Application of response surface methodology for adsorption of Cr(VI) from wastewater streams by chitosan

S Bhuvaneshwari, V Sivasubramanian*, K Sankar, M Aswathi & B Harish

Department of Chemical Engineering National Institute of Technology, Calicut, Kerala 673 601, India
E-mail: siva@nitc.ac.in

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The performance of chitosan as an adsorbent in the removal of chromium ion (Cr(VI)) from wastewater in batch and continuous modes has been investigated. The column performance of Cr(VI) adsorption onto chitosan has been studied at different bed height (3-9 cm) and flow rate (50-200 mL/min). The column has been designed based on the break through curves. Initially, adsorption tests of Cr(VI) on chitosan have been carried out in batch modes. The effects of pH, chitosan concentration, Cr(VI) concentration, contact time and shaking speed on the removal of Cr(VI) from synthetic and industrial wastewater have been studied. The highest adsorption capacity of 99.2% has been observed in the recycle column. An ideal experimental design has been carried out based on central composite design (CCD) with response surface methodology (RSM) using the design expert software 8.0.6.1 to evaluate the effect of the different parameters on Cr (VI) adsorption capacity in batch mode and continuous mode. A multiple response method is applied for optimization of process parameters.

Keywords: Adsorption capacity, Chitosan, Cr(VI), Central composite design, Response surface methodology

An increase in population initiating rapid industrialization was found to consequently increase the effluents and the domestic wastewater into the aquatic ecosystem. Heavy metals are major toxicants found in industrial wastewaters; they may adversely affect the biological treatment of wastewater\textsuperscript{1,2}. Conventional physico-chemical treatment methods for removing heavy metals from the waste streams became generally ineffective or expensive\textsuperscript{3}. Thus, there is a need for cheaper methods for effluent treatment. Biosorption is a process that utilizes biological materials as adsorbents. This method has been studied by several researchers as an alternative technique to conventional methods for heavy metal removal from wastewater\textsuperscript{4}. Various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents can subsequently bind the heavy metals. Chitosan is a biodegradable and biocompatible polymer. Chitosan displays the basic properties that impart it with unique physico-chemical characteristics. It is an excellent chelating agent for removing heavy toxic metals from sewage\textsuperscript{5,6}. The amino group is responsible for the polycationic character of chitosan\textsuperscript{7}. Metal biosorption is a rather complex process affected by several factors\textsuperscript{8}. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials\textsuperscript{9-11}.

Chromium VI is generally produced by industrial processes, and is used in such industries as pigment manufacturing, leather tanning, wood treatment and chrome plating\textsuperscript{12}. Due to its toxicity and suspected carcinogenicity, however, chromium is heavily regulated to human health and the environment\textsuperscript{13}. The batch studies for the biosorption of chromium (VI) from wastewater are being influenced by the operating conditions such as temperature, pH, biosorbent dose, initial metal concentrations, contact time and agitation speed\textsuperscript{14}. The design of a continuous packed bed column for biosorption of heavy metal depends on parameters such as adsorbent size, column bed height, flow rate of metal solution into the column, initial concentration of metal solution, temperature and pressure of the operating system\textsuperscript{15}.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response. RSM has a important application in the process design and optimization, as well as in the improvement of the existing design\textsuperscript{16}. The RSM provides functions and data types for the coding and decoding of factor levels. Appropriate coding is an important element of response-surface analysis. There are good commercial softwares
available to help in designing and analyzing response-surface experiments. The most popular among them include Design-Expert (Stat-Ease, Inc. 2009), JMP (SAS Institute, Inc. 2009), and Statgraphics (Stat Point Technologies, Inc. 2009). All these help in generating Box-Behnken and central-composite designs, fitting first- and second-order response surfaces, and visualizing them.\(^\text{17}\)

**Experimental Section**

**Reagents**

All the chemicals used were of analytical grade and the samples were prepared using double distilled water.

- **Synthetic metal solution**
  Synthetic wastewater containing Cr (VI) was prepared by dissolving 2.8287 g of potassium dichromate ($K_2Cr_2O_7$) in 1000 mL of deionized water i.e. 1000 ppm chromium solution. 1 mL of the standard solution was made in 100 mL distilled water for a 10 ppm solution. This solution was further mixed in the ratios 2:8, 4:6, 6:4, 8:2 with distilled water to form 2, 4, 6, 8 ppm solutions respectively.

- **Industrial effluent**
  Wastewater from TMS leathers, Cochin was obtained. The Cr(VI) concentration and pH of the untreated wastewater were 25.7 mg/L and 3 respectively.

- **Chitosan**
  Present experiments were carried out using pelletized form of chitosan (donated by Central Institute of Fisheries Technology, Cochin).

**Instrumentation**

The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (Thermo scientific AA 303). Centrifugation and filtration were done before atomic adsorption measurements to remove suspended particles and thus to avoid turbidity problems. FT-IR spectra were recorded on a Thermo Nicolet Model-Avater 320 FTIR spectrophotometer. FT-IR analysis has been used to examine the role of hydroxyl and amine groups of chitosan structure involved in the mechanism of chromium adsorption. The surface morphology of chitosan was examined using a Scanning Electron Microscope, (Hitachi SU 6600 Japan). The EDX spectra of adsorbent were analyzed using Energy Dispersive Spectrophotometer (Horiba EMAX, 13 ev).

**Experimental methods**

The adsorption experiments in this work were divided into three parts. The first part of the study was aimed at investigating the effect of experimental parameters such as $pH$ (2-10), chitosan concentration (10-70 mg), Cr(VI) concentration (2-10 ppm), contact time (20-150 min) and shaking speed (30-150 rpm) on Cr(VI) adsorption from synthetic Cr(VI) solutions. Borosil glass conical flasks of 250 mL capacity with 50 mL of wastewater of desired Cr(VI) concentration, chitosan concentration, $pH$, contact time and shaking speed were used. The second part of the study examined the applicability of chitosan for removal of Cr(VI) from industrial wastewater (TMS leathers, Cochin). In the tests, the $pH$ (1-12) was adjusted and a given mass of chitosan (10-80 g/L) was added to the solution by maintaining the contact time in the range of 30-150 min and shaking speed time in the range of 30-270 rpm.

For the above two studies the resultant suspension was paddle stirred at a constant rpm for a specified amount of time. Upon completion a sample of the suspension was removed from the flask and filtered through a Whatman No 1 filter paper to remove the adsorbed particles. The filtrate was analyzed for residual Cr(VI) using an atomic absorption spectrophotometer and the amount of Cr(VI) removed by the adsorbent was calculated using the Equation (1).\(^\text{18,19}\)

\[
\text{% Adsorption} = \left(\frac{C_{\text{in}} - C_0}{C_{\text{in}}}\right) \times 100
\]

where $C_{\text{in}}$ and $C_0$ are the Cr (VI) concentration in aqueous solutions before and after adsorption (mg/L), respectively.

The optimum conditions that achieve the maximum amount of chromium removal was determined for the above two studies and illustrated in Table 1.

Third part of the study examined the experimental and theoretical investigation on the potential of chitosan as a bioreductant for reducing Cr(VI) in a continuous fixed bed column made of acrylic tube of 1.1 cm inner diameter and 12 cm height. The schematic diagram of fixed-bed column for Cr(VI) adsorption is shown in Fig. 1. The column performance of Cr (VI) adsorption was studied using chitosan as adsorbent at different bed height (3-9 cm) and flow rate (50-200 mL/min). The breakthrough time, exhaustion time and adsorption capacity has been found to decrease with...
The maximum adsorption of 99.2% was observed in the recycle process. Preliminary experiments were carried out with single column without recycle. The % adsorption in a 9 cm single stage column without recycle was 94.33%. The calculations have been done as follows:

\[
\text{Metal removal (\% Adsorption)} = \left( \frac{C_i - C_b}{C_i} \right) \times 100
\]

\[
\text{Maximum adsorption capacity, } q_C \text{ in mg/g} = \frac{\int_0^t (C_i - C_t) \, dt}{V_o (C_i - C_1)} - \left( \frac{V e C_1}{m} \right)
\]  

where \( C_i \) is the initial concentration of Cr(VI) in feed (mg/mL), \( C_b \) is the break point concentration of Cr(VI) (mg/mL), \( C_i \) is the instantaneous concentration of Cr(VI) leaving the bed (mg/mL), \( dt \) is the time interval (min), \( V_o \) is the volumetric flow rate through the bed (mL/min) and \( M \) is the weight of adsorbent (g).

Application of response surface methodology

Development of mathematical models and experimental design

The mathematical-statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA). This work employed two/three test variables, following the second-order polynomial equation:

\[
y = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_1 \alpha_2 x_1 x_2 + \alpha_1 \alpha_3 x_1 x_3 + \alpha_2 \alpha_3 x_2 x_3 + \epsilon
\]

where \( y \) is the response, \( \alpha_0 \) is the constant term, \( \alpha_1 \) and \( \alpha_2 \) represent the coefficients of the linear parameters, \( \alpha_1 \alpha_2 \) represents the coefficient of the interaction parameter, \( \alpha_1^2 \) and \( \alpha_2^2 \) represent the coefficients of the quadratic parameters and \( \epsilon \) is the residual associated with the experiments.

Optimization

Optimization studies for the batch adsorption of Cr(VI) by chitosan were carried out by studying the effect of different variables including chitosan dose, initial Cr(VI) concentration, \( pH \) of solution, shaking time and agitation speed by means of a central composite design (CCD) and the response surface methodology (RSM). Similarly, the optimization
studies for the continuous adsorption of Cr(VI) by chitosan were carried out by studying the effect of bed height and flow rate on break through time and adsorption capacity. The numerical optimization found a point that maximizes the desirability function. The importance of each goal was changed in relation to the other goals.

Results and Discussions

Model fitting for batch study

The empirical relationship for adsorption (%) versus the two/three test variables (adsorbent dosage, Cr(VI) concentration and pH) in actual units obtained by the application of RSM is given as:

\[
\text{Adsorption (\%)} = +72.74+0.38x_1+2.59x_2+0.04x_1x_2
-7.83E-003x_1^2-0.012x_2^2
\]

\[\cdots (5)\]

\[
\text{Adsorption (\%)} = +25.81+0.3lx_1+4.29x_2+21.02x_3
+0.023x_1x_2+0.033x_1x_3-7.79E-003x_1^2
-0.15x_2^2-2.96x_3^2
\]

\[\cdots (6)\]

where \(Y\) (response) is the adsorption(\%), \(x_1, x_2\) and \(x_3\) are the actual values of the tests variables, adsorbent dosage \((x_1)\), Cr(VI) concentration \((x_2)\) and \(pH\) \((x_3)\). The results of the % adsorption as a function of the tests variables, adsorbent dosage, Cr(VI) concentration and \(pH\) showed that this regression is statistically significant.

The fit of the model was checked by the determination of coefficient \(R^2 = 0.8855\) for % adsorption as a function of the two tests variables, adsorbent dosage and Cr (VI) concentration. Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 15.55 indicates an adequate signal. The value of \(R^2 = 0.944\) for % adsorption as a function of the three tests variables, adsorbent dosage, Cr (VI) concentration and \(pH\) indicates that 5.60% of the total variable is not explained by the model. The Adeq Precision ratio of 34.43 indicates an adequate signal. Polynomial regression analysis has been conducted for second-order response surface model and the results are given in Table 2 and Table 3. Response surface and contour plots for % adsorption versus adsorbent dosage, Cr (VI) concentration and \(pH\) are shown in Fig. 3. It is observed from Table 3 that \(pH\) is most significant term.

Model fitting for continuous column study

The empirical relationship for break through time and adsorption capacity \((y)\) versus the two test variables (Bed height and flow rate) in coded units obtained by the application of RSM is given as:

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Fig. 2 — Breakthrough curves of Cr (VI) adsorption onto chitosan at a varying bed height (a) and feed flow rate (b).
Table 2 — ANOVA test for % adsorption as a function of two test variables using the CCD

<table>
<thead>
<tr>
<th>Model term</th>
<th>Coefficient estimate</th>
<th>Sum of square</th>
<th>Standard Error</th>
<th>DF</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$ Intercept</td>
<td>93.77</td>
<td>675.57</td>
<td>0.78</td>
<td>9</td>
<td>21.48</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>$\alpha_1$ Dosage</td>
<td>1.58</td>
<td>4.17</td>
<td>1.44</td>
<td>1</td>
<td>1.19</td>
<td>0.0285</td>
</tr>
<tr>
<td>$\alpha_2$ Cr(VI) concentration</td>
<td>0.16</td>
<td>0.035</td>
<td>1.58</td>
<td>1</td>
<td>9.88E-003</td>
<td>0.0925</td>
</tr>
<tr>
<td>$\alpha_1 \alpha_2$</td>
<td>-0.051</td>
<td>0.026</td>
<td>0.60</td>
<td>1</td>
<td>7.356E-003</td>
<td>0.9323</td>
</tr>
<tr>
<td>$\alpha_1^2$</td>
<td>-2.31</td>
<td>19.79</td>
<td>0.97</td>
<td>1</td>
<td>5.66</td>
<td>0.0253</td>
</tr>
<tr>
<td>$\alpha_2^2$</td>
<td>-9.18</td>
<td>489.11</td>
<td>0.78</td>
<td>1</td>
<td>139.97</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>

Std. Dev : 1.87  
Mean : 87.29  
C.V. % : 2.14  
R-Squared : 0.8855  
Adeq Precision : 15.551

Fig. 3 — Response surface and contour plots for batch adsorption as a function of test variables.
Break through time \( (y) = + 46.88 + 21.88 x_1 - 8.33 x_2 - 0.62 x_1 x_2 + 4.17 x_1^2 + 0.83 x_2^2 \)
\[ \text{...(7)} \]

Adsorption capacity \( (y) = + 55.7 + 5.09 x_1 - 6.70 x_2 + 0.17 x_1 x_2 - 0.59 x_1^2 + 0.26 x_2^2 \)
\[ \text{...(8)} \]

where \( y \) (response) is the break through time and adsorption capacity, \( x_1 \) and \( x_2 \) are the coded values of the tests variables, bed height \( (x_1) \) and flow rate \( (x_2) \). Polynomial regression analysis has been conducted for second-order response surface model and the results are given in Tables 4 and 5.

The results of the breakthrough time \( (t_b) \) and Cr (VI) adsorption capacity \( (q_c) \) as a function of the test variables, bed height \( (x_1) \) and flow rate \( (x_2) \) showed that this regression is statistically significant. In the case of breakthrough time, the value of \( R^2 = 0.9885 \) indicates that 1.15% of the total variable is not explained by the model. The Adeq Precision ratio of 22.158 indicates an adequate signal. The value of \( R^2 = 0.9684 \) for Cr(VI) adsorption capacity indicates that 3.16% of the total variable is not explained by the model. The Adeq Precision ratio of 11.984 indicates an adequate signal. The Response surface and contour plots for Cr(VI) adsorption capacity and breakthrough time are shown in Fig. 4. It is observed from Tables 4 and 5 that bed height is most significant term in the case of breakthrough time and flow rate is most significant term in the case of adsorption capacity.

**Optimization using desirability functions**

A multiple response method was applied for optimization of adsorbent dosage, Cr(VI) concentration, contact time, agitation speed and % adsorption.

**Table 4 — ANOVA test for break through time using the CCD**

<table>
<thead>
<tr>
<th>Model term</th>
<th>Coefficient estimate</th>
<th>Sum of square</th>
<th>Standard Error</th>
<th>DF</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_0 ) Intercept</td>
<td>46.88</td>
<td>4009.03</td>
<td>2.52</td>
<td>5</td>
<td>51.70</td>
<td>0.0041</td>
</tr>
<tr>
<td>( \alpha_1 ) Bed Height</td>
<td>21.88</td>
<td>1984.95</td>
<td>1.93</td>
<td>1</td>
<td>127.99</td>
<td>0.0015</td>
</tr>
<tr>
<td>( \alpha_2 ) Flow rate</td>
<td>-8.33</td>
<td>416.67</td>
<td>1.61</td>
<td>1</td>
<td>2.57</td>
<td>0.0139</td>
</tr>
<tr>
<td>( \alpha_1^2 )</td>
<td>4.17</td>
<td>34.72</td>
<td>6.09</td>
<td>1</td>
<td>0.32</td>
<td>0.2315</td>
</tr>
<tr>
<td>( \alpha_2^2 )</td>
<td>0.83</td>
<td>85.71</td>
<td>1.03</td>
<td>1</td>
<td>0.37</td>
<td>0.1002</td>
</tr>
<tr>
<td>( \alpha_1 \alpha_2 )</td>
<td>-0.62</td>
<td>14.58</td>
<td>1.08</td>
<td>1</td>
<td>0.33</td>
<td>0.4037</td>
</tr>
</tbody>
</table>

Std. Dev : 3.94  
Mean : 42.78  
C.V. % : 9.21  
R-Squared : 0.9885  
Adeq Precision : 22.158

**Table 5 — ANOVA test for Cr adsorption capacity using the CCD**

<table>
<thead>
<tr>
<th>Model term</th>
<th>Coefficient estimate</th>
<th>Sum of square</th>
<th>Standard Error</th>
<th>DF</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_0 ) Intercept</td>
<td>55.07</td>
<td>1940.25</td>
<td>2.94</td>
<td>5</td>
<td>18.41</td>
<td>0.0185</td>
</tr>
<tr>
<td>( \alpha_1 ) Bed Height</td>
<td>5.09</td>
<td>107.43</td>
<td>2.25</td>
<td>1</td>
<td>5.10</td>
<td>0.1092</td>
</tr>
<tr>
<td>( \alpha_2 ) Flow rate</td>
<td>-6.70</td>
<td>269.07</td>
<td>1.87</td>
<td>1</td>
<td>12.77</td>
<td>0.0375</td>
</tr>
<tr>
<td>( \alpha_1^2 )</td>
<td>0.59</td>
<td>0.59</td>
<td>3.25</td>
<td>1</td>
<td>0.033</td>
<td>0.8681</td>
</tr>
<tr>
<td>( \alpha_2^2 )</td>
<td>0.26</td>
<td>0.26</td>
<td>0.41</td>
<td>1</td>
<td>0.38</td>
<td>0.5799</td>
</tr>
<tr>
<td>( \alpha_1 \alpha_2 )</td>
<td>0.17</td>
<td>0.17</td>
<td>0.75</td>
<td>1</td>
<td>0.054</td>
<td>0.8311</td>
</tr>
</tbody>
</table>

Std. Dev. : 4.59  
Mean : 46.60  
C.V. % : 9.85  
R-Squared : 0.9684  
Adeq Precision : 11.984
Ramp desirability was generated using Design Expert 8.0.6.1. Numerical optimization found a point that maximizes the desirability function. A minimum level of biosorbent (chitosan) dosage (25.27 mg), agitation speed (69.88 rpm), a maximum level of initial Cr(VI) concentration (8.18 mg/L) and shaking time (103.82 min) resulted in 99.3 % of Cr(VI) removal at the initial pH 4 for synthetic Cr(VI) solutions. A minimum level of biosorbent (chitosan) dosage (52 mg), shaking time (91 min) and a maximum level of agitation speed (141.89 pm) resulted in 99.5% of Cr(VI) removal at the initial pH with in a range of 10 for industrial wastewater (Table 1).
Conclusion

From the experiments discussed above, the following conclusions can be drawn.

- The batch study results reveal that the rate of adsorption is controlled by adsorbent dosage, and pH compared to other factors like Cr(VI) concentration, shaking time and shaking speed.
- Chitosan reduces the Cr(VI) concentration in industrial wastewater to 0.055 mg/L, which is on par with the designated standards of WHO, US EPA and CPCB, India for effluent discharge.
- The effect of the bed depth and flow rate on Cr(VI) adsorption capacity and breakthrough time has been evaluated by means of CCD using RSM. The fit of the model is checked by the determination of coefficient ($R^2$). The value of the multiple correlation coefficient for breakthrough time and adsorption capacity response ($R^2 = 0.9885$ and $0.9684$) indicate that 1.15% and 3.16% of the variation is not explained by the model. Similarly, the effect of the adsorbent dosage, pH and Cr(VI) concentration on % adsorption in batch studies has been evaluated by means of CCD using RSM. The fit of the model is checked by $R^2$.
- Chitosan is a cheaply available cationic polymer and a characteristic ideal for the binding of metal anions such as chromate.

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References


