Optimization of adsorption process parameters by response surface methodology for hexavalent chromium removal from aqueous solutions using *Annona reticulata* Linn peel microparticles

N. Saranya, E. Nakeeran, M. S. Giri Nandagopal and N. Selvaraju

**ABSTRACT**

Fruit peel microparticles of *Annona reticulata* Linn were used as biosorbent for the sequestration of hexavalent chromium (Cr(VI)). Characterization of the biosorbent was done using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDXS), Fourier transfer infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GCMS), carbon, hydrogen, nitrogen and sulphur (CHNS) elemental analysis, mercury intrusion porosimetry and point of zero charge. Influential parameters were optimized using response surface methodology (RSM) with a total of 17 experimental runs based on the Box-Behnken design and found to be pH 1.0, temperature 25 °C and 100 mg/L initial chromium concentration. pH and concentration were found to be more influential than temperature. The analysis of variance indicated that a second-order polynomial regression equation was the most suitable for fitting the experimental data. The experimental runs showed a good correlation with the predicted responses ($R^2 = 0.9956$). The biosorption process fitted well with the Langmuir isotherm with an adsorption capacity of 108.32 mg/g out of the other isotherms such as Freundlich and Dubinin-Radushkevich that were analyzed. Non linear pseudo first order, pseudo second order, and intraparticle diffusion kinetics were applied to describe the interaction between the biosorbent and Cr(VI). Desorption and regeneration performances showed that fruit peels of *Annona reticulata* Linn can be an environmental friendly option for hexavalent chromium removal from aqueous solutions.

**Key words** | *Annona reticulata*, Box-Behnken design, desorption and regeneration, hexavalent chromium, isotherms and kinetics

**INTRODUCTION**

Immense urbanization, industrialization and exploitation of natural resources by humans have created stress to the global environment by generating toxic pollutants (Kuppusamy *et al.* 2015). Owing to the property of passivation, chromium has been an important metal in several industrial processes such as metal plating and polishing, leather tanning, textile dyeing, inorganic chemical production, wood preservation, etc. (Tofihy & Mohammadi 2011). In solution, the common oxidation states of chromium are +2, +3 and +6, while the other unstable forms are 0, +1, +4 and +5 (Mohan & Pittman 2006). Out of them, Cr(VI) has been found to be highly toxic and carcinogenic to flora and fauna when it exceeds permissible limits (Kalidhasan *et al.* 2016). It is considered as a major soil and water contaminant also. Most surface waters contain between 1 and 10 μg of chromium per litre (Handa 1988). As per the United States Environmental Protection Agency (US EPA), the permissible limit for Cr in drinking water is 0.05 mg/l, max. Above this limit, Cr can be carcinogenic (Amdur *et al.* 1991). Many methods such as coagulation (Parga *et al.* 2005), precipitation (Round hill & Koch 2002), membrane separation (Ozaki *et al.* 2002), extraction (Salazar *et al.* 1992) evaporation (Tels 1987), etc., are utilized for the detoxification and removal of anionic metal species like Cr(VI). Owing to several constraints such as complexity in design, cost, sludge production, difficulty in regeneration and metal recovery, these techniques are not considered as superior options (Crini 2005; Zheng *et al.* 2012). Several zero cost green sorbents have been used to remove or reduce hexavalent chromium from aqueous solutions.
chromium in contaminated water (Ajmal et al. 1996; Dakily et al. 2002; Yu et al. 2003; Sumathi & Naidu 2005; Parab et al. 2006). Green waste comprises food, forestry, garden, agricultural and biological industrial wastes. It is estimated that 140 billion metric tonnes of biomass are generated globally every year from agriculture (Centore et al. 2014). Out of them, lignocellulosic and phytochemical bound biosorbents have been tremendously explored since they naturally contain several diverse functional groups that would readily interact with heavy metals and other inorganic substances. *Annona reticulata* is a deciduous, semi-evergreen tree belonging to the family Annonaceae, known for its fruit, called the custard apple. It is cultivated and naturalized in many parts of the world including Southeast Asia, Taiwan, India, Australia, and West Africa (Aluka 2008). Fruit peels of *Annona reticulata* are lignocellulosic and polyphenol rich food waste with no commercial value, thus they can be abstracted for heavy metal sequestration. Modeling and optimization techniques have been profoundly used to study the deep insights into the Cr removal mechanism and the effect of each parameter that drives the process (Anupam et al. 2011; Mofarrah et al. 2014; Mandal et al. 2015). Since adsorption of Cr(VI) relies on several parameters, the study focused on utilizing the predictive response surface methodology (RSM) model for modeling and optimization of hexavalent chromium removal from simulated aqueous solution through the utilization and regeneration of *Annona reticulata* fruit peel waste non living biomass, which has not been utilized before. Whilst being a commonly used predictive model, having its own advantages and disadvantages, it was believed that the model equation from the Box-Behnken design would give a clear relationship between the parameters analyzed and Cr removal rate. The study also considered the kinetic, equilibrium and thermodynamic behavior of hexavalent chromium biosorption onto the biosorbent. Desorption and regeneration studies were also documented, which highlighted the ascendency of the biosorbent in reutilization.

**MATERIALS AND METHODS**

**Preparation of fruit peel microparticles**

*Annona reticulata* fruit peels were collected and washed thoroughly with deionized water to remove dirt. They were then dried in an oven at 70 °C for 48 hrs and pulverized using an electrical blender. The powdered biomass was sieved through different sized meshes, and 54–63 μm particles were collected. The *Annona reticulata* fruit peel biosorbent (ARPB) thus prepared was checked for hexavalent chromium adsorption without any modification to check the native effect of biosorbent and to avoid extra expenditure.

**Stock chromate solution**

Stock solution of 1,000 mg L⁻¹ is prepared by dissolving 2.828 g of potassium dichromate salt (AR grade) in double distilled water. The working solutions of 100, 200, 300, 400 and 500 mg/L were prepared by diluting the stock solution appropriately in double distilled water. Quality assurance/quality control analysis was performed, and standardization was done before starting the batch experiments.

**Biosorbent characteristics study**

Elementary analysis of ARPB was done using a CHNS Analyzer (Vario EL III, Elementar, Germany). The surface area and pore volume of the biosorbent was determined using a Mercury Intrusion Porosimeter (Quantachrome ASAP 2200, Micromeritics, USA). The volatile organic constituents predominantly present in the biosorbent were characterized using gas chromatography-mass spectrometry (GCMS) (Agilent Technologies). Acetone and methanolic extracts of the biosorbent were filtered with Whatman filter paper (No. 1) and injected in an Agilent Technologies 7890A GC System fitted with a DP-5/HP5 silicon based capillary column (30 mm length 0.25 mm inner diameter, 0.25 μm film thickness; maximum temperature, 350 °C), coupled to an Agilent Technologies 5975C MS. Ultra-high purity helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The initial temperature was 40 °C for 5 min then raised up to 250 °C at 5 °C/min at the injection port. An AgilentHP-5MS capillary column loaded with 5% (v/w) phenyl-substituted methyl siloxane stationary phase connected to the thermally stable capillary wall was used. The identification and characterization of chemical compounds in various crude extracts was based on GC retention time. The mass spectra were matched with those of standards available in mass spectral libraries. The zero point charge was measured by preparing 0.1 N KNO₃ solutions of varying pH ranges from 1.0 to 8.0 using 0.1 N HCl and 0.1 N NaOH. 0.1 g of biosorbent was added to the solutions and agitated overnight, and a final pH (pHₑ) was measured. A plot between the initial pH (pHᵢ) and the difference between the final and initial pH (∆pH = pHᵢ – pHₑ) was made and the zero point charge was determined using the point at which ∆pH is zero. The structural characteristics of the biosorbent before and after Cr(VI) biosorption were analysed using a Scanning Electron Microscope (SEM) (JSM – 6390LV, JEOL, USA). Energy-dispersive X-ray spectroscopy
The quantitative form of the methodology is as follows:

\[ Y = f(x_1, x_2, x_3, \ldots x_n) \]

where \( Y \) is the response, which is the removal percentage of Cr(VI), and \( x_1, x_2, x_3 \) and \( x_n \) are the independent variables or parameters that influence the process. The lower order polynomial function that describes the value of \( Y \) can be described as

\[ Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ij} X_i X_j + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ijk} X_i X_j + \epsilon \]

Where \( Y \) is the response (removal %), \( X_i \) and \( X_j \) are the real or coded variables, \( \beta_0, \beta_i, \beta_{ij}, \beta_{ijk} \) are the coefficients of regression and \( \epsilon \) is the random error. Design Expert 10.0.3 (Stat-Ease, Inc., USA, 2016) was used for the analysis, and the experimental results at coded conditions were fitted to a second-order polynomial regression model with linear, quadratic and interaction coefficient terms. A three parameter Box-Behnken model was used with the three influencing parameters as independent variables [pH (\( X_1 \)), temperature (\( X_2 \)) and initial chromium concentration (\( X_3 \))] for the response (Removal %). Table 1 gives the parameters and their coded levels. After the regression model of the experimental design was obtained, the statistical significance and regression parameters were evaluated by using analysis of variance (ANOVA), by which the experimental and calculated values are compared.

Desorption and regeneration studies

The regeneration capacity of the biosorbent in removing Cr(VI) was determined after desorption with different concentrations of NaOH. Successive desorption-biosorption experiments were repeated for up to six cycles. Different concentrations of NaOH (0.1 N, 1.0 N and 2 N) were used as a desorbing agent, and the experiments were conducted for up to 24 hrs. Desorption out of adsorption was calculated by

\[ \% \text{Desorption} = \frac{C_{\text{des}}}{C_{\text{ads}}} \times 100 \]

where \( C_{\text{des}} \) is the chromium desorption concentration at time ‘t’ (mg/L), \( C_{\text{ads}} \) is the adsorbed chromium concentration at the same time ‘t’ (mg/L).

**Table 1** Independent variables with their coded values

<table>
<thead>
<tr>
<th>Factors</th>
<th>Symbols</th>
<th>Low level</th>
<th>Medium</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>( X_1 )</td>
<td>1</td>
<td>4.5</td>
<td>8</td>
</tr>
<tr>
<td>Temperature</td>
<td>( X_2 )</td>
<td>25</td>
<td>37.5</td>
<td>50</td>
</tr>
<tr>
<td>Initial concentration</td>
<td>( X_3 )</td>
<td>100</td>
<td>300</td>
<td>500</td>
</tr>
</tbody>
</table>

EDX (JED–2300, JEOL, USA) was used for analyzing adsorption of Cr ions onto ARPB. A Fourier transform infrared (FTIR) spectrophotometer (Jasco 1033, FT/IR-4700 type A India) identified the predominant functional groups present and involved in Cr(VI) binding in the range of 400–4,000 cm\(^{-1}\).

Batch adsorption studies

250 ml stoppered conical flasks were used with 50 ml of 100 mg/L potassium dichromate solution for experimental studies. Thorough analysis was performed to know the effects of biosorbent size, biosorbent dose, contact time, temperature, agitation speed, and initial chromium solution concentration. Adjustments to the pH were made with 0.1 mol/L HCL and 0.1 mol/L NaOH. A rotary shaker with incubator (model GeNei, SLM-INC-OS-250, India) was used for mixing the reactants. The concentration of the Cr(VI) after adsorption was determined using a UV-Visible spectrophotometer (Perkin-Elmer Lambda 650, USA) after reacting with 1,5-diphenyl carbazide and concentrated H\(_2\)SO\(_4\) at 540 nm (Rangabhashiyam et al. 2016). Milligrams of Cr(VI) adsorbed per gram of biosorbent at time ‘t’ was calculated as

\[ q_t = \frac{(C_0 - C_t)V}{m} \]

(1)

where \( q_t \) is the adsorption capacity at time ‘t’ (mg/g), \( C_0 \) is the initial Cr(VI) concentration (mg/L), \( C_t \) is the Cr(VI) concentration (mg/L) at time ‘t’, \( m \) is the adsorbent dry weight (g) and \( V \) is the volume of the Cr(VI) solution (L). The removal percentage was represented by

\[ \% \text{Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]

(2)

where \( C_e \) is the equilibrium concentration of Cr(VI) (mg/L). All the experiments were carried out in triplicates and the experimental results were expressed as means ± SD.

Numerical optimization of experimental design using response surface methodology

Response surface methodology is one of the basic tools in optimizing experimental design where large number of parameters influence the process (Ranjan et al. 2009). The quantitative form of the methodology is as follows:

\[ Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ij} X_i X_j + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ijk} X_i X_j + \epsilon \]

where \( Y \) is the response (removal %), \( X_i \) and \( X_j \) are the real or coded variables, \( \beta_0, \beta_i, \beta_{ij}, \beta_{ijk} \) are the coefficients of regression and \( \epsilon \) is the random error. Design Expert 10.0.3 (Stat-Ease, Inc., USA, 2016) was used for the analysis, and the experimental results at coded conditions were fitted to a second-order polynomial regression model with linear, quadratic and interaction coefficient terms. A three parameter Box-Behnken model was used with the three influencing parameters as independent variables [pH (\( X_1 \)), temperature (\( X_2 \)) and initial chromium concentration (\( X_3 \))] for the response (Removal %). Table 1 gives the parameters and their coded levels. After the regression model of the experimental design was obtained, the statistical significance and regression parameters were evaluated by using analysis of variance (ANOVA), by which the experimental and calculated values are compared.

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RESULTS AND DISCUSSION

Physico chemical characterization of biosorvents

The basic elemental composition of the *Annona reticulata* biosorbent shown in Table 2 revealed that the biomass is cellulosic in nature (Rangabhashiyam & Selvaraju 2015a).

The SEM image of the biosorbent (Figure 1(a)) before Cr(VI) adsorption clearly depicts that the surface of the biosorbent is irregular, and highly porous with a total porosity of 12.68%, with striated ups and downs that can hold ligands upon them. Figure 1(b), the EDXS image, represents the binding of Cr(VI) upon the surface of the biosorbent with distinct peaks for Cr ions, thus confirming the adsorption of Cr(VI) ions by the biosorbent.

The predominant chemical constituents of volatile matter, long chain, branched chain hydrocarbons, alcohol acids and esters, etc. of the biosorbent were estimated by GCMS. From the gas chromatography analysis, the biosorbent was found to contain several organic volatiles such as Ephedrine 3-Octanol, and Phthalic acid isobutyl ester, which showed that the biosorbent comprises organic phytochemicals with diverse functional groups reliable for Cr(VI) binding. The presence of acetone dimethyl acetal groups and methane oxybis [dichloro- compounds reveals that the biosorbent is lignocellulosic and phytochemical in nature. The molecular formulae of the compounds are presented in Table 3.

The spectral analysis of the biosorbent before and after adsorption was done using FTIR and is shown in Figure 2. The significant positional band shift in the fingerprint region of 500 to 1,500 cm\(^{-1}\) is mainly owing to hydroxyl

### Table 2 | Physico chemical analysis of the biosorbent

<table>
<thead>
<tr>
<th>Parameters</th>
<th><em>Annona reticulata</em> peel biosorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C%</td>
<td>40.68</td>
</tr>
<tr>
<td>H%</td>
<td>5.79</td>
</tr>
<tr>
<td>N%</td>
<td>1.98</td>
</tr>
<tr>
<td>S%</td>
<td>Nil</td>
</tr>
<tr>
<td>Total pore volume (cc/g)</td>
<td>5.634</td>
</tr>
<tr>
<td>Total surface area (m(^2)/g)</td>
<td>4.852</td>
</tr>
<tr>
<td>Total porosity %</td>
<td>12.68</td>
</tr>
<tr>
<td>pH(_{ZPC})</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 1 | SEM-EDS images of the biosorbent (a) before adsorption and (b) after adsorption.
groups of phenols exposed on the surface of the biosorbent. Disappearance of a vibrational band in the region 582.76 cm\(^{-1}\) after adsorption is due to the C-C-C bend of alkanes. A slight shift of peak at 846.32 cm\(^{-1}\) is due to the stretch of alkyl halides. The appearance of a stretch at 906.11 cm\(^{-1}\) clearly depicts the accumulation of Cr(VI) onto the surface of the biosorbent (Ren et al. 2016). The shift of the peak at 1,055.17 cm\(^{-1}\) after adsorption clearly depicts the involvement of the \(-\text{C}-\text{N}-\) stretch of aliphatic amines (Nakkeeran et al. 2016). The appearance of a peak at 1,139.99 cm\(^{-1}\) after adsorption, which is meant for alkyl halides, reveals the involvement of alkyl groups of biosorbent. The appearance of small sharp peaks at 1,357 and 1,403.55 cm\(^{-1}\) corresponds to the C-H bend of alkanes. The disappearance of the peak at 1,496.58 cm\(^{-1}\) clearly depicts the involvement of the N-O symmetric stretch of nitro compounds. The appearance of a sharp peak at 1,565.89 cm\(^{-1}\) after Cr(VI) adsorption might be due to the fact that binding of Cr ions upon the aromatic hydrocarbon compounds of the AR biosorbent would have undergone interactions, thus producing a weak C-C stretch (WH Freeman). The Narrowing of the broad peak at 3,400 cm\(^{-1}\) after adsorption clearly depicts the involvement of hydroxyl groups of biosorbent (Rangabhashiyam et al. 2016). Hence, the functional groups involved in the biosorption process are found to be the hydroxyl, amino, alkane and nitro groups.

**Effect of biosorbent dosage**

The effect of biosorbent dose was checked using different doses ranging from 0.05 g to 0.3 g with the other parameters fixed. A maximum removal of 85.04% and a maximum adsorption capacity of 42.52 mg/g were obtained at about 0.1 g, and no considerable increase was shown for a further increase in the sorbent dose (Figure 3). The adsorption capacity values decreased with the increase in the adsorbent dose due to the unavailability of Cr ions, which would have been adsorbed upon the largely available binding sites (Nakkeeran et al. 2016). Hence 0.1 g of biosorbent was considered to be the optimum dose for maximum removal of 100 mg/L of Cr(VI) solution until equilibrium.

**Effect of contact time**

Contact time is an essential and influencing factor for the biosorption process between the biosorbent and adsorbate. Batch experiments were conducted with different contact time from 30 mins to 180 mins. Figure 4 shows the effect of contact time on the removal of different initial Cr(VI) concentration ranges from 100 to 500 mg/L. The removal

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**Table 3** Organic volatiles identified in Annona reticulata linn. fruit peel biomass by GCMS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Retention time (min)</th>
<th>Compound</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanolic</td>
<td>1.690</td>
<td>(R*, S*)-2-(methylamino)-1-phenylpropan-1-ol</td>
<td>C(<em>{10})H(</em>{15})NO</td>
</tr>
<tr>
<td>extract</td>
<td></td>
<td>(Ephedrine)</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>2.389</td>
<td>Acetone dimethyl acetal</td>
<td>C(<em>{2})H(</em>{12})O(_{2})</td>
</tr>
<tr>
<td>extract</td>
<td>2.149</td>
<td>Methane, oxybis [dichloro-</td>
<td>C(<em>{2})H(</em>{4})Cl(_{2})</td>
</tr>
<tr>
<td></td>
<td>5.054</td>
<td>3-Octanol</td>
<td>C(<em>{6})H(</em>{12})</td>
</tr>
<tr>
<td></td>
<td>30.879</td>
<td>Phthalic acid, diisobutyl ester</td>
<td>C(<em>{16})H(</em>{24})O(_{4})</td>
</tr>
</tbody>
</table>

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**Figure 2** FTIR spectra of Annona reticulata biomass before and after Cr(VI) adsorption.

**Figure 3** Effect of biosorbent dose on Cr(VI) adsorption capacity at 100 mg/L initial concentration, 100 rpm, pH 1.0 and 303 K.
percentage increased rapidly in the first 30 min, gradually increased with the passage of time, and equilibrium was reached in approximately 120 mins. The increase in removal percentage of Cr(VI) at the initial stage is owing to increased availability if the number of functional binding sites upon the adsorbent surface. After 120 mins, adsorption was not accountable owing to sorption site unavailability.

**Effect of agitation speed**

Adsorption studies were carried out at different agitation speed ranges from 25 to 150 rpm for about 120 mins. 33.51% removal was obtained when the sorbent-sorbate mixture was allowed to spin at 25 rpm, and increased gradually and attained maximum at 100 rpm (Figure 5). Hence 100 rpm was selected as the optimum speed for the study. Above optimum speed there was a little decrease in the removal percentage, most probably due to boundary layer limitations (McKay 1985) and non exposure of all the available functional groups of biosorbent to the chromium ions, spinning at a high speed. Furthermore, higher agitation speed lowered the removal percentage, due to insufficient contact time for the Cr ions to be adsorbed on the adsorbent surface. In addition, desorption might have occurred due to the high speed, which would have decreased the removal percentage of Cr(VI) ions.

**RSM model fit**

**Box-Behnken statistical analysis**

In accordance with the design produced, experiments were conducted for all 17 runs with different ranges of pH, temperature and initial chromium concentration. The actual observed and predicted values were in the maximum and minimum ranges of 77.50 to 6.0, and are shown in the Table 4. The ratio of the maximal value to the minimal value was 12.06.

<table>
<thead>
<tr>
<th>Runs</th>
<th>Factor 1: pH</th>
<th>Factor 2: temperature</th>
<th>Factor 3: concentration</th>
<th>Actual values removal%</th>
<th>Predicted values removal%</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5</td>
<td>25</td>
<td>500</td>
<td>12</td>
<td>12.06</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>50</td>
<td>300</td>
<td>43.8</td>
<td>44.31</td>
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<tr>
<td>3</td>
<td>1</td>
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<td>77.5</td>
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<td>5</td>
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<td>17</td>
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<td>37.5</td>
<td>500</td>
<td>31.8</td>
<td>31.37</td>
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</table>
value is 12.91, with a mean and standard deviation of 23.32 and 19.11 respectively implying that the model design is feasible and acceptable. From the design, the optimum parameters were determined as pH 1.0, temperature 37.5 °C and an initial concentration of 100 mg/L for a maximum removal of 77.5%.
Analysis of variance

The interaction between design factors and responses was clearly depicted using ANOVA. The predicted data for the ANOVA are shown in the supplementary material as Table S1 (available with the online version of this paper).

The ‘probability > F’ values of most of the terms from ANOVA results are less than 0.05, and 2,435.90 F-value indicated that the model is significant. According to the model, $X_1$, $X_2$, $X_3$, $X_1X_2$, $X_1X_3$, $X_2X_3$, $X_1^2$ and $X_2^2$ were significant model terms. Owing to certain systematic variations unaccounted for in this model, lack of fit also became significant. The model Equation (6) developed by the software showed explicitly the relationship between the independent factors considered and the removal percentage of Cr(VI)

$$Y = +113.11 - 20.725X_1 + 0.199X_2 - 0.211X_3$$
$$+ 0.0257X_1X_2 + 0.016X_1X_3 - 5.66 \times 10^{-4}X_2X_3$$
$$+ 1.01X_1^2 - 3.44 \times 10^{-3}X_2^2 + 1.709 \times 10^{-4}X_3^2$$

The positive and negative sign in front of the independent and interactive factors in the equation represents the increase and decrease in the response due to those factors respectively. Although the negative symbol in front of the pH and concentration terms implies a non-linear relationship between the parameters and the response, the coefficient values of those terms (20.725 and 0.211) depicted that pH and concentration are the most influential factors of the Cr(VI) adsorption process. On the other hand, the positive symbols of the interactive and quadratic factors showed that they tend to influence the removal percentage in a proportional manner (Kaoah et al. 2018). In addition, the quadratic model predicted the regression value of 0.9956, which was in good agreement with the real regression value of 0.9997. A plot of the actual and predicted values is presented in the supplementary material, Figure S1 (available with the online version of this paper). This implies that Annona reticulata linn peels can be used as an effective biosorbent for Cr(VI) removal. In addition, the adequate precision ratio of 180.384 represented less noise with an adequate signal, and thus the model can be used to navigate the design space.

Optimization of parameters

Numerical optimization was performed using the software with a goal of maximizing the removal percentage by applying the lower and upper limits as 6.0 and 100, respectively. From the solution obtained, the optimum parameters were determined as pH 1.0, temperature 25 °C and an initial concentration of 100 mg/L for the increased removal of 77.632, with a desirability value of 0.844. Figure 6(a) shows the percentage removal of Cr(VI) at a constant initial concentration of 100 mg/L at different pH and temperatures ranging from 1.0 to 8.0 and 25 °C to 50 °C, respectively. The maximum removal was at a pH of 1.0 and a temperature of 25 °C. When the pH and temperature increase, the removal percentage gradually decreases. When the pH was increased to 8.0, the removal percentage was only 13.2%. This behavior might be due to the fact that at high pH, anions predominate in solution and hence there is a repulsion between the Cr(VI) anionic species ($\text{HCrO}_4^-$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{CrO}_4^{2-}$) and the hydroxyl ions in the solution. Conversely, at low pH, the mobility and attraction of Cr species with that of the cations present in the solution would be high, and adsorption over the surface of the biosorbents would be relatively greater (Ofomaja & Ho 2007). Box-Behnken design had suggested the optimum combination of parameters for Cr(VI) adsorption onto the Annona reticulata linn biosorbent. From the contour plots of the optimization results it is clear that the optimum temperature is from 25 °C for increased removal of 77.632% and above the optimum temperature, the removal was reduced. From the experiments, it was depicted that the removal percentage was 77.5 at 37.5 °C at pH 1.0 and an initial concentration of 100 mg/L.

The reason for this could be that the optimum mobility of the chromium ions is high enough to make

![Image](https://iwaponline.com/wst/article-pdf/75/9/2094/453358/wst075092094.pdf)
interaction with the surface functional groups of the biosorbent at low temperatures ranging from 25 °C to 37.5 °C. At temperatures higher than the optimum values, the removal percentage decreased to half of its maximum owing to the possibility of desorption that could have taken place due to the fast mobility of Cr ions, which bounced off from the surface functional groups. The percentage removal of Cr increases with the decrease in the chromium concentration, and vice versa, as depicted in the 2D and 3D plots. At the optimum concentration of 100 mg/L, the active sites on the surface of the biosorbent were free enough to accommodate the Cr species and hence maximum removal was attained (Daoud et al. 2015). When the concentration increased, the surface active sites were exhausted where there was creation of a charge balance between the metal ions and the functional groups that drive the process to attain equilibrium. Hence, from the analysis, the optimum pH, temperature and initial concentration were found to be 1.0, 25 °C and 100 mg/L, respectively.

Validation experiments post analysis

To check the validity of the model, three batch experiments were conducted with different sets of operating conditions (Run 1: pH 1.0, temperature 50 °C and 318 mg/L concentration; Run 2: pH 1.0, temperature 35 °C and 100 mg/L concentration; Run 3: pH 7.0, temperature 37 °C and 500 mg/L concentration) produced from the optimization step, and the results were compared. The experimental removal percentages were 40.50, 74.80 and 9.20, which are appreciably comparable with optimized response outcomes such as 42.17, 76.639, and 9.8 removal percentages, respectively. This implies that the model developed by RSM was highly suitable for Cr(VI) removal from aqueous solutions using *Annona reticulata* Linn biosorbent.

Biosorption isotherms

Biosorption isotherms are frequently used for quantification of the biosorption capacity of a biosorbent (Bhattacharya et al. 2017). The biosorption process is analyzed using the following two parameter models, and the parameters were calculated.

**Langmuir model**

Monolayer adsorption upon a homogeneous surface can be well predicted by the Langmuir adsorption model represented as

\[ q_e = \frac{Q_0 K_L C_e}{1 + K_L C_0} \]  

(7)

where \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) is the equilibrium biosorption capacity at time ‘t’ (mg/g), \( Q_0 \) is the monolayer adsorption capacity (mg/g) and \( K_L \) is the Langmuir isotherm constant. A dimensionless constant called the separation factor, \( R_L \), represents the nature of the process given by

\[ R_L = \frac{1}{1 + K_L C_0} \]  

(8)

If \( R_L \) lies between 0 and 1, the adsorption process is said to be favourable, if it is 1, adsorption will be unfavourable and \( R_L = 0 \) represents irreversible adsorption. Non linear regression analysis has been done, and the parameters have been analysed (Barrow 2008). Values of R² (0.978) indicate the better fit of the isotherm to the biosorption process. The monolayer biosorption capacity was found to be 108.32 ± 4.4 mg/g for the removal of hexavalent chromium. The Langmuir isotherm constant \( K_L \) was calculated as 0.02 (L/mg). Such a low value showed the high affinity of Cr(VI) anions towards the biosorbent. The decrease in the \( K_L \) value with the increase in concentration revealed the exothermic and physical nature of the adsorption (Febrianto et al. 2009). The \( R_L \) values between 0 and 1 (Table 5) confirmed Cr(VI) biosorption onto the biosorbent is suitable and reversible.

**The Freundlich isotherm**

The Freundlich model describes a multilayer adsorption over a heterogeneous surface of the adsorbent and considers that each ion attached to the active site will have an effect over the neighbouring ions at the adjacent sites with an exponential decrease in adsorption energy.

The following equation was used and the parameters were determined and represented in Table 5.

\[ q_e = K_F C_e^{1/n} \]  

(9)

where \( K_F \) is the Freundlich constant (mg/g)(L/mg)\(^{1/n}\) and \( n \) is the Freundlich exponent, which depicts the strength of adsorption (dimensionless) and extent of deviation from linearity of the adsorption. The low value of 1/n represented that the adsorption of chromium over ARPB is favourable. The regression value of 0.975 represented a least fit of the Freundlich isotherm than the Langmuir isotherm.
The Dubinin-Radushkevich (DR) isotherm is based on the Polanyi potential adsorption theory, which defines whether the process is driven by physical or chemical forces (Hutson & Yang 1997). The non-linear form of the DR model is represented by the following equation

\[ q_e = Q_m \exp\left(-\frac{K\varepsilon^2}{C_0}\right) \]  

(10)

where \( Q_m \) is the maximum adsorption capacity (mg/g), and \( K \) is the activity coefficient (mol/J). \( \varepsilon \), the Polanyi potential is equal to \( RT \ln(1 + 1/C_e) \), where \( R \) (J/mol K) is the universal gas constant and \( T \) is the absolute temperature (K). The non-linear plot of \( q_e \) versus \( C_e \) gives the value of \( Q_m \) and \( K \) (Figure 7). The apparent energy of adsorption (E) is given by

\[ E = \frac{1}{\sqrt{2k}} \]

(11)

describes whether the adsorption is of physical, chemical or ion exchange. If the value is less than 8 kJ/mol, physical adsorption prevails, if it is greater than 16 kJ/mol, then chemical adsorption occurs, values between 8 and 16 kJ/mol represent ion exchange. The Dubinin-Radushkevich constants are shown in Table 5. An E-value of 0.142 kJ/mol represents the possibility of physisorption and the involvement of weak forces holding the adsorbents over the biosorbent surfaces. A regression value of 0.946 represents the least fit to the experimental data (Vaghetto et al. 2008).

**Kinetic studies**

**Pseudo first order model**

The non-linear pseudo first order kinetic model takes the following form as

\[ q_t = q_e(1 - e^{-k_1t}) \]  

(12)

where \( q_t \) is the number of Cr ions adsorbed (mg/g) at time \( t \) (sec), \( q_e \) is the chromium adsorbed at equilibrium (mg/g) and \( k_1 \) is the equilibrium rate constant (min\(^{-1}\)). From the non-linear plot of \( q_t \) vs \( t \), the kinetic constants were determined (Simonin 2016) and shown in Table 6.

**Pseudo second order model**

The linear form of the pseudo second order model is as follows:

\[ q_t = \frac{k_2q_e^2}{1 + k_2q_e t} \]  

(13)

where \( k_2 \) is the rate constant of the pseudo second order model (g/mg/min). The kinetic parameters for the removal of hexavalent chromium using Annona reticulata Linn peel biomass are shown in Table 6.
where \( k_2 \) (g/mg/min) is the pseudo second order constant. Figure 8 shows that the plots of non linear form of the pseudo second order kinetic model at different Cr(VI) concentrations are in the range of 100 to 500 mg/L, respectively. The calculated \( q_e \) values are well correlated, and the kinetic rate constants for Cr(VI) biosorption by peel biosorbent are given in Table 6. Considering the coefficient of determination, biosorption of Cr(VI) using Annona reticulata peel biosorbent followed the pseudo second order model and most likely is controlled by the chemisorption process.

**Intraparticle diffusion model**

Rate controlling steps limiting the biosorption process can be represented using the following equation

\[
q_t = K_{id}t^{1/2} + C
\]

where \( K_{id} \) is the intra-particle diffusion rate constant (mg/g/min\(^{1/2}\)) and C is the model intercept. From the kinetic analysis, it was known that the pseudo second order kinetic model fits better than the other kinetic models such as the pseudo first order and intraparticle diffusion models analyzed over a wide range of concentrations at regular time intervals. The calculated \( q_e \) values were close to the experimental values at optimum concentration using the pseudo second order model. The pseudo second order plot between t and \( q_t \) produced linear curves with high regression values, clearly depicting that the adsorption of Cr(VI) on ARPB is likely to be controlled by chemisorption (Rangabhashiyam & Selvaraju 2015b). The plot between \( t^{1/2} \) and \( q_t \) produced a multilinear curve, which showed that the adsorption process was not only influenced by diffusion but also by other mechanisms.

**Thermodynamics of the biosorption process**

To determine the spontaneity, stability and thermal behavior of the adsorption process, the change in free energy (\( \Delta G \)), enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) were calculated from the following equations:

\[
\Delta G^o = -RT \ln K_C
\]

where \( T \) is the absolute temperature (K), \( R \) is the universal gas constant (8.314 J/mol/K) and \( K_C \) is the coefficient of distribution given by

\[
\ln K_C = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]

\[
K_C = \frac{q_e}{C_e}
\]

![Figure 8](image)

Figure 8 | Pseudo second order plot of Annona reticulata biomass for Cr(VI) removal at different concentrations.

<table>
<thead>
<tr>
<th>( C_e ) (mg/L)</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (kJ/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293 K</td>
<td>303 K</td>
<td>313 K</td>
<td>323 K</td>
</tr>
<tr>
<td>100</td>
<td>10.97</td>
<td>0.035</td>
<td>-0.052</td>
</tr>
<tr>
<td>200</td>
<td>7.880</td>
<td>0.035</td>
<td>-0.055</td>
</tr>
<tr>
<td>300</td>
<td>12.17</td>
<td>0.050</td>
<td>-0.050</td>
</tr>
<tr>
<td>400</td>
<td>9.403</td>
<td>0.040</td>
<td>-0.040</td>
</tr>
<tr>
<td>500</td>
<td>8.621</td>
<td>0.040</td>
<td>-0.040</td>
</tr>
</tbody>
</table>

The thermodynamic parameters calculated from the analysis (Bhaumik et al. 2016) are presented in Table 7, and the plot between 1/T and ln K is represented as Figure S2 in the supplementary material (available with the online version of this paper). The increase in the \( \Delta G \) values with the increase in temperature clearly describes that the spontaneity of the interactions would be lost at higher temperatures. This is due to the fact that at temperatures above optimum, rapid mobility of Cr ions occurs, resulting in increased randomness.
Also, the increase in the Δ\(G\) values with the increase in concentration shows that the spontaneity of the process would be lost if there is a increase in randomness in the sorbent-sorbate interface owing to an increase in Cr(VI) ions (Ali et al. 2016). The negative ΔH values clearly depicted that the reaction was exothermic, and negative ΔS represented a decrease in the randomness at the sorbent-sorbate interface during the adsorption of Cr(VI) on Annona reticulata peel microparticles.

**Desorption studies**

Reusability of the biosorbent was checked by repeated adsorption and desorption experiments using different Normality NaOH solutions as desorbing agents. Biosorption-desorption cycles of Cr(VI) were repeated for up to three runs for 12 hrs at 100 rpm and 298 K. Maximum desorption and equilibrium were attained at about 4 hrs. Adsorption experiments were done with 100 mg/L Cr(VI) solution at 1.0 pH, 298 K and 100 rpm. Table 8 presented the percentage desorption for each cycle with different concentrations of NaOH. 2 N NaOH was found to be suitable for maximum desorption of Cr(VI) ions rather than 0.1 N and 1 N NaOH. This might be due to the cation exchange reaction that would have taken place when the adsorbed Cr(VI) anions were introduced into NaOH solution. Saturation of the biosorbent occurs due to structural changes on the surface of the biosorbent and deposition of some of the Cr(VI) ions into the pores of the biosorents, and thus the desorption percentage decreases.

**CONCLUSION**

In the research undertaken, biosorbent prepared from Annona reticulata linn peels was analyzed for removal of hexavalent chromium from simulated aqueous solution. SEM-EDX and FTIR analysis proved that hexavalent chromium can be removed by biosorption. Response Surface Box–Behnken analysis depicted the influence of pH, initial chromium concentration and temperature in the removal of hexavalent chromium, and optimized those parameters for maximum removal. The Langmuir models fitted better than the other models analyzed. The monolayer adsorption capacity of Annona reticulata peels was considerably high, with a value of 108.34 ± 4.4 mg/g more than other fruit peels in Cr(VI) removal (Table 9). Kinetic studies showed that the adsorption was most likely influenced by chemisorption. Thermodynamic studies revealed that the process was exothermic, stable and spontaneous. Desorption and regeneration experiments depicted that the selected biosorbent can be a better option for sequestration of Cr(VI) from aqueous solutions. Batch studies produced considerable performance in Cr(VI) removal under optimized conditions, and further investigation in continuous column studies with industrial effluents has to be carried out for large scale applications.

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