estimate whether *F* was large enough to indicate the statistical significance. The *p*-values less than 0.05 indicate the model terms are significant, whereas the values of *p* greater than 0.10 specify insignificance [27]. In this study, all the *p*-values of the terms of X_1, X_3, X_1X_3, X_1^2 (Table 6), X_1, X_3, X_1^2 (Table 7), X_1, X_2, X_3, X_1X_2, X_1X_3, X_1^2, X_2^2 (Table 8), and X_1, X_3, X_1^2 (Table 9), respectively, are less than 0.05 represents the significant model terms. The developed mathematical models were found to be highly significant owing to their higher *F*-values and lower *p*-values.

3.4. Effect of interactive variables and 3-D Mesh study

The mutual interactive effects of the combination of independent variables such as pH, temperature, and initial chromium concentration on Cr(VI) and total chromium percentage removal using ESA and EPS were illustrated using 3-D Mesh diagrams (Figs. 3 and 4). In order to construct the 3-D Mesh plots, one variable was kept constant and others two variables were varied within the experimental range. The composed influence of temperature and pH on the Cr(VI) % removal by the ESA was shown in Fig. 3(a). The Cr (VI) percentage removal decreased with an increase in pH and increased with an increase in temperature. Cr (VI) may exist in three different ionic forms ($HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}) in aqueous solutions and the stability of these ions mainly dependent on the solution pH. The decrease in the percentage removal of Cr(VI) at higher pH may be due to the competitiveness of the chromium oxyanions [28]. Temperature has a direct influence over the adsorption process, which affects the metal ions diffusion rate and the number of adsorption sites [29]. The impact of initial Cr(VI) concentration and pH for Cr(VI) removal on ESA was presented in Fig. 3(b). The results indicated that at the lower initial Cr(VI) concentration and solution pH, better removal of Cr(VI) was attained. The decrease in the Cr(VI) percentage removal with an increase in initial Cr(VI) concentration may be because of the limited ESA active sites, which would have saturated beyond a certain Cr(VI) concentration [30]. In Fig. 3(c), the effect of the interaction between temperature and pH on total Cr removal using ESA is depicted. The total chromium percentage removal was increased with an increase in solution pH; however temperature had slight impact on total chromium percentage removal. High selectivity for the removal of total chromium was favored at $pH > 4$, this was due to the reduction coupled mechanism of Cr(III) adsorption process [31]. Fig. 3(d) depicts the effect initial Cr(VI) concentration and pH on the total chromium percentage removal by ESA. The total chromium percentage removal was decreased with an increase in initial Cr(VI) concentration and increased with an increase in solution pH. Fig. 3(e) represents the impact of initial Cr(VI) concentration and temperature for total chromium removal on ESA. Higher removal of total chromium was achieved at low initial Cr(VI) concentration and at higher temperature. In Fig. 4(a), the effect of the interaction between temperature and pH on Cr(VI) % removal using EPS is illustrated. It was observed that the percentage removal of Cr(VI) was higher at lower pH and higher temperature. Fig. 4(b) represent the response surface plot for initial Cr(VI) concentration and pH for Cr(VI) percentage removal using EPS. The Cr(VI) % removal was higher at low initial Cr (VI) concentration and low solution pH. The effect of initial Cr(VI) concentration and temperature for Cr (VI) removal on EPS was shown in Fig. 4(c). The results indicated that higher removal of Cr(VI) was attained at lower initial Cr(VI) concentration and at higher temperature. Fig. 4(d) shows the 3-D response surfaces representing the composed influence of temperature and pH on total chromium removal by EPS. Better removal of total chromium was attained at higher solution pH. The temperature parameter had shown negligible impact on total chromium removal. Fig. 4(e) represents the combined effect of initial Cr (VI) concentration and pH on total chromium removal by EPS. Higher percentage removal of total chromium was attained at low initial Cr(VI) concentration and higher solution pH. The impact of initial Cr(VI) concentration and temperature for total chromium removal on EPS was shown in Fig. 4(f). The results indicated that the higher removal of total chromium was attained at the low initial Cr(VI) concentration.

4. Conclusions

In the present investigation, a potential use ESA and EPS was checked for the chromium removal. Box–Behnken design was employed to study and optimize chromium removal process variables, such as pH, temperature, and initial chromium concentration for the adsorption process. According to ANOVA and response surface analyses, the experiment data were excellent fitted to the quadratic model. The optimum conditions were found to be pH of 2.0, temperature of 318 K, and 20 mg/L initial chromium concentration for Cr(VI) removal by ESA, EPS, and pH of 8, temperature of 318 K, and 20 mg/L initial chromium concentration for total chromium removal by ESA, EPS, respectively. The results of the present study suggested that use of ESA and EPS can be good alternative adsorbents for the removal of chromium ions from aqueous solution.

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