REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION USING POLYANILINE: MODELING AND OPTIMIZATION

Saeb Ahmadi1, Seyed Omid Rastegar2, Pouran Makhdoumi3, Hooshyar Hossini4*, Nezam Mirzaei5,6

1Chemical engineering department, Tarbiat Modares University, Tehran, Iran.
2Chemical Engineering Group, Department of Engineering, Kurdistan University, Sanandaj, Iran.
3Student Research Committee, Department of Pharmacology and Toxicology, Faculty of Pharmacy, Mashhad University of Medical Sciences, Mashhad, Iran.
4Department of Environmental Health Engineering, Faculty of Health, Kermanshah University of Medical Sciences, Kermanshah, Iran.
5Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran.
6Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran.

Email: h.hosseini@kums.ac.ir

Received on 06-08-2016

Abstract

The aim of this work was the application of polyaniline as adsorbent for removal of hexavalent chromium from aqueous solution. Response surface method (RSM) as a mathematical technique was used for modeling and optmized the considerable parameters. The operating parameters such as initial chromium concentration, adsorption time and pH were evaluated. Maximum chromium removal was 11.51 mg/g at the optimum condition of initial pH 6.23, initial Cr\textsuperscript{6+} concentration 92.52 mg/L, and contact time about 19 min. According to statistical analysis, \(R^2\) (0.75), Adjusted \(R^2\) (0.52), the mean adsorption uptake (8.25 mg/g) and standard deviation (2.09) were calculated.

Key words:Hexavalent chromium, Adsorption, Polyaniline, Optimization, Modeling.

1. Introduction

Due to highly toxic, carcinogenic and mutagenic effect of chromium, its discharge to surface water has been limited to below 0.05 mg/L by the united state environmental protection agency (US EPA) and the European Union, while total, tri/hexavalent and its other chromium forms, is regulated to below 2 mg/L (1). Other adverse health effect of chromium is including liver, kidney, lung disorders and gastrointestinal cancer. Based on literature review, the industrial sources of chromium are encompassing pigments, tanning, electroplating, fertilizers, mining and metallurgical process(2). Among the treatment techniques such as chemical precipitation, membrane filtration, liquid extractions, ion exchange, because of the cost-effective in operation and investment and easy to use, absorption process is considered more seriously. Today conducting polymer finds widely applications in various fields such as
microelectronics, composite materials, optics and biosensors and as adsorbent (3, 4). Polyaniline as a representative of the family of conducting polymers in the conditions of aniline polymerization is produced. Due to the high stability to the environmental exposition, the facility in preparation procedures, desired structures and properties of polyaniline have provided the usage in various fields of science and engineering (5,6). There is many parameters affective in the optimization of the adsorption process such as initial pH, initial concentration, contact time, adsorbent dosage, mixing velocity and etc. Using traditional method such as one factor at a time need many time, cost and investment.

Response surface methodology (RSM) is a method to optimized parameters in addition thier interaction. According to the literature and available database, there is no information regarding the optimization of effective parameters based on RSM for the adsorption of chromium from aqueous solution using polyaniline. Therefore, the aim of this work is described as following: (1) determination of adsorption capacity potential of chromium by polyaniline, (2) modeling the adsorption process by response surface methodology and (3) Optimization of the effective parameters to find the maximum chromium uptake by polyaniline.

2. Materials and Methods

2.1. Materials

All chemicals and regents encompassing aniline, H$_2$SO$_4$, 1, 5 diphenylcarbazide, NaOH, HCl, acetone were prepared from analytical grade. Hexavalent chromium stock solution was prepared by adding 0.1414 g of potassium dichromate in one liter deionized water. Desirable concentrations of Cr (VI) were prepared by stock dilution.

2.2. Experimental methods

The pH of solution monitored by adding 1 M HCl and 1 M NaOH solution as per required pH value. Aniline was purified by vacuum distillation before than polymerization. To understand the morphology of adsorbent, the samples were gold sputter coated and the scanning electron microscopic (SEM) micrograph was taken (SEM, XL30). The residual Chromium was determined via a colorimetric method using 1, 5 diphenylcarbazide [CO(NH$_2$NH)$_2$H$_2$] regent by utilizing of a UV/Visible spectrophotometer (Rayleigh UV 9200, China) set at 540 nm (2). For increasing the contact between adsorbent and chromium, a rotary shaker at 100 rpm were considered. The chromium uptake (mg/g) was calculated using the following relationship, Eq. (1):

\[
\text{Uptake (mg/g)} = \frac{(C_0 - C_f)}{m \times V}
\]

Where $C_0$ and $C_f$ (mg/L) are the initial and final chromium concentration. And m is the adsorbent dosage (g) and V is the volume of backer (L).
2.3. Statistical method

The Response Surface Methodology (RSM) is a collection of the mathematical-statistical algorithm for optimization and model development. At first step, we were evaluated suitable approximately function between responses and set of independent variables. This approximate function must be polynomial of independent variables. Also the behavior of the system is explained by the following quadratic equation (6-8):

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \epsilon
\]

where \(Y\) is the response, \(\beta_0, \beta_i, \beta_{ii}, \beta_{ij}\): are the regression coefficients, \(\epsilon\): is the error value and \(X_j\): coded variables of the system. To estimate the polynomial regression the least squares method and central composite design (CCD) was used.

As can be seen from Table 1 the CCD for the natural and coded parameters (as; \(A\): time, \(B\): pH and \(C\): initial concentration).

Table 1. Experimental variables at different levels used for polyaniline adsorption experiment.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Code</th>
<th>Low axial (-(\alpha=1.63))</th>
<th>Low factorial (-1)</th>
<th>Central (0)</th>
<th>High factorial (+1)</th>
<th>High axial (+(\alpha=+1.63))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>A</td>
<td>1</td>
<td>7</td>
<td>15.5</td>
<td>24.5</td>
<td>30</td>
</tr>
<tr>
<td>pH</td>
<td>B</td>
<td>5</td>
<td>6</td>
<td>7.6</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Chromium (mg/L)</td>
<td>C</td>
<td>50</td>
<td>80</td>
<td>125</td>
<td>170</td>
<td>200</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Scanning electron microscopy

Scanning electron microscopy (SEM) is a versatile, non-destructive technique that reveals detailed information about the morphology and composition of natural and manufactured materials (9). As seen from the Fig. 1, the high levels of porosity and higher surface area is provided, and it confirmed the ordered arrangement of pores on the surface of the polyaniline.

Fig. 1. SEM image of the polyaniline at 10000X magnification.
3.2. Analysis of variables (ANOVA)

A total 20 runs for three variables based on the RSM- CCD was designed that showed in the Table 2. The ANOVA for the predicted quadratic model are presented in Table 3. With regard, the model $F$-value of 3.37 and a low probability value ($p$-value< 0.036) offer that the model is significant with regard to 95% confidence interval. A significant lack of fit (<0.0001) recommends that there may be some systematic variation unaccounted for in the hypothesized model. According to statistical analysis, $R^2$ (0.75), Adjusted $R^2$ (0.52), the Mean uptake (8.25 mg/g) and standard deviation (2.09) were calculated.

### Table 2. Experimental plan based on CCD and the results of metals recoveries.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>pH</th>
<th>Initial conc. (mg/L)</th>
<th>Uptake (mg/g) Actual</th>
<th>Uptake (mg/g) Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.68</td>
<td>0</td>
<td>0</td>
<td>4.1</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>6.3</td>
<td>8.4</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>3.8</td>
<td>4.1</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>3.9</td>
<td>3.6</td>
</tr>
<tr>
<td>5</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>6.1</td>
<td>7.4</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.2</td>
<td>10.3</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.1</td>
<td>10.3</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>1.68</td>
<td>0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.4</td>
<td>10.3</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>-1.68</td>
<td>12.5</td>
<td>10.1</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.2</td>
<td>10.3</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>0</td>
<td>1.68</td>
<td>9.9</td>
<td>9.1</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>-1.68</td>
<td>0</td>
<td>14</td>
<td>10.4</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>6.2</td>
<td>7.1</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>8.2</td>
<td>10.8</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>8.1</td>
<td>10.1</td>
</tr>
<tr>
<td>20</td>
<td>1.68</td>
<td>0</td>
<td>0</td>
<td>10.2</td>
<td>8.0</td>
</tr>
</tbody>
</table>

### Table 3. Analysis of variance (ANOVA) for response surface quadratic model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F-Value</th>
<th>p-value</th>
<th>significant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>131.79</td>
<td>9</td>
<td>14.64</td>
<td>3.37</td>
<td>0.03</td>
<td>significant</td>
</tr>
</tbody>
</table>
Generally, the adequacy of a model is evaluated by diagnostic plots, such as a normal probability plot of the studentised residuals and a plot of predicted versus actual values. As observed from Fig. 2a, the normal probability plots of the studentised residuals for chromium adsorption is presented. Fig. 2b represents the predicted versus the actual efficiency data.

![Normal Plot of Residuals](image1)

![Predicted vs. Actual Efficiency](image2)

**Fig. 2.** Normal probability plots of the studentised residuals (a) and actual vs. predicted values plots (b) for chromium adsorption.
The final quadratic model regression in terms of coded factors and actual is represented as follows.

Final equation in terms of coded factors:

\[
\text{Uptake (mg/g)} = +10.34 +1.42 \times A -1.89 \times B -0.30 \times C +0.16 \times A \times B +0.063 \times A \times C +0.11 \times B \times C -1.69 \times A^2 -1.12 \times B^2 -0.25 \times C^2
\]

Final equation in terms of actual factors:

\[
\text{Uptake (mg/g)} = -14.45 +0.75 \times \text{Time} +5.93 \times \text{pH} +0.01 \times \text{Initial Concentration} +0.013 \times \text{Time} \times \text{pH} +1.63E-004 \\
\times \text{Time} \times \text{Initial Concentration} +1.69E-003 \times \text{pH} \times \text{Initial Concentration} -0.023 \times \text{Time}^2 -0.51 \times \text{pH}^2 -1.28E-004 \times \text{Initial Concentration}^2
\]

### 3.3. Interaction between parameters

Fig.3 showed the three-dimensional (3D) response surfaces of chromium uptake (mg/g) of the relationship among different parameters. Regard to Fig. 3(a), there is a combined effect of initial chromium concentration with adsorption time at the constant pH of 7.5. The effect of contact time is evaluated by its influence on the interactions between pollutant and adsorbent (2).

Figure shows that increasing in time and decreasing in chromium concentration have positive effect on uptake. The maximum chromium uptake (10.7 mg/g) was observed for chromium concentration of 102 mg/L and the time about 19 min.

At lower chromium concentrations, the adsorption rate (mg/g) is increased. It can be concluded from ion competition and decrease of electronic repulsion(10). The relationship between contact time and amount of pH for chromium uptake is illustrated in Fig. 3 (b).

Accordingly, a maximum uptake rate of chromium around 11.37 mg/g was observed in amount of pH 6.37 and contact time 18.9 min at the constant initial chromium concentration of 125 mg/L. However, the amount of chromium removal would be increased with time increasing from 1 to 19 min and decreasing the pH from 10 to 5. Heavy metal adsorption researches have been showed that pH is an important parameter affecting the sorption process (11). The pH dependence of metal adsorption can largely be related to type and ionic state of these functional groups and also on the metal chemistry in solution (12).

As seen in Fig. 3 (c), the relationship between initial chromium concentration and pH variations is represented. At the constant time 15.5 min, the effect of pH is more influenced on the chromium adsorption rather than concentration changes.
Fig. 3. 3D-plots of the interactive effect for chromium adsorption (a) Effect of time and initial chromium concentration at the constant pH 7.5, (b) effect of pH and time at the constant initial chromium concentration 125 mg/L, and (c) effect of pH and initial chromium concentration at the constant time 15.5 min.

3.4. Determination of optimum conditions

The goal of optimization is to find a proper set of experimental conditions. The optimal conditions proposed by the model were time 18.5 min, pH 6.23, and chromium concentration 92.5 mg/L, where maximum uptake of 11.5 mg/g was achieved. This optimal point is shown in Fig. 4.

Fig. 4. Desirability plots of optimal point.

Accordingly, the results of the experiment conducted at the optimal conditions showing the verification experiment with a 95% confidence and prediction intervality (Table 4). To evaluate the validity of the optimal point given by the model, a test was carried out at actual condition. Under optimal condition, experimental test was conducted and the chromium uptake was determined. The chromium uptake about 10.5 was obtained that this amount was set between 95% CI and PI values.
Table 4. Verification of optimum condition.

<table>
<thead>
<tr>
<th>Response</th>
<th>Prediction (low)</th>
<th>95% CI (low)</th>
<th>Prediction (high)</th>
<th>95% CI (high)</th>
<th>Prediction (low)</th>
<th>95% PI (low)</th>
<th>Prediction (high)</th>
<th>95% PI (high)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uptake (mg/g)</td>
<td>11.5</td>
<td>9.22</td>
<td>13.81</td>
<td>6.33</td>
<td>16.69</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion

Adsorption of hexavalent chromium from aqueous solution was studied using polyaniline as adsorbate material and RSM for optimize the main considered parameters. The optimum condition amounts were time 18.5 min, pH 6.23, and chromium concentration 92.5 mg/L, where maximum uptake of 11.5 mg/g was achieved. Based on results of this work, polyaniline can be successfully applied for adsorption the hexavalent chromium from aqueous solutions.

Acknowledgment

The authors acknowledge all non-financial supports provided by Kermanshah University of Medical Sciences. The authors declare that there is no conflict of interest.

References


Corresponding Author:
Hooshyar Hossini

Email: hoo.hosseini@gmail.com