

Statistical optimization of process parameters for the simultaneous adsorption of Cr(VI) and phenol onto Fe-treated tea waste biomass

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Abstract In this study, simultaneous removal of Cr(VI) and phenol from binary solution was carried out using Fe-treated tea waste biomass. The effect of process parameters such as adsorbent dose, pH, initial concentration of Cr(VI) (mg/L), and initial concentration of phenol (mg/L) was optimized. The analysis of variance of the quadratic model demonstrates that the experimental results are in good agreement with the predicted values. Based on experimental design at an initial concentration of 55 mg/L of Cr(VI), 27.50 mg/L of phenol, pH 2.0, 15 g/L adsorbent dose, 99.99% removal of Cr(VI), and phenol was achieved.

Keywords Binary solution · Cr(VI) · Phenol · Response surface methodology · Fe-treated tea waste biomass

Introduction

Heavy metals are generally present with phenolic compounds in the environment cause adverse effects on flora and fauna, including human beings (Aksu and Akpınar 2001). Precipitation/coagulation (Wang et al. 2011), chemical oxidation (Dittert et al. 2014), biodegradation (Annadurai et al. 2008), adsorption (Jain et al. 2011), ion exchange (Cavaco et al. 2007), membrane processing (Lin et al. 2014), electrolytic methods (Hamdan and El-Naas 2014), carbon nanomaterial (Salam et al. 2012), etc. are

some important methods which have been used to remove the heavy metal ion and phenolic contents together. These components are generally present in the effluents of various industries such as leather tanning, electroplating, and alloying extra (Gładysz-Plaska et al. 2012). Cr(VI) and its copollutants such as phenol, naphthalene, and trichloroethylene discharge from these industries contaminate ground water aquifers, lake, river sediments, and soil (Yen-Hui et al. 2009). Much research has been carried out on the adsorption of a single pollutant nevertheless the fact that organic pollutants also exist with multiple metallic species (Repo et al. 2011; Gupta and Balomajumder 2015); therefore, in the recent year, simultaneous removal of heavy metals and organic compounds has gained a great attention in wastewater treatment processes (Mani et al. 2015). Adsorption of pollutant using commercial granular activated carbon is conventional method, but due to its high cost, this method is not economical (Suresh et al. 2011). Adsorption is proved to be most promising conventional or traditional methods for the simultaneous removal of organic compound and heavy metal ions from wastewater in comparison with other treatment methods such as precipitation, ion exchange, catalytic reaction, etc. (Quintelas et al. 2006; Aksu and Akpınar 2001). Modification of biosorbent by metal impregnation (Talreja et al. 2014) and acid treatment (Garg et al. 2009) improves the percentage removal of pollutants (Kuo and Bembenek 2008; Fonseca-Correa et al. 2013; Owlad et al. 2010; Cronje et al. 2011). Chromium is found in the environment predominantly in two forms Cr(III) and Cr(VI) out of which Cr(VI) is most mutagenic and carcinogenic to the living organism (Acar and Malkoc 2004; Baral et al. 2009). Chromium sulfate [Cr(III)] is used as a tanning agent which can be converted to Cr(VI) and causes severe contamination of ground water (El-Sherif et al. 2013). Phenol is highly toxic and

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recalcitrant organic compound used as a biocide in the leather tanning process (Srivastava et al. 2007; Hank et al. 2014). According to WHO, the maximum permissible limit of Cr(VI) in drinking water is 0.05 mg/L (Bansal et al. 2009). According to the US environmental protection agency, the maximum permissible limit of discharge of phenol by various process industries is 0.005 mg/L (Banerjee and Ghoshal 2011). The aim of this work is to optimize the process parameters such pH, contact time, adsorbent dose for the simultaneous removal of Cr(VI), and phenol in a multicomponent simulated synthetic wastewater using Box–Behnken design of response surface methodology (RSM). Characterization of Fe-treated tea waste biomass before and after adsorption was also carried out to confirm the simultaneous adsorption of Cr(VI) and phenol using various techniques such as FTIR, FE-SEM, EDX, and BET surface area.

Materials and methodology

Preparation of biosorbent

Tea waste biomass was collected from local tea stall Roorkee. A soluble sugar and dirt present in tea waste biomass was removed by boiling in distilled water about for 30 min. After boiling, tea waste biomass was washed with distilled water in triplicate and then dried in hot air oven at 50 °C for 12 h. Furthermore, the dried biomass was sieved to the desired particle size 0.5–2 mm (Gupta and Balomajumder 2015).

5 g of tea waste biomass was added to 50 mL solution of 2 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 mL conical flask. It was kept on a magnetic stirring plate at 100 °C for the impregnation of Fe ions onto the surface of tea waste. 0.1 M of NaOH was added dropwise to the conical flask by the help of burette to increase the pH 4–5 for the precipitation of ferrous sulfate. This process was carried out continuously 3–4 h. Upon cooling, the tea waste biomass was covered with a thick layer of orange color iron oxide. Then, tea waste biomass was washed with distilled water to remove extra quantity of precipitate. Finally, this Fe-treated tea waste biomass was dried in an oven at 50 °C for 2 h and then sieved to obtain homogeneous particle size (Nethaji et al. 2013).

Preparation of solutions

All chemicals used for the experimentation purpose including potassium dichromate and phenol were AR grade having more than 99% purity. Stock solutions of Cr(VI) and phenol were prepared by dissolving known quantity of phenol and potassium dichromate in 1 L of Millipore

water. To avoid photo-oxidation of phenol, stock solution was stored in brown glass bottle (Chaudhary and Balomajumder 2014). Based on industrial wastewater such as tannery and electroplating, 2:1 ratio of Cr(VI) and phenol were taken for conducting the present experiments, because these components are generally present in the wastewater in this composition (Aksu and Akpınar 2001; Gupta and Balomajumder 2015).

Batch experiments

Batch adsorption studies were carried out in 250 mL round bottom flasks with working volume of 100 mL. The synthetic, simulated binary wastewater was prepared in the laboratory by mixing the necessary amount of $\text{K}_2\text{Cr}_2\text{O}_7$ and phenol in 2:1 ratio (Anupam et al. 2011). RSM (response surface methodology) using Box–Behnken design was used for the optimization of process parameters. Box–Behnken design does not contain any corner point in the design; therefore, number of experimental run generated is comparatively less than CCD. A range of process parameters was selected as pH (2–8), adsorbent dose (0.5–1.5 g), initial concentration of Cr(VI) (10–100 mg/L), and initial concentration of phenol (5–50 mg/L). The experiments were carried out in an incubator shaker at temperature 30 °C until the equilibrium condition was achieved. The pH of binary solution was controlled by adding 0.1 N HCl and 0.1 N NaOH. When equilibrium was attained, the sample was filtered using the standard Whatman filter paper (Cat No. 1001 125). Thereafter, concentration of Cr(VI) and phenol in the filtrate was analyzed using a UV spectrophotometer.

The percentage removal of phenol and Cr(VI) was calculated by the following equation:

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100, \quad (1)$$

where C_i and C_f are the initial and final concentrations of the pollutant, respectively.

Analytical method

The residual concentration of Cr(VI) and phenol in the filtrate was analyzed using UV spectrophotometer made of Hach (model no: DR 5500). The residual concentration of Cr(VI) was measured by reacting 10 mL of filtrate with a 200 μL diphenyl carbazide solution and 500 μL H_2SO_4 and let them stand for 10 min for full color development and its absorbance was noted at 540 nm. For the analysis of phenol, 10 mL of phenol sample was mixed with 0.7 mL of sodium bicarbonate (pH 8), 0.1 mL of 4-amino antipyrine (20.8 mM), and 0.1 mL of potassium ferricyanide

(83.4 mM) and let them stand for full color development and its absorbance was noted at 510 nm (Srihari and Das 2008). Both phenol and $K_2Cr_2O_7$ do not interact with each other as there was no effect on the absorbance of both components and can be measured for the same filtrate in UV spectrophotometer at 510 and 540 nm, respectively.

Characterization of biosorbent

FTIR of tea waste biomass before and after adsorption

The FTIR spectrum is an important tool used for the identification of characteristic functional groups responsible for the adsorption of Cr(VI) and phenol onto the surface of Fe-treated tea waste biomass. The FTIR spectrum of tea waste biomass before surface modification, after surface modification, and after simultaneous adsorption of Cr(VI) and phenol is shown in Fig. 1a–c, respectively. FTIR study suggested that functional groups such as N–H, O–H, C=O, and C–O were present onto the surface of tea waste biomass (Golbazi et al. 2014). The FTIR spectrum of tea waste biomass before adsorption (Fig. 1a) indicates the strong band of O–H functional groups at 3612.29 cm^{-1} wavelength (Kamsonlian et al. 2011; Srivastava et al. 2015). Adsorption band at around $1989\text{--}1654.67\text{ cm}^{-1}$ indicates the C=O group (Moussavi and Barikbin 2010). Furthermore, peaks at 1396.67 and 1095.67 cm^{-1} were significance of C–O and N–H stretching (Mohan et al. 2006). After surface modification of tea waste biomass shown in Fig. 1b, there is a change in the vibration of the O–H functional group at 3443.04 cm^{-1} which became broad after simultaneous adsorption of Cr(VI) and phenol, as shown in Fig. 1c. A peak of the C–H functional group at 2923.82 cm^{-1} was observed after surface modification of tea waste biomass (Quintelas et al. 2009). Furthermore, the shift in the functional groups such as C=O, C–O, and N–H was observed after surface modification and after simultaneous adsorption of Cr(VI) and phenol, as shown in Fig. 1b, c, respectively. Changes in the peak of functional group after surface modification shown in Fig. 1b depict that the surface of tea waste biomass was modified as iron was impregnated. Furthermore, the changes in the peak of functional group shown in Fig. 1c confirm the simultaneous adsorption of Cr(VI) and phenol onto the surface of Fe-treated tea waste biomass.

SEM and EDX analysis

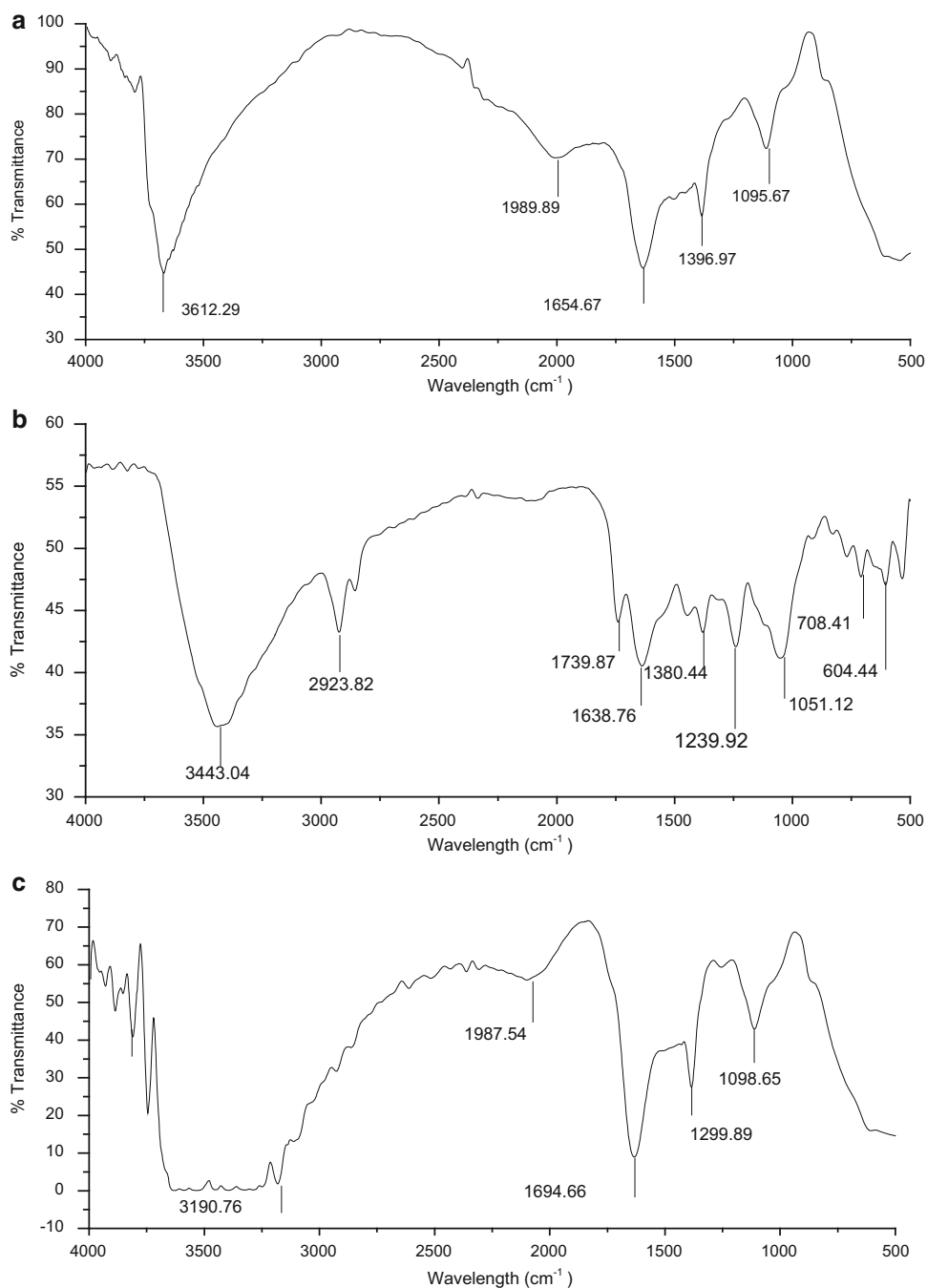
FE-SEM shows the morphology of tea waste biomass before surface modification, after surface modification, and after simultaneous adsorption of Cr(VI) and phenol onto the surface of Fe-treated tea waste biomass, as shown in Fig. 2a–c,

respectively. The composition of various elements present onto the surface of tea waste biomass was obtained by EDX analysis. It is clear from SEM analysis that (Fig. 2a), before the surface modification, surface was highly porous and homogeneous as large number of pores was observed. The surface morphology of tea waste biomass after surface modification was different from before surface modification. After surface modification, it was covered with a layer of Fe ions. After simultaneous adsorption of Cr(VI) and phenol onto the surface of Fe-treated tea waste biomass, the surface became rough and bulky, which was due to the fact that all the active pores were filled with Cr(VI) and phenol anion. The adsorption of Cr(VI) and phenol anions was due to strong electrostatic force between negatively charged Cr(VI) and phenol anions and positively charged tea waste biomass surface (Zuo and Balasubramanian 2013). The EDX of tea waste biomass before surface modification, after surface modification, and after simultaneous adsorption of Cr(VI) and phenol is shown in Fig. 3a–c, respectively. The results of the EDX analysis showed a sharp peak of elements such as C, O, and Ca before surface modification, but after surface modification, a peak of Fe in K and L shell of tea waste biomass was observed which confirms that iron was impregnated onto the surface of tea waste biomass. After simultaneous adsorption of Cr(VI) and phenol, a peak of Cr in K and L shell was observed which confirms the adsorption of Cr(VI). The changes in the peaks of carbon and oxygen in the EDX spectrum before and after adsorption confirm the adsorption of phenol. The weight % of elements present onto the surface of tea waste biomass before surface modification, after surface modification, and after simultaneous adsorption of Cr(VI) and phenol is given in Tables 1, 2, and 3, respectively. From Tables 1, 2, and 3, it is clear that after surface modification with $FeSO_4 \cdot 7H_2O$, the weight % of C was decreased, while weight % of O was increased. After simultaneous adsorption of Cr(VI) and phenol, a peak of 4.87 weight % of Cr and changes in the weight % of C and O were observed in the EDX spectra which confirm the simultaneous adsorption of Cr(VI) and phenol (Kumar et al. 2012).

BET surface area analysis

BET surface area and total pore volume of the tea waste biomass before and after surface modification, and after simultaneous adsorption of Cr(VI) and phenol are given in Table 4. The surface area of tea waste biomass was calculated using surface area analyzer ASAP 2010 Micrometrics, USA). The surface area of tea waste biomass was ($23.658\text{ m}^2/\text{g}$). After surface modification, the surface area was slightly decreased ($20.196\text{ m}^2/\text{g}$), because iron was impregnated onto the surface of tea waste biomass. After simultaneous adsorption of Cr(VI) and phenol, the surface area was reduced ($2.456\text{ m}^2/\text{g}$), because all the pores were filled by Cr(VI) and phenol anions.

Fig. 1 **a** FTIR of tea waste biomass before surface modification, **b** FTIR of tea waste biomass after surface modification, and **c** FTIR of tea waste biomass after simultaneous adsorption of Cr(VI) and phenol



Experimental design and procedure

The Box–Behnken design matrix has been applied for the simultaneous adsorption of Cr(VI) and phenol using the design expert software 6.0.8. The interactive effects of four most important operating variables, pH (X_1), adsorbent dose (X_2), initial concentration of Cr(VI) (X_3), and initial concentration of phenol (X_4), were determined onto the percentage removal of Cr(VI) and phenol. A total of 29 experiments was carried out in the present study as

suggested by Box–Behnken design for the construction of quadratic equation model for the two responses Y_1 [percentage removal of Cr(VI)] and Y_2 (percentage removal of phenol). An orthogonal 2^4 Box–Behnken design (BBD) with five replicates at the center point was used to optimize the selected key variables (X_1 , X_2 , X_3 , and X_4) (Singh et al. 2013). The coded values of the process parameters were determined by the following equation (Rajasimman et al. 2009; Satapathy and Das 2014; De Sales et al. 2013):

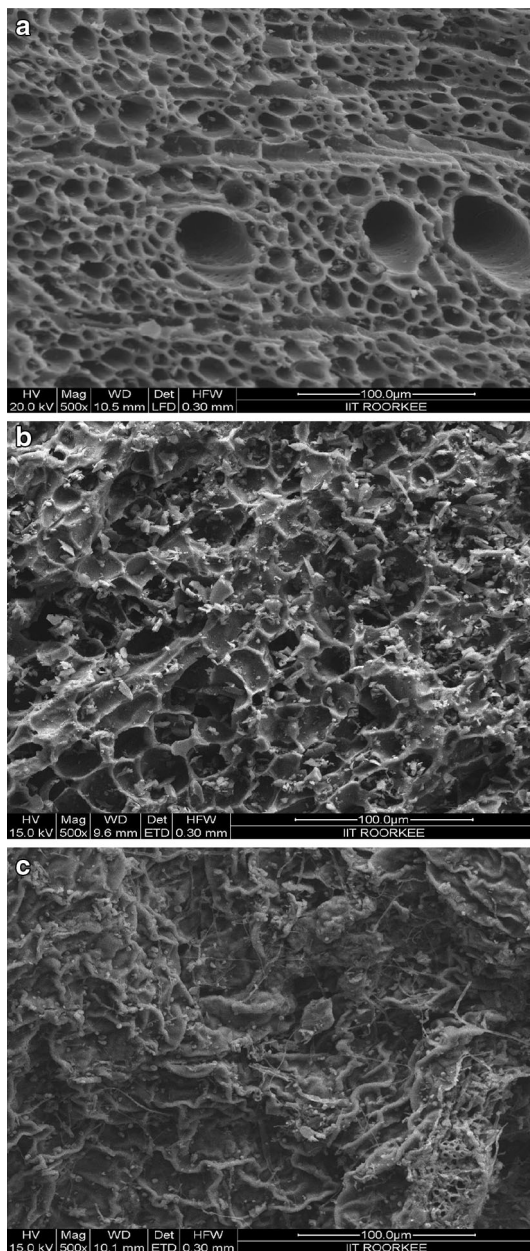


Fig. 2 a SEM image of tea waste biomass before surface modification, b SEM image of tea waste biomass after surface modification, and c SEM image of tea waste biomass after simultaneous adsorption of Cr(VI) and phenol

$$x_i = \frac{X_i - X_o}{\Delta x}, \tag{2}$$

where x_i is the coded value of the i th variable, X_i is the uncoded value of the i th test variable, and X_o is the uncoded value of the i th test variable at center point. The range and level of individual variables selected are given in Table 5. The Box–Behnken experiment design for the simultaneous adsorption of Cr(VI) and phenol onto the Fe-treated tea waste biomass is given in Table 6 which shows

that the experimental data are close to the predicted value (Park et al. 2011).

Model and statistical analysis

The experimental data were analyzed using ANOVA (Analysis of variance) and validated for two responses of interest percentage removal of Cr(VI) (Y_1) and percentage removal of phenol (Y_2). A second-order polynomial equation was developed to study the interactive effect of four process parameters ($X_1, X_2, X_3,$ and X_4) onto the percentage removal of Cr(VI) (Y_1) and Y_2 (percentage removal of phenol) (Chaudhary and Balomajumder 2014; Abigail et al. 2015).

$$Y_i = \alpha_o + \sum_{i=1}^n \alpha_i x_i + \left(\sum \alpha_{ii} x_i^2 \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \alpha_{ij} x_i x_j, \tag{3}$$

where Y_i is the predicted value of the response of interest, α_o is intercept coefficient, α_i is linear coefficient, α_{ii} is quadratic regression coefficient, and α_{ij} is regression coefficients of interaction. Some insignificant terms of the above model can be neglected based on the statistical analysis for the accurate prediction of response (Cao et al. 2014).

Results and discussion

The effect of process variable on response of interest was investigated by conducting a total of 29 experiments suggested by the Box–Behnken design of design expert software (Ferreira et al. 2007). Batch experiments were conducted for visualizing the effects of independent variables on responses of interest. Multiple regression analysis using response surface methodology was carried out to generate the following regression equation for the two responses of interest Y_1 and Y_2 (Xu et al. 2013):

$$\begin{aligned} Y_1 (\text{Percentage removal of Cr(VI)}) &= 123.22342 - 11.94269 X_1 + 3.94889 X_2 - 0.68007 X_3 \\ &\quad - 0.44198 X_4 + 0.69796 X_1^2 + 14.13167 X_2^2 \\ &\quad + 0.00421379 X_3^2 + 0.00945021 X_4^2 - 2.33167 X_1 X_2 \\ &\quad - 0.024093 X_1 X_3 - 0.025926 X_1 X_4 + 0.011111 X_2 X_3 \\ &\quad - 0.20000 X_2 X_4 + 0.00592593 X_3 X_4, \end{aligned}$$

$$\begin{aligned} Y_2 (\text{Percentage removal of Phenol}) &= 60.80 - 22.17 X_1 + 8.42 X_2 - 2.25 X_3 - 12.33 X_4 \\ &\quad + 3.97 X_1^2 - 0.40 X_2^2 - 2.15 X_3^2 + 6.73 X_4^2 \\ &\quad - 3.75 X_1 X_2 - 2.75 X_1 X_3 - 4 X_1 X_4 \\ &\quad + 1.25 X_2 X_3 - 1.75 X_2 X_4 - 4.25 X_3 X_4. \end{aligned}$$

The regression equation coefficients were calculated and the data fitted to a second-order polynomial equation for

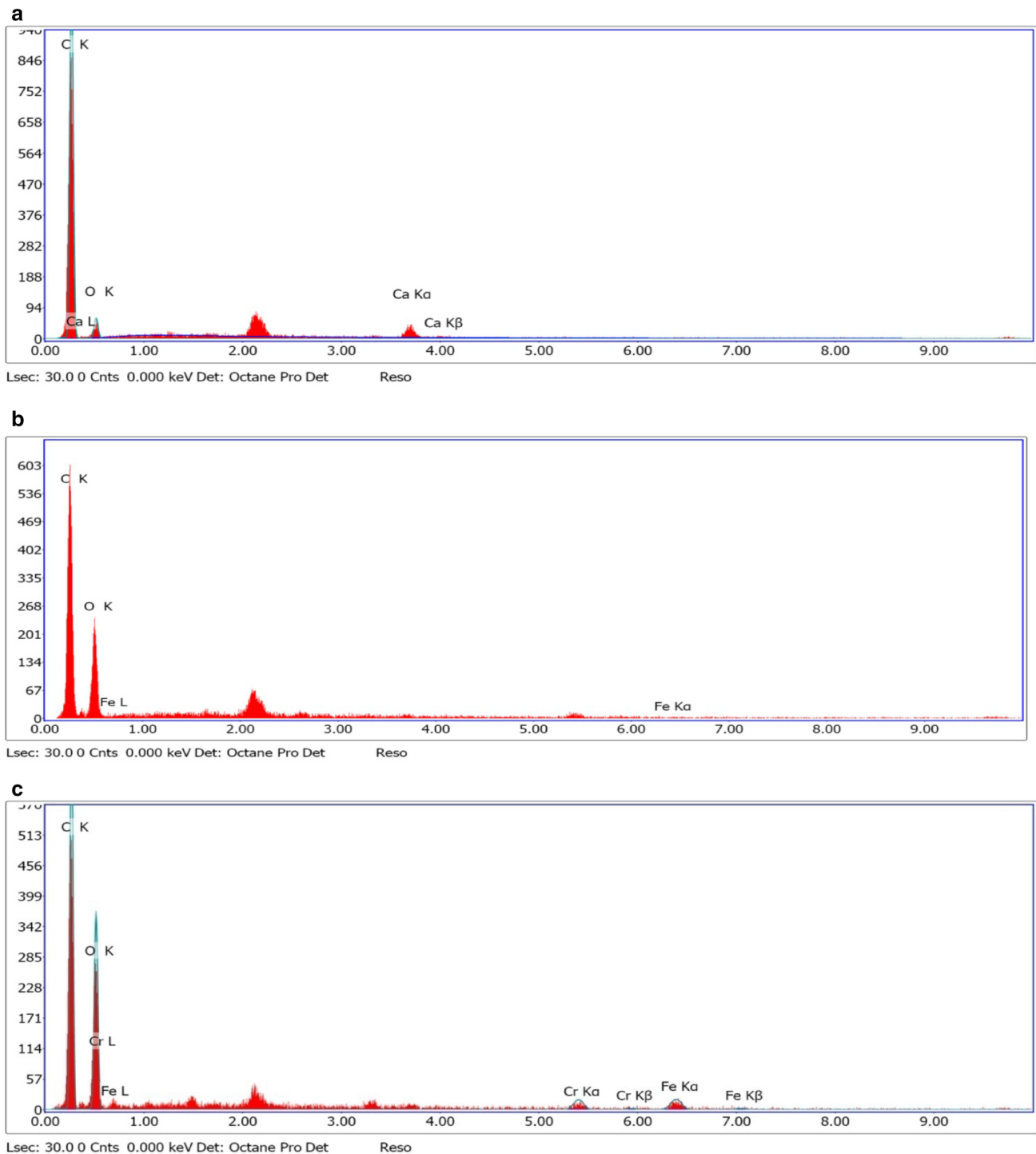


Fig. 3 **a** EDX image of tea waste biomass before surface modification, **b** EDX image of tea waste biomass after surface modification, and **c** EDX image of tea waste biomass after simultaneous adsorption of Cr(VI) and phenol

simultaneous removal of Cr(VI) and phenol. The results of ANOVA for the response Y_1 [percentage removal of Cr(VI)] and Y_2 (percentage removal of phenol) are given in Tables 7 and 8, respectively. The significance of the second-order quadratic equation developed depends upon the coefficient of determination (R^2) and F test (Gonen and

Aksu 2009). Values of “ $P > F$ ” less than 0.05 indicate that model terms are significant for the simultaneous removal of Cr(VI) and phenol (Pavlovic et al. 2014). The value of the mean squares is calculated by dividing the sum of squares of each variable by their respective degree of freedom. The F (Fishers’ variance ratio) value is calculated by taking the

Table 1 Various elements present onto the tea waste biomass surface before surface modification

Element	Weight (%)	Atomic (%)	Net int.	Error (%)
C K	80.62	87.27	294.02	3.95
O K	13.2	10.73	16.77	16.42
Ca K	6.18	2.01	25.21	13.89

Table 2 Various elements present onto the tea waste biomass after surface modification

Element	Weight (%)	Atomic (%)	Net int.	Error (%)
C K	60.86	67.8	222.57	5.44
O K	38.24	31.98	87.14	11.26
Ca K	0.9	0.22	1.5	66.77

Table 3 Various elements present onto the tea waste biomass after simultaneous adsorption of Cr(VI) and phenol

Element	Weight (%)	Atomic (%)	Net int.	Error (%)
C K	51.48	63.98	184.44	6.84
O K	34.48	32.17	107.46	10.32
Cr K	4.87	1.4	16.18	6.36
Fe K	9.17	2.45	18.32	6.27

Table 4 Surface properties of tea waste biomass

Biosorbent	BET surface area (m ² /g)	Monolayer volume (cm ³ /g)	Total pore volume (m ³ /g)
Tea waste biomass before surface modification	23.658	5.187	0.0355
Tea waste biomass after surface modification	20.196	1.467	0.0230
Tea waste biomass after simultaneous adsorption of Cr(VI) and phenol	2.456	0.578	0.00245

Table 5 Different levels of process variables selected for the simultaneous adsorption of Cr(VI) and phenol

Independent variables	Range and levels		
	−1	0	+1
pH	2	5	8
Adsorbent dose (mg/g)	0.5	1	1.5
Initial concentration of Cr(VI) (mg/L)	10	55	100
Initial concentration of phenol (mg/L)	5	27.50	50

ratio of the mean square owing to regression and the mean square owing to error. F values show the variation in the experimental and predicted values of the variables about the mean. Here, the ANOVA of the regression model for response Y_1 [percentage removal of Cr(VI)] and response Y_2 (percentage removal of phenol) shows that the model is highly significant which is confirmed by the calculated F value for response Y_1 (79.53) and response Y_2 (50.11)

and a very low probability value ($P \leq 0.0001$) was obtained for both responses Y_1 and Y_2 (Cao et al. 2014). The lack of fit F value for response Y_1 (147.32) and Y_2 (185.22) depicts that the lack of fit is significant. There is only a 0.01% chance of “Lack of Fit F value” (Kumar et al. 2009). The predicted R^2 for response Y_1 (0.9285) is in reasonable agreement with the adjusted R^2 of 0.9752. Similarly, for response Y_2 , the predicted R^2 (0.8873) is in

Table 6 Experimental design matrix developed by Box–Behnken design for removal of chromium

Standard order	Run no.	Actual variables				Removal efficiency (%) Cr(VI)		Removal efficiency (%) Phenol	
		X_1	X_2	X_3	X_4	Experimental	Predicted	Experimental	Predicted
14	1	5	1.5	10	27.5	76	78.5	68	67.67
11	2	2	1.0	55	50	90	94.08	84	85.33
24	3	5	1.5	55	50	69	67.17	60	61.46
19	4	2	1	100	27.50	90	90.33	86	85.29
5	5	5	1	10	5	78	76.58	80	75.71
23	6	5	0.5	55	50	56	56	50	48.13
3	7	2	1.5	55	27.50	99.99	100	99.99	98.70
29	8	5	1	55	27.50	52	51.60	63	63
8	9	5	1	100	50	68	65.25	44	46.54
28	10	5	1	55	27.50	52	51.60	63	63
12	11	8	1	55	50	30	34.58	38	33
9	12	2	1	55	5	89	87.25	98	100
27	13	5	1	55	27.50	52	52	63	63
25	14	5	1	55	27.50	52	52	63	63
20	15	8	1	100	27.50	25	27.83	30	35.46
1	16	2	0.5	55	27.50	80	78.08	75	74.38
18	17	8	1	10	27.50	48	49	42	45.46
7	18	5	1	10	50	72	67.92	58	59.54
22	19	5	1.5	55	5	67	68.33	85	89.62
13	20	5	0.5	10	27.50	60	63.42	51	53.33
2	21	8	0.5	55	27.50	34	29.02	38	37.54
4	22	8	1.5	55	27.50	40	37.75	48	46.88
10	23	8	1	55	5	36	34.75	68	65.67
15	24	5	0.5	100	27.50	48	48.25	47	46.33
16	25	5	1.5	100	27.50	65	64.42	69	65.67
26	26	5	1	55	27.50	52	52	63	63
21	25	5	0.5	55	5	45	48.17	68	69.29
6	28	5	1	100	5	50	49.92	83	79.71
17	29	2	1	10	27.50	99.99	98.49	87	84.29

good agreement with adjusted R^2 (0.9606) (Sahu et al. 2009). “Adequate Precision” measures the signal-to-noise ratio, and a ratio greater than 4 is desirable (Gonen and Aksu 2009). Here, the ratio of 31.253 for response Y_1 and 26.376 for response Y_2 indicates an adequate signal.

Interaction effects of independent variables (X_1 , X_2 , X_3 , and X_4 on responses Y_1 and Y_2)

RSM is a statistical method for the analysis of interactive effects of operating variables onto the response of interest. The effects of independent process variables were evaluated by 3D plots shown in Fig. 4a, b for response Y_1 [percentage removal of Cr(VI)] and Fig. 5a, b for response Y_2 (percentage removal of phenol). For response Y_1 , the linear effects of the process variables X_1 (pH), X_2 (adsorbent dose), X_3 (initial concentration of Cr(VI)) are highly significant, given in

Table 5, which is confirmed by high F values and low P value ($P < 0.0001$) (Fereidouni et al. 2009; Singh et al. 2013), but the effect of X_4 (initial concentration of phenol) was not highly significant as the P values obtained were $P > 0.005$. Similarly, the linear effects of process variables (X_1 , X_2 , X_3 , and X_4) were examined onto the percentage removal of phenol (response Y_2) given in Table 6 which shows that effect of pH (X_1), adsorbent dose (X_2), and initial concentration of phenol (X_4) was highly significant. The effect of process variable X_3 [initial concentration of Cr(VI)] onto the percentage removal of phenol was not highly significant. Therefore, the percentage removal of Cr(VI) and phenol in the binary mixture using Fe-treated tea waste biomass was not affected by the presence of each other. It can be concluded that Cr(VI) and phenol can be easily removed from binary mixture using Fe-treated tea waste biomass. The effects of X_1^2 , X_2^2 , X_3^2 , and X_4^2 onto the responses Y_1 and Y_2 were

Table 7 Results of ANOVA for the percentage removal of Cr(VI) using Fe-treated tea waste biomass

Source	Sum of squares	DF	Mean square	F value	P > F
Model	11,716.44	14	836.89	79.53	<0.0001 significant
X ₁	9406.88	1	9406.88	893.96	<0.0001
X ₂	736.18	1	736.18	69.96	<0.0001
X ₃	645.19	1	645.19	61.31	<0.0001
X ₄	33.33	1	33.33	3.17	0.0968
X ₁ ²	239.91	1	239.91	22.80	0.0003
X ₂ ²	72.05	1	72.05	6.85	0.0203
X ₃ ²	450.41	1	450.41	42.80	<0.0001
X ₄ ²	136.31	1	136.31	12.95	0.0029
X ₁ X ₂	48.93	1	48.93	4.65	0.0489
X ₁ X ₃	42.32	1	42.32	4.02	0.0647
X ₁ X ₄	12.25	1	12.25	1.16	0.2988
X ₂ X ₃	0.25	1	0.25	0.024	0.8797
X ₂ X ₄	20.25	1	20.25	1.92	0.1871
X ₃ X ₄	144.00	1	144.00	13.68	0.0024
Residual	147.32	14	10.52		
Lack of fit	147.32	10	14.73		
Pure error	0.000	4	0.000		
Cor total	11,863.76	28			

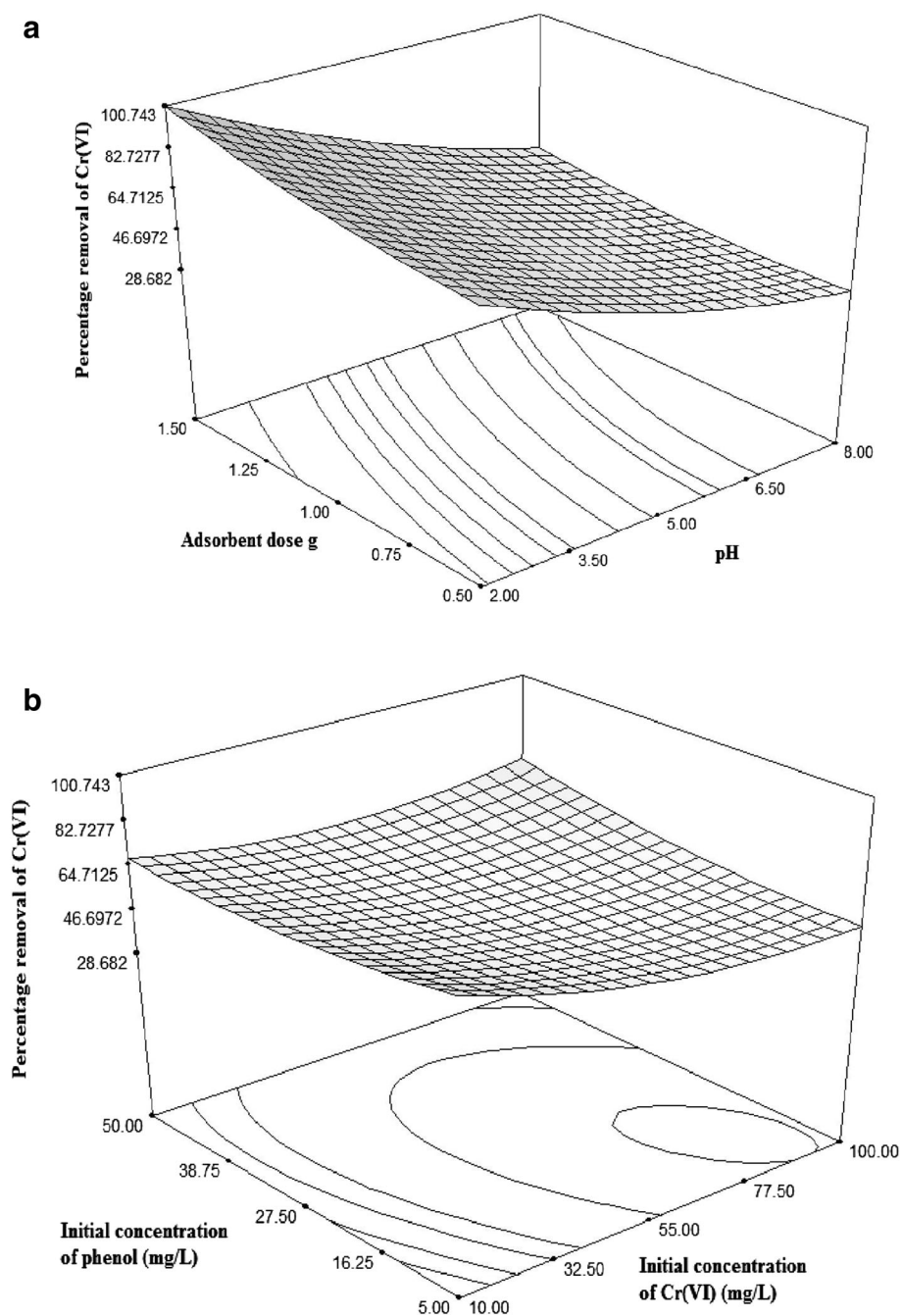
Table 8 Results of ANOVA for the percentage removal of phenol using Fe-treated tea waste biomass

Source	Sum of squares	DF	Mean square	F value	P > F
Model	9281.24	14	662.95	50.11	<0.0001 significant
X ₁	5895.89	1	5895.89	445.64	<0.0001
X ₂	849.92	1	849.92	64.24	<0.0001
X ₃	60.75	1	60.75	4.59	0.0502
X ₄	1825.33	1	1825.33	137.97	<0.0001
X ₁ ²	53.58	1	53.58	4.05	0.0638
X ₂ ²	14.61	1	14.61	1.10	0.3111
X ₃ ²	68.50	1	68.50	5.18	0.0391
X ₄ ²	205.27	1	205.27	15.51	0.0015
X ₁ X ₂	56.18	1	56.18	4.25	0.0584
X ₁ X ₃	30.25	1	30.25	2.29	0.1528
X ₁ X ₄	64.00	1	64.00	4.84	0.0452
X ₂ X ₃	6.25	1	6.25	0.47	0.5031
X ₂ X ₄	12.25	1	12.25	0.93	0.3523
X ₃ X ₄	72.25	1	72.25	5.46	0.0348
Residual	185.22	14	13.23		
Lack of fit	185.22	10	18.52		
Pure error	0.000	4	0.000		
Cor total	9466.46	28			

also appreciated. The combined effects of adsorbent dose and pH (X₁X₂), initial concentration of Cr(VI), and initial concentration of phenol (X₃X₄) onto the responses Y₁ and Y₂ were also observed. Based on the response surface design, it is evident that at an initial concentration of 55 mg/L of Cr(VI), 27.50 mg/L of phenol, pH 2.0, adsorbent dose 15 g/

L, and 99.99% removal of both Cr(VI) and phenol was obtained. The response surface curves were plotted, as shown in Fig. 4a, b which depicts the effect of independent variables onto the percentage removal of Cr(VI). Figure 5a, b shows the effects of independent variables onto the percentage removal of phenol. The circular nature of the contour

Fig. 4 **a** 3D response surface plots showing the effects of (a) pH (b) adsorbent dose onto the percentage removal of Cr(VI). **b** 3D response surface plots showing the effects of (a) initial concentration of Cr(VI) and (b) initial concentration of phenol onto the percentage removal of Cr(VI)



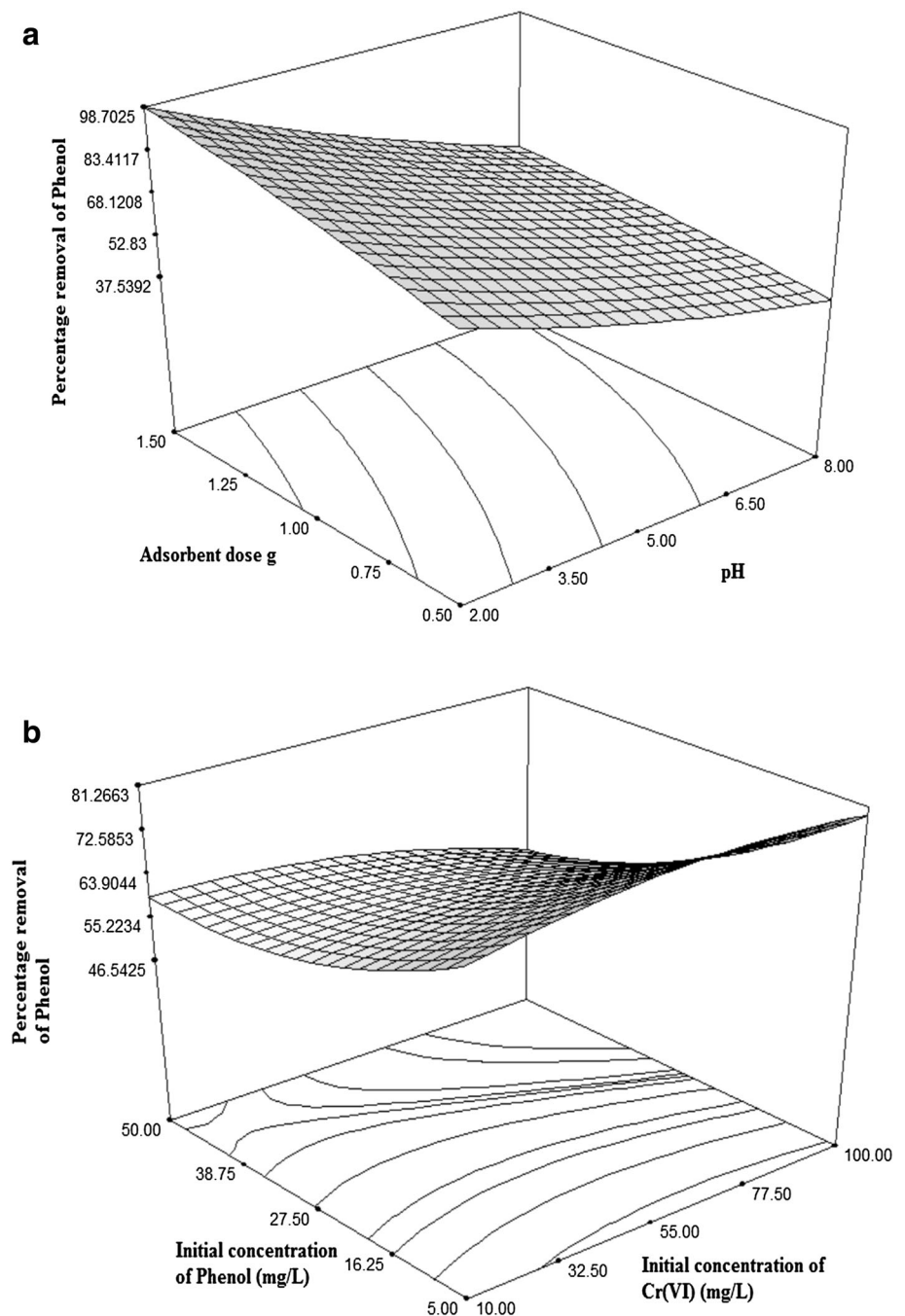
signifies that the effect of initial concentration of phenol onto the percentage removal of Cr(VI) and initial concentration of Cr(VI) onto the percentage removal of phenol was not significant, as shown in Figs. 4b and 5b, respectively. The percentage removal of Cr(VI) decreases with the increase in the initial concentration of Cr(VI) and percentage removal of phenol decreases with the increase in the initial concentration of phenol. The effects of adsorbent dose, pH, and initial concentration of Cr(VI) onto the percentage removal of Cr(VI) were found significant. Similar effects of these independent variables onto the percentage removal of phenol

were observed. The percentage removal of Cr(VI) and phenol was decreased with increasing pH and increases with increase in adsorbent dose. The possible reason of these phenomena is given below.

Effect of pH onto the percentage removal of Cr(VI) and phenol

pH is an important parameter for the simultaneous removal of Cr(VI) and phenol. At low pH value, the percentage removal of Cr(VI) and phenol was maximum,

Fig. 5 **a** 3D response surface plots showing the effects of (a) adsorbent dose and (b) pH onto the percentage removal of phenol. **b** 3D response surface plots showing the effects of (a) initial concentration of Cr(VI) and (b) initial concentration of phenol onto the percentage removal of phenol



because at low pH value, the surface of Fe-treated tea waste biomass becomes more protonated. At low pH, Cr(VI) was in the form of $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , while phenol was present in the form of $\text{C}_6\text{H}_5\text{O}^-$ (Chaudhary and Balomajumder 2014). Therefore, there is a strong electrostatic interaction between negatively charge chromate, dichromate, and phenolate anions to the positively charged surface of Fe-treated tea waste biomass. At high pH value, after pH 6, a rapid decrease in the percentage removal of Cr(VI) and phenol was observed, because at

this pH, the surface of biosorbent becomes negatively charged which repel the Cr(VI) and phenol anions. Favorable adsorption occurs between pH (2–5). There was also a competition between negatively charged phenolate and chromate anions for adsorption to the vacant positively charged active sites. When all the vacant active sites are filled, equilibrium was established between negatively charged chromate and phenolate anions present in the synthetic binary solution and positively charged surface.

Effects of adsorbent dose onto the percentage removal of Cr(VI) and phenol

Fe-treated tea waste biomass is used as a adsorbent for the simultaneous adsorption of Cr(VI) and phenol. The simultaneous adsorption of both Cr(VI) and phenol from a binary mixture increases with the increase in adsorbent dose (mg/g) due to increase in possible active sites and surface area for adsorption. After reaching optimum adsorbent dose, simultaneous removal of both Cr(VI) and phenol becomes constant and then decreases. The decrease in percentage removal after reaching the optimum dose was due to all the vacant seats which were filled (Garg et al. 2004).

Conclusion

In this study, Fe-treated tea waste biomass was used for the simultaneous removal of Cr(VI) and phenol from binary mixture using Fe-treated tea waste biomass. Impregnation of Fe ions onto the surface of tea waste biomass improves the morphology of adsorbent and thus the percentage removal of Cr(VI) and phenol. Response surface methodology (RSM) using Box–Behnken design was used for the determination of optimum conditions for adsorption of Cr(VI) and phenol from binary mixture. The experimental and predicted values were in good agreement for both responses Y_1 [percentage removal of Cr(VI)] and Y_2 (percentage removal of phenol). A second-order quadratic equation was developed to predict the effects of independent variables onto the percentage removal of Cr(VI) and phenol from binary mixture. The application of statistical design using RSM for the adsorption of Cr(VI) and phenol from a binary mixture reduces the time and overall cost, and improved the efficiency of the process.

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