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Process optimization for Cr(VI) removal by *Mangifera Indica* seed powder: a response surface methodology approach

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ABSTRACT

In this study, *Mangifera Indica* (mango) seed kernel powder was used as an adsorbent for chromium(VI) removal. The interactive effects between the process variables such as pH, temperature, adsorbent concentration, chromium concentration, and stirring speed (RPM) on chromium(VI) removal have been studied. In order to optimize the process, the experiments were designed using central composite design under response surface methodology by MINI-TAB 16.0 software. Based on the study, the optimum conditions for maximum removal of chromium(VI) from synthetic solution were obtained as: pH 1, temperature 27.5 °C, adsorbent concentration 3.5 g/L, chromium concentration 100 ppm, and RPM 75. The statistical analysis of the data shows that experiments are statistically significant with a regression coefficient (R^2) value of 0.95.

Keywords: Chromium removal; Mango seed kernel powder; 1-5,Diphenyl carbazide; Response surface methodology; Central composite design

1. Introduction

Contamination due to heavy metals is of major concern in the recent decades due to its toxicity and global occurrence [1]. These pollutants are of significant concern since they are carcinogenic, highly toxic, and nonbiodegradable [2]. Chromium is one such heavy metal that exists in two forms namely trivalent chromium and hexavalent chromium in the aquatic environment. Scientific studies established extreme impact of chromium on human life, as it causes skin rashes, upset stomach and ulcers, respiratory problems, kidney and liver damage, lung cancer etc. [3]. Hexavalent chromium is five hundred times more toxic than trivalent chromium [4]. The maximum

permissible levels for trivalent chromium and hexavalent chromium in wastewater are 5 and 0.05 mg/L respectively, whereas, maximum permissible level for chromium in drinking water set by World Health Organization is 0.05 mg/L [5]. Several industries use chromium in its processes and hence, a huge amount of chromium-contained wastewater is let into the environment. The sources of chromium waste causing water pollution includes tanning, steel fabrication, wood treatment units, mining, electroplating, and aluminum conversion coating operations [6–8]. precipitation, chemical oxidation and Chemical reduction, ion exchange, filtration, electrochemical treatment, and evaporative recovery are the conventional methods available for removal of dissolved heavy metal ions. These methods have their own

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limitation which includes ineffective metal removal, need for sophisticated equipments, monitoring systems, and disposal of toxic sludge produced during the process [7]. Adsorption is the most reliable and widely employed technique for removing metal ions [9,10]. Adsorption using activated carbon is a suitable method for treating water and wastewater. Activated carbon is expensive which limits its use in wastewater treatment [11]. Many locally available low-cost adsorbents have been widely investigated for removal of Cr(VI) [12]. The adsorbents include palm fiber [12], coconut coir pith [13], Ocimum americanum seed pods [14], Hydrilla verticillata [15], Tamarindus indica seeds [16], wheat bran [17], Azadirachta indica leaf powder [18], Spirogyra condensata and Rhizoclonium hieroglyphicum [19], Helianthus annuus stem waste [20]. corn stalks [21], sugarcane bagasse [22,23], and Borassus aethiopum flower [1]. A detailed literature survey showed that Mangifera indica seed kernel powder has not been used as an adsorbent so far for the removal of chromium(VI). Further, mango seeds are the waste material from the juice manufacturing units and hence, an attempt has been made to study the feasibility of using mango seed kernel powder to remove hexavalent chromium from aqueous solutions. Generally, in batch mode studies, influence of individual factors (viz. pH, temperature, adsorbent concentration, chromium concentration) have been reported by keeping other factors involved at an undetermined constant level, which does not depict the overall effect of all factors on chromium removal. In addition, this approach needs ample number of experiments which also consumes more time to establish optimum levels. However, these shortcomings can be eradicated by optimizing all the factors overall by statistical experimental design such as response surface methodology (RSM). Hence, in the present work the overall effect of five process variables (viz, pH, adsorbent concentration, temperature, stirring speed (RPM), and chromium(VI) concentration) on the removal of chromium from synthetic solutions by M. indica seed powder have been studied by employing central composite design (CCD) using RSM.

2. Materials and methods

2.1. Adsorbent preparation

Mango seeds were collected locally from the market and the seeds were washed several times with water to remove the dust and dried in the sun. The dried seeds were powdered in a laboratory mixer grinder and sieved through sieve size of $300 \ \mu\text{m}$; the powder was stored in airtight container. Characteristics of mango Table 1

| Physical propertie | s of mango seec | i kernel powder |
|--------------------|-----------------|-----------------|
|--------------------|-----------------|-----------------|

| Property | Value |
|--------------------------|-------|
| Moisture content (%) | 6.49 |
| Volatile matter (%) | 33.05 |
| Ash content (%) | 27.54 |
| Fixed carbon content (%) | 32.92 |
| Bulk density (g/cc) | 0.50 |

seed kernel powder were determined and the results are presented in Table 1.

2.2. Cr(VI) solution preparation

Cr(VI) solution of 1,000 mg/L concentration was prepared by dissolving 2.8287 g of potassium dichromate in 1,000 mL of distilled water. The standard solutions were made to get the desired range of Cr(VI) concentration. The concentration of Cr(VI) was determined by following the standard procedure prescribed in diphenylcarbazide method (APHA, 1995) [24] using an UV–spectrophotometer (Cyberlab, USA) at a wavelength corresponding to maximum absorbance (540 nm). 0.1 N HCl or NaOH is used to adjust the pH of the solution. All the reagents and chemicals used were of analytical grade.

2.3. Response surface methodology (RSM)

RSM is a fusion of mathematical and statistical techniques which is used for developing, enhancing, and optimizing the process and used to find the mutual significance of various process parameters even when complex interactions are present. Determination of optimum operational conditions of the process is the main aim of RSM. There are three steps in RSM (a) design and experiments, (b) response surface modeling through regression, and (c) optimization [25].

Independent process parameters can be represented in quantitative form using RSM as:

$$Y = f(X_1, X_2, X_3...X_n) \pm \varepsilon$$
⁽¹⁾

where, *Y* represents the response (yield), *f* is the response function, ε is the experimental error, and *X*₁, *X*₂, *X*₃ ... *X*_n are independent parameters.

A surface, known as the response surface is obtained by plotting the expected response of Y. The form of f may be very complex and unknown. Thus, RSM aims at approximating f by a suitable lower ordered polynomial in some region of the independent

process variables. If the response can be well-suited by a linear function of the independent variables, the function (Eq. (1)) can be written as:

$$Y = C_0 + C_1 X_1 + C_2 X_2 + \ldots + C_n X_n \pm \varepsilon$$
(2)

2.4. Experimental procedure

Adsorption of Cr (VI) ions onto mango seed kernel powder from aqueous solutions was performed on the batch scale. All the experiments was performed in 250-mL conical flasks containing 50 mL of chromium (VI) solution with adsorbent concentration ranging from 0.1–0.25 g per 50 mL each, which was scaled up in g/L as shown in Table 2 in order to study the interactive effect of the variables (pH, temperature, adsorbent concentration, chromium concentration, and RPM) on the maximum removal of Cr(VI). Since the number of independent variables is five in the present study, a 2⁵ fractional factorial CCD, consisting of 16 factorial points, 10 axial points and six replicates at the center points were employed. Altogether, 32 sets of experiments under the CCD with suitable combinations of pH, temperature, adsorbent concentration, chromium concentration, and RPM using response surface method were calculated by the Eq. (3) and the details are presented in Table 3.

$$N = 2^{k-1} + 2k + n_0 \tag{3}$$

where N is the total number of experiments and k is the number of factors. The experiments were designed from CCD under RSM using MINITAB 16.0. In order to demonstrate the nature of the response surface in the experimental design and to find out the optimal conditions of the most significant independent variables, the CCD under RSM was used. pH, temperature, adsorbent concentration, chromium

Table 2Level of independent variables and experimental range

| | Design | Rar leve | Range and levels | | |
|-------------------------|-----------|-------------|---------------------|-----|--|
| Independent variables | variables | -1 | 0 | +1 | |
| pH | X_1 | 2 | 3 | 4 | |
| Temperature | X_2 | 25 | 27.5 | 30 | |
| Adsorbent concentration | X_3 | 2 | 3.5 | 5 | |
| Chromium concentration | X_4 | 50 | 100 | 150 | |
| RPM | X_5 | 50 | 75 | 100 | |

concentration, and RPM were taken as independent variables and the chromium removal rate (%) was taken as dependent output response variable in this study.

The experimental design matrices of five individual variables with regard to their uncoded and coded values are given in Table 3. Estimation of quality of fit of the model is done through coefficient determination and analysis of variances. A mathematical model in form of second-order polynomial Eq. (4) was used to fit the experimental results as a function of independent variables involving their interactions.

$$Y = C_0 + C_1 X_1 + C_2 X_2 + C_3 X_3 + C_4 X_4 + C_5 X_5 + C_{11} X_1^2 + C_{22} X_2^2 + C_{33} X_3^2 + C_{44} X_4^2 + C_{55} X_5^2 + C_{12} X_1 X_2 + C_{13} X_1 X_3 + C_{14} X_1 X_4 + C_{15} X_1 X_5 + C_{23} X_2 X_3 + C_{24} X_2 X_4 + C_{25} X_2 X_5 + C_{34} X_3 X_4 + C_{35} X_3 X_5 + C_{45} X_4 X_5$$
(4)

where, Y represents the dependent variable (chromium removal rate); X_1 , X_2 , X_3 , X_4 , X_5 represents the independent variable; C₀ represents the regression coefficient at center point; C1, C2, C3, C4, C5 represents the linear coefficients; C₁₁, C₂₂, C₃₃, C₄₄, C₅₅ represents the quadratic coefficients; and C_{12} , C_{13} , C_{14} , C_{15} , C_{23} , C₂₄, C₂₅, C₃₄, C₃₅, C₄₅ represents the second-order interaction coefficients. The obtained regression model was estimated by interpreting the regression coeffivalues, analysis of variance (ANOVA), cient *p*- and *F*-values. The coefficient of determination R^2 was used to express the goodness of fit of the polynomial model equation. To identify the experimental design and to generate a regression model to find the optimum combinations considering the effects of linear, quadratic, and interactive effects on removal of chromium, the statistical software package (MINITAB 16.0) was used.

2.5. Scanning electron microscopy (SEM) analysis

The surface morphology of the raw and chromium-loaded samples of adsorbent were studied by employing SEM technique (JEOL, Japan). The samples were placed on stubs using double-faced adhesive tape and images were captured with different magnifications.

2.6. Fourier transform infrared radiation (FTIR) analysis

The surface chemistry of the adsorbent can be examined by employing FTIR [26]. The FTIR spectroscopy (SHIMADZU, Japan) was used to determine the

| Run | X_1 | X_2 | X_3 | X_4 | X_5 | pН | Temp (°C) | Ads conc. (g/L) | Cr conc. (mg/L) | RPM |
|-----|-------|-------|-------|-------|-------|----|-----------|-----------------|-----------------|------|
| 1 | -1 | -1 | -1 | -1 | 1 | 2 | 25.0 | 2.0 | 50.0 | 100 |
| 2 | 1 | -1 | -1 | -1 | -1 | 4 | 25.0 | 2.0 | 50.0 | 50.0 |
| 3 | -1 | 1 | -1 | -1 | -1 | 2 | 30.0 | 2.0 | 50.0 | 50.0 |
| 4 | 1 | 1 | -1 | -1 | 1 | 4 | 30.0 | 2.0 | 50.0 | 100 |
| 5 | -1 | -1 | 1 | -1 | -1 | 2 | 25.0 | 5.0 | 50.0 | 50.0 |
| 6 | 1 | -1 | 1 | -1 | 1 | 4 | 25.0 | 5.0 | 50.0 | 100 |
| 7 | -1 | 1 | 1 | -1 | 1 | 2 | 30.0 | 5.0 | 50.0 | 100 |
| 8 | 1 | 1 | 1 | -1 | -1 | 4 | 30.0 | 5.0 | 50.0 | 50.0 |
| 9 | -1 | -1 | -1 | 1 | -1 | 2 | 25.0 | 2.0 | 150 | 50.0 |
| 10 | 1 | -1 | -1 | 1 | 1 | 4 | 25.0 | 2.0 | 150 | 100 |
| 11 | -1 | 1 | -1 | 1 | 1 | 2 | 30.0 | 2.0 | 150 | 100 |
| 12 | 1 | 1 | -1 | 1 | -1 | 4 | 30.0 | 2.0 | 150 | 50.0 |
| 13 | -1 | -1 | 1 | 1 | 1 | 2 | 25.0 | 5.0 | 150 | 100 |
| 14 | 1 | -1 | 1 | 1 | -1 | 4 | 25.0 | 5.0 | 150 | 50.0 |
| 15 | -1 | 1 | 1 | 1 | -1 | 2 | 30.0 | 5.0 | 150 | 50.0 |
| 16 | 1 | 1 | 1 | 1 | 1 | 4 | 30.0 | 5.0 | 150 | 100 |
| 17 | -2 | 0 | 0 | 0 | 0 | 1 | 27.5 | 3.5 | 100 | 75.0 |
| 18 | 2 | 0 | 0 | 0 | 0 | 5 | 27.5 | 3.5 | 100 | 75.0 |
| 19 | 0 | -2 | 0 | 0 | 0 | 3 | 22.5 | 3.5 | 100 | 75.0 |
| 20 | 0 | 2 | 0 | 0 | 0 | 3 | 32.5 | 3.5 | 100 | 75.0 |
| 21 | 0 | 0 | -2 | 0 | 0 | 3 | 27.5 | 0.5 | 100 | 75.0 |
| 22 | 0 | 0 | 2 | 0 | 0 | 3 | 27.5 | 6.5 | 100 | 75.0 |
| 23 | 0 | 0 | 0 | -2 | 0 | 3 | 27.5 | 3.5 | 0.0 | 75.0 |
| 24 | 0 | 0 | 0 | 2 | 0 | 3 | 27.5 | 3.5 | 200 | 75.0 |
| 25 | 0 | 0 | 0 | 0 | -2 | 3 | 27.5 | 3.5 | 100 | 25.0 |
| 26 | 0 | 0 | 0 | 0 | 2 | 3 | 27.5 | 3.5 | 100 | 125 |
| 27 | 0 | 0 | 0 | 0 | 0 | 3 | 27.5 | 3.5 | 100 | 75.0 |
| 28 | 0 | 0 | 0 | 0 | 0 | 3 | 27.5 | 3.5 | 100 | 75.0 |
| 29 | 0 | 0 | 0 | 0 | 0 | 3 | 27.5 | 3.5 | 100 | 75.0 |
| 30 | 0 | 0 | 0 | 0 | 0 | 3 | 27.5 | 3.5 | 100 | 75.0 |
| 31 | 0 | 0 | 0 | 0 | 0 | 3 | 27.5 | 3.5 | 100 | 75.0 |
| 32 | 0 | 0 | 0 | 0 | 0 | 3 | 27.5 | 3.5 | 100 | 75.0 |

 Table 3

 Fractional factorial CCD matrix with code and real variables

functional groups present in the adsorbent. FTIR was done both for raw and chromium-loaded samples of mango seed kernel powder. The infrared spectrum of mango seed kernel powder was recorded as KBr discs in the range of $4,000-400 \text{ cm}^{-1}$.

3. Results and discussion

3.1. CCD: response surface estimation

The chromium removal results of various design variables (pH, temperature, adsorbent concentration, chromium concentration, and RPM) are shown in the Table 4. Experimental results of maximum chromium removal (%) from the calculated regression coefficients are fitted to a second-order polynomial Eq. (4). The Eq. (4) with regression coefficient for removal of chromium is given as Eq. (5). $Y = 70.1452 - 8.3417X_1 - 0.6583X_2 + 4.2433X_3$ + 4.6767X_4 + 1.6442X_5 + 1.1660X_1^2 - 0.0165X_2^2 - 3.1552X_3^2 - 12.5590X_4^2 - 0.1027X_5^2 + 0.7225X_1X_2 + 3.0637X_1X_3 + 0.6775X_1X_4 - 0.1800X_1X_5 - 1.3613X_2X_3 - 0.9750X_2X_4 - 4.5275X_2X_5 + 1.9837X_3X_4 - 3.2913X_3X_5 - 1.0450X_4X_5 (5)

3.2. Response surface methodology (RSM)

The predicted response was correlated with the experimental data with the help of regression coefficient. The proportion of variation in the response that is given by the model is denoted by the R^2 and adjusted R^2 values, where *R* indicates the amount of variation in the observed responses. The measure of fit of the model is also given by the value of R^2 and

| Table 4 | |
|--|------------|
| Fractional factorial CCD matrix and the output response for chromi | um removal |

| Run | pН | Temp (°C) | Ads conc. (g/L) | Cr conc. (mg/L) | RPM | Cr removal (%) exp | Cr removal (%) pre |
|-----|----|-----------|-----------------|-----------------|-----|--------------------|--------------------|
| 1 | 2 | 25.0 | 2.0 | 50 | 100 | 71.98 | 70.3570 |
| 2 | 4 | 25.0 | 2.0 | 50 | 50 | 27.45 | 23.7303 |
| 3 | 2 | 30.0 | 2.0 | 50 | 50 | 61.65 | 59.9470 |
| 4 | 4 | 30.0 | 2.0 | 50 | 100 | 45.23 | 40.1320 |
| 5 | 2 | 25.0 | 5.0 | 50 | 50 | 57.45 | 56.6778 |
| 6 | 4 | 25.0 | 5.0 | 50 | 100 | 55.34 | 51.1728 |
| 7 | 2 | 30.0 | 5.0 | 50 | 100 | 54.45 | 52.2995 |
| 8 | 4 | 30.0 | 5.0 | 50 | 50 | 56.34 | 52.0928 |
| 9 | 2 | 25.0 | 2.0 | 150 | 50 | 53.34 | 57.0520 |
| 10 | 4 | 25.0 | 2.0 | 150 | 100 | 50.67 | 50.9870 |
| 11 | 2 | 30.0 | 2.0 | 150 | 100 | 60.87 | 63.2037 |
| 12 | 4 | 30.0 | 2.0 | 150 | 50 | 44.23 | 44.4670 |
| 13 | 2 | 25.0 | 5.0 | 150 | 100 | 73.45 | 76.7145 |
| 14 | 4 | 25.0 | 5.0 | 150 | 50 | 61.23 | 62.3978 |
| 15 | 2 | 30.0 | 5.0 | 150 | 50 | 71.12 | 74.3045 |
| 16 | 4 | 30.0 | 5.0 | 150 | 100 | 52.32 | 52.1095 |
| 17 | 1 | 27.5 | 3.5 | 100 | 75 | 95.80 | 91.4927 |
| 18 | 5 | 27.5 | 3.5 | 100 | 75 | 51.45 | 58.1260 |
| 19 | 3 | 22.5 | 3.5 | 100 | 75 | 71.67 | 71.3960 |
| 20 | 3 | 32.5 | 3.5 | 100 | 75 | 66.12 | 68.7627 |
| 21 | 3 | 27.5 | 0.5 | 100 | 75 | 47.45 | 49.0377 |
| 22 | 3 | 27.5 | 6.5 | 100 | 75 | 65.23 | 66.0110 |
| 23 | 3 | 27.5 | 3.5 | 0 | 75 | 0.00 | 10.5560 |
| 24 | 3 | 27.5 | 3.5 | 200 | 75 | 37.45 | 29.2627 |
| 25 | 3 | 27.5 | 3.5 | 100 | 25 | 66.56 | 66.4460 |
| 26 | 3 | 27.5 | 3.5 | 100 | 125 | 70.54 | 73.0227 |
| 27 | 3 | 27.5 | 3.5 | 100 | 75 | 70.54 | 70.1452 |
| 28 | 3 | 27.5 | 3.5 | 100 | 75 | 70.54 | 70.1452 |
| 29 | 3 | 27.5 | 3.5 | 100 | 75 | 70.54 | 70.1452 |
| 30 | 3 | 27.5 | 3.5 | 100 | 75 | 70.54 | 70.1452 |
| 31 | 3 | 27.5 | 3.5 | 100 | 75 | 70.54 | 70.1452 |
| 32 | 3 | 27.5 | 3.5 | 100 | 75 | 70.54 | 70.1452 |

the model is compared with different independent variables by the adjusted R^2 values. The regression coefficient evaluates correlation between experimental and predicted values. The experimental values and predicted values obtained from the model Eq. (5) are depicted in Fig. 1.

In the figure, the linear line in the scatter plot has been obtained with regression analysis based on minimization of squared errors [27]. The regression coefficient value ($R^2 = 0.9564$) obtained is closer to 1, which indicates the perfect fit of the data presented in Table 5. The obtained R^2 value indicates that 95.64% of variability in chromium removal could be explained by the model. Also, if the model has high degree of adequacy for predicting the experimental results, the computed *F*-value from the model should be greater than tabulated *F*-value [28].

From the Table 5, the obtained *F*-value for chromium removal is 12.06, which is greater than F

tabulated value (2.64). The calculated regression coefficient for chromium removal is given in Table 6, together with their corresponding *p*-value and *T*-value. From the Table 6, the coefficient for single effect of pH (C_1), adsorbent concentration (C_3), and chromium concentration (C_4) are significant (p < 0.050); the square effects of (C_{33}), (C_{44}) and interactive effects of (C_{25}), (C_{35}) are significant.

3.3. SEM analysis

The SEM images captured at different magnifications on the adsorbent before and after adsorption are presented in Fig. 2.

3.4. FTIR analysis

The FTIR spectra of raw and chromium-loaded mango seed kernel powder are presented Fig. 3(a)



Fig. 1. Experimental values vs. predicted values for chromium (VI) removal.

Table 5ANOVA for fit of chromium removal (%) from CCD

| Sources of variation | Sum of squares | Degree of freedom | Mean square | <i>F</i> -value | р | | |
|---|-------------------|-------------------|----------------|-----------------|-------|--|--|
| Regression | 8,474.77 | 20 | 423.74 | 12.06 | 0.000 | | |
| Total | 386.46 8861.23 | 11 | 33.13 | | | | |
| $R^2 = 95.64\%; R^2 \text{ (adjusted)} = 87.71\%$ | | | | | | | |

Table 6 Estimated regression coefficients for removal of chromium (%)

| Term | Coefficient | Standard error | Т | р |
|------------------------|-------------|----------------|---------|-------|
| C_0 | 70.1452 | 2.364 | 29.670 | 0.000 |
| C_1 | -8.3417 | 1.210 | -6.895 | 0.000 |
| C_2 | -0.6583 | 1.210 | -0.544 | 0.597 |
| C_3 | 4.2433 | 1.210 | 3.507 | 0.005 |
| C_4 | 4.6767 | 1.210 | 3.865 | 0.003 |
| C_5 | 1.6442 | 1.210 | 1.395 | 0.201 |
| <i>C</i> ₁₁ | 1.1660 | 1.094 | 1.065 | 0.309 |
| C ₂₂ | -0.0165 | 1.094 | -0.015 | 0.988 |
| C ₃₃ | -3.1552 | 1.094 | -2.883 | 0.015 |
| C_{44} | -12.5590 | 1.094 | -11.476 | 0.000 |
| C_{55} | -0.1027 | 1.094 | -0.094 | 0.927 |
| C_{12} | 0.7225 | 1.482 | 0.488 | 0.635 |
| C ₁₃ | 3.0637 | 1.482 | 2.068 | 0.063 |
| C_{14} | 0.6775 | 1.482 | 0.457 | 0.656 |
| C_{15} | -0.1800 | 1.482 | -0.121 | 0.906 |
| C_{23} | -1.3613 | 1.482 | -0.919 | 0.378 |
| C_{24} | -0.9750 | 1.482 | -0.658 | 0.524 |
| C_{25} | -4.5275 | 1.482 | -3.055 | 0.011 |
| C_{34} | 1.9837 | 1.482 | 1.339 | 0.208 |
| C_{35} | -3.2913 | 1.482 | -2.221 | 0.048 |
| C ₄₅ | -1.0450 | 1.482 | -0.705 | 0.495 |

and (b). From Fig. 3(a), the peaks at 3,566.3 and 3,305.9 cm⁻¹ indicates the presence of –OH group and –NH group. The peak at 2,918.3 cm⁻¹ indicates the

presence of asymmetric CH₂ group and the peak at 1,710.8 cm⁻¹ represents C=O stretching. In Fig. 3(b), the downshift of wave number from 3,566.3 to 3,543.2 cm⁻¹ shows that –OH group is involved in chromium adsorption. The up shift of wave number from 3,305.9 to 3,317.5 cm⁻¹ is attributed to –NH stretching. The down shift of wave number from 1,710.8 to 1,708.9 cm⁻¹ indicates that C=O is involved in chromium adsorption. The new peak at 1,664.5 cm⁻¹ is due to C=O stretching of carboxyl group [29,30].

3.5. Interpretation of response surface plots

3.5.1. Effect of pH and temperature on chromium(VI) removal

pH and temperature plays an important role in estimating the removal efficiency of an adsorbent. The maximum removal takes place at acidic pH, as the pH increases removal efficiency decreases. H2CrO4, $HCrO_4^-$, CrO_4^{2-} , and $Cr_2O_7^{2-}$ are the different forms of Cr(VI) that exists in aqueous solution. HCrO₄⁻ is the active form of Cr(VI) adsorbed on the adsorbent. It is stable only at low pH range, thus leading to high uptake of chromium. When pH is increased the concentration of this form decreases, so at higher pH chromium uptake decreases [14]. From Fig. 4 it can be noted that as the pH increases with increase in temperature, the removal efficiency was very low which is due to fact that with an increase in pH, the hydroxides hinders the diffusion of chromium(VI) anions [31]. Also, as the pH decreases at initial level of temperature there was a maximum removal of Cr (VI) but as the temperature increases there was decrease in chromium(VI) removal which may be due to the fact that the desorption occurs during increase in temperature where temperature induces higher mobility of the adsorbate causing desorption [32].



Fig. 2. SEM images of raw adsorbent (a), (b) and chromium-loaded adsorbent (c), (d).

3.5.2. Effect of adsorbent concentration and pH on chromium(VI) removal

From Fig. 5, it has been observed that at low pH and low adsorbent concentration, the percentage removal was high; as the pH increases with an increase in adsorbent concentration, the removal efficiency was low, this is due to fact that only at low pH the chromium ions ($HCrO_4^-$) is in active form of Cr(VI) which will be available for adsorption onto the adsorbent. It is not that the pH is only significant factor for chromium removal; at low pH when the adsorbent concentration increases, there was maximum removal in the middle and with further increase in adsorbent concentration the removal decreases which may be due to desorption.

3.5.3. Effect of chromium concentration and pH on chromium(VI) removal

From Fig. 6, it can be noted that at low pH as the chromium concentration increases, to a certain point the removal efficiency was high but as the concentration increases there was decrease in the removal efficiency. This could be due to the fact that the chromium(VI) removal is dependent on initial concentration as the ratio of available surface to the initial chromium(VI) concentration is larger at low

concentration, whereas, at higher concentration this ratio is low and hence, the low percentage removal. This observation is consistent with the results reported in the literature [33].

3.5.4. Effect of RPM and pH on chromium(VI) removal

The stirring speed (RPM) plays an important role in the mass transfer of chromium ions from the solution into the adsorbent [14,15]. From Fig. 7, it can be clearly noted that at low pH values as the RPM increases there was maximum removal, whereas the chromium removal was low at higher pH and higher RPM. This observation is consistent with the results reported in the literature [14].

3.5.5. Effect of adsorbent concentration and temperature on chromium(VI) removal

Temperature is also one of the major factors in chromium removal. It can be observed from Fig. 8 that at low temperature, when the adsorbent concentration increases the chromium removal was high and when temperature increases there was a decrease in the chromium removal which could be due to the fact that increase in thermal energy causes desorption [32,34]. Also, higher adsorbent concentration leads to greater



Fig. 3. FTIR spectra of raw (a) and chromium loaded (b) mango seed powder.



Fig. 4. Effect of pH and temperature on chromium(VI) removal.

availability of exchangeable sites for metal ions and greater surface area. As the adsorbent concentration increases the removal efficiency decreases, beyond a point which could be due to overlapping of adsorption sites [33].



Fig. 5. Effect of adsorbent concentration and pH on chromium(VI) removal.



Fig. 6. Effect of chromium concentration and pH on chromium(VI) removal.



Fig. 7. Effect of RPM and pH on chromium(VI) removal.

3.5.6. Effect of chromium concentration and temperature on chromium(VI) removal

It can be observed from Fig. 9 that at low temperature as the chromium concentration increases there was a high removal of chromium to certain level, and then decreases. At lower adsorbent concentration, there is no significant change in chromium removal with increase in temperature. The chromium(VI)



Fig. 8. Effect of adsorbent concentration and temperature on chromium(VI) removal.

removal is dependent on initial concentration as the ratio of available surface to the initial chromium(VI) concentration is larger at low concentration. The results obtained are consistent with the results reported in the literature [33].

3.5.7. Effect of RPM and temperature on chromium(VI) removal

From Fig. 10, it can be noted that at low temperature, when the RPM increases the removal efficiency was low, whereas at high RPM and low temperature the maximum removal was observed which could be due to the fact that high mass transfer rate leads to more adsorption of chromium on to the adsorbent.

3.5.8. Effect of chromium concentration and adsorbent concentration on chromium(VI) removal

It can be observed from Fig. 11 that when the adsorbent concentration increases with initial chromium concentration the removal efficiency was low, whereas at high adsorbent concentration the removal was high to a certain range of chromium



Fig. 10. Effect of RPM and temperature on chromium(VI) removal.

concentration and then there was a decrease which may be due to desorption as the capacity of adsorbent to absorb the chromium is limited.

3.5.9. Effect of RPM and adsorbent concentration on chromium(VI) removal

Fig. 12, depicts the effect of RPM and adsorbent concentration on chromium(VI) removal. It can be noted from the figure that at low RPM when the adsorbent concentration increases there is an increase in chromium removal, whereas at higher adsorbent concentration, increase in RPM decreases the chromium removal.

3.5.10. Effect of RPM and chromium concentration on chromium(VI) removal

From Fig. 13, it can be noted that when the chromium concentration increases the increase in removal efficiency was observed at all RPM levels. However, there was decrease in chromium removal at higher levels of chromium concentration which could be due



Fig. 9. Effect of chromium concentration and temperature on chromium(VI) removal.



Fig. 11. Effect of chromium concentration and adsorbent concentration on chromium(VI) removal.



Fig. 12. Effect of RPM and adsorbent concentration on chromium(VI) removal.



Fig. 13. Effect of RPM and chromium concentration on chromium(VI) removal.

to the fact that the mass transfer was high at certain range of chromium concentration and hence the higher removal efficiency.

4. Conclusion

The objective is to study the effects of variables, such as pH, temperature, adsorbent concentration, chromium concentration, and RPM on hexavalent chromium removal by mango seed powder using CCD under RSM with statistical analysis. From the results it is observed that optimum condition for chromium removal is obtained at pH 1, temperature 27.5 °C, adsorbent concentration 3.5 g/L, chromium concentration 100 ppm, and RPM 75. The predicted value for maximum chromium removal is 91.45% which is near to the experimental value of 95.8% with a regression coefficient (R^2) value of 0.95 which shows that experiments are statistically significant.

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