Chapter 5

Adsorption study of Cr(VI) on Af-NPC
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5.1 Introduction
Chromium commonly exists in environment in two stable oxidation states, trivalent and hexavalent chromium (Cr(III) and Cr(VI)). Cr(VI) is more toxic and mobile and prevails in oxidizing environments. In an aqueous medium predominant anionic forms of Cr(VI) are HCrO$_4^-$ at p$\text{H}<$ 6.5 and CrO$_4^{2-}$ at p$\text{H} >$ 6.5 [1]. As discussed in chapter 1 the permissible limit for Cr(VI) in industrial wastewaters is 0.1 mg/l and 0.05 mg/l for drinking water. Concentration of Cr(VI) above 0.05 mg/l limit in drinking water can be hazardous. Hence Cr(VI) must be removed from water. This chapter presents and discusses the results obtained on the removal of Cr(VI) from aqueous medium by Af-NPC synthesized from grass as an adsorbent. The adsorption capabilities of both acid functionalized and unfunctionalized NPC are compared. The influence of the important parameters such as solution pH, contact time, initial concentration and interfering ions are discussed in detail. Adsorption isotherm and kinetic models are used to describe the adsorption process. The mechanism of Cr(VI) adsorption is also discussed. The ability of Cr(VI) to desorb from Af-NPC is also examined.

5.2 Adsorption experiments
All the chemicals used in the present study were of analytical grades. Cr(VI) stock solutions of 1000 mg/L was prepared by mixing required amounts of potassium dichromate (K$_2$Cr$_2$O$_7$) in deionized water. Solutions of required arsenic concentrations were freshly prepared by diluting the stock solutions.

NPC and Af-NPC were examined separately for removal of Cr(VI) with respect to pH between 2-10 in batch mode experiments using Erlenmeyer flask. For this 10 ml of 10 mg/L solution of Cr (VI) was mixed with 0.5 g/L of NPC and Af-NPC separately and the flasks were rotated on a rotary shaker for about 1h at 150 rpm. The pH adjustment of all the reaction mixtures were done by adding appropriate amounts of aqueous solution of 0.1N HCl and 0.1N NaOH. After 1 h samples were filtered through 0.45µm syringe filters. The initial and residual concentrations of metal ions in aqueous medium
were measured by inductively coupled plasma-atomic emission spectrometer (ICP-AES, ARCOS from M/s. Spectro, Germany). As Af-NPC indicated better removal efficiency for Cr(VI) from water when compared with pristine NPC further detailed study with respect to various factors was carried out using Af-NPC as an adsorbent.

Adsorption kinetic study was done in batch mode by stirring 10 mg of Af-NPC with 20 ml of 1, 5 and 10 mg/L metal ion solutions separately at 150 rpm for predetermined time intervals (5, 10, 15, 20, 30, 60 and 120 min) at room temperature and pH 2.5. In order to evaluate the effect of initial metal ion concentration, solution of 20 ml of Cr(VI) with different initial concentrations of 1, 2, 3, 5, 10, 15, 20 and 25 mg/L were mixed with 10 mg of Af-NPC separately and rotated at 150 rpm for an adsorption period of 1 h at pH of 2.5 and room temperature. Removal efficiency of Af-NPC was further investigated in presence of competing ions like chloride and sulphate with concentration ranging between 0.02 - 0.1M at initial concentration of 15 mg/L of Cr(VI) while keeping other parameters constant. In all adsorption experiments initial and final concentrations of Cr(VI) were determined by ICP-AES.

In order to examine recycling capacity of Af-NPC, adsorption-desorption cycles were performed using NaOH for three consecutive cycles and 5 mg/L of initial concentration of Cr(VI). To study the effect of NaOH concentration the desorption process was carried out by mixing 35 mg of used Af-NPC with 10 ml of 0.05 M, 0.1 M and 0.2 M NaOH solution separately. The solutions were sonicated and filtered through 0.2 µm membrane filters. The adsorbents were reconstituted in order to use in succeeding cycles by thoroughly washing with double distilled water and drying. The study was done for three consecutive cycles. Concentrations of Cr(VI) in filtrates were determined by ICP-AES.

5.3 Data analysis

All the adsorption experiments were carried out in three sets and the average values were reported. The percentage removal efficiency (% R) and metal adsorption capacity q_e (mg/g) were calculated by the following equations.
\[ \%R = \frac{C_0 - C_e}{C_0} \times 100 \] \hspace{1cm} (5.1)

\[ q_e = \frac{(C_0 - C_e)V}{M} \] \hspace{1cm} (5.2)

Where \( C_0 \) and \( C_e \) are the initial and final equilibrium concentrations of metal ions (mg/L) in aqueous medium, \( V \) is the total volume of solution (L) and \( M \) is the adsorbent mass (g).

### 1.4 Results and discussion

#### 5.4.1 Adsorption of Cr(VI) on NPC and Af-NPC at various pH

The percentage removal efficiency of Cr(VI) by Af-NPC was higher than only NPC (Fig. 5.1). Maximum percentage removal efficiency of Af-NPC was 87 % and that of NPC was 33% for Cr(VI) with an initial metal ion concentration of 10 mg/L at pH 2. As per EDS analysis the percentage oxygen content of NPC was 7.32 % and that of Af-NPC was 19.85 % (Table 4.4). High oxygen content indicates formation of oxygen containing functional groups on the surface of Af-NPC after treatment with aqua regia. These oxygen containing functional groups on the surface of Af-NPC acts as good active sites for adsorption of Cr(VI) thereby improving the removal efficiency of Af-NPC. Treatment of NPC with acid has improved the removal efficiency of Af-NPC due to introduction of oxygen containing functional groups on the surface, as good active sites for adsorption of Cr(VI). Removal of hexavalent Cr(VI) reduces with increase in pH and the maximum removal was observed below pH 4. At low pH the surface of Af-NPC was positive due to presence of \( H^+ \) ions on the surface and Cr(VI) exist as an oxyanion \( (HCrO_4^-) \). Hence adsorption of Cr(VI) was taking place by electrostatic forces of attraction in acidic pH. In the pH range above 6.5 Cr(VI) prevails as \( CrO_4^{2-} \) but at the same time more \( OH^- \) ions were present in the solution and the surface of Af-NPC becomes negative. The affinity of \( OH^- \) with carbon was better than \( CrO_4^{2-} \) hence
adsorption of Cr(VI) reduces due to competition and repulsion with OH- ions for adsorption sites in alkaline medium.

**Figure 5.1** % Removal of Cr(VI) by NPC and Af-NPC at different pH 2-10

(C₀ = 10 mg/L)

### 5.4.2 Sorption kinetic study

Sorption kinetic study of Cr(VI) on the surface of Af-NPC was analyzed by Lagergren pseudo first-order model and Ho’s pseudo-second-order reaction rate models [2]. Mathematical equations of these models are given in equations below (5.3) and (5.5) respectively.

Lagergren pseudo-first-order equation:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

The integrated linear form of equation 5.3 can be given as below
The integrated and simplified form of equation no. 5.5 can be expressed as follows

\[ t/q = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

(5.6)

Where \( q_t \) is the adsorption capacity of an adsorbent at any time \( t \). \( k_1 \) and \( k_2 \) are the first order rate constant (\( \text{min}^{-1} \)) and the second-order rate constant (\( \text{g/mg min} \)) respectively and \( t \) is the time (min). The initial adsorption rate (\( h \)) at \( t = 0 \) min was also calculated from the \( t/q_t \) vs \( t \) plot, using the following equation.

\[ h = k_2 q_e^2 \]  

(5.7)
Figure 5.2 (a) Time profile of Cr(VI) adsorption on Af-NPC for different metal ion concentration. (b) Pseudo first order kinetics model and (c) Pseudo-second-order kinetics model for adsorption of Cr(VI) on Af-NPC ($C_0 = 1, 5$ and $10$ mg/L)
Table 5.1 Pseudo-first and second order rate constants for sorption of Cr(VI) on the surface of Af-NPC at room temperature

<table>
<thead>
<tr>
<th>Co  (mg/L)</th>
<th>qe (mg/g)</th>
<th>k1 (min⁻¹)</th>
<th>R²</th>
<th>qe (mg/g)</th>
<th>k2 (g/mg min)</th>
<th>h (mg/g min)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.445</td>
<td>0.22x10⁻¹</td>
<td>0.506</td>
<td>1.977</td>
<td>1.256</td>
<td>4.911</td>
<td>0.999</td>
</tr>
<tr>
<td>5</td>
<td>0.057</td>
<td>6.31x10⁻²</td>
<td>0.438</td>
<td>9.65</td>
<td>0.237</td>
<td>22.07</td>
<td>0.999</td>
</tr>
<tr>
<td>10</td>
<td>0.302</td>
<td>5.36x10⁻²</td>
<td>0.346</td>
<td>19.08</td>
<td>0.155</td>
<td>56.497</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Time profile of Cr(VI) adsorption on Af-NPC, first order rate plot and second order rate plot are given in Fig 5.2. Pseudo first and second order rate parameters calculated from kinetic plots are presented in table 5.1. From the slope and intercept of first order kinetic plot (log (q_e-q_t) vs t), first order rate constant k_1 and adsorption capacity q_e were calculated respectively. Second order rate constants k_2 and q_e were calculated from intercept and slope of the plot of t/q_t vs t respectively. The adsorption of Cr(VI) on Af-NPC was described well by second order kinetics as the correlation coefficients are higher than first order kinetics. Pseudo second order kinetics implies that the adsorption of Cr(VI) was taking place through chemisorption. The process of adsorption reached equilibrium within 10 min. In the initial 5 min 75 % of Cr(VI) was adsorbed by Af-NPC. High surface area of Af-NPC provides more number of active sites for adsorption and mesoporous nature increases the rate of diffusion of metal ions inside the pores thereby increasing the overall rate of adsorption.

5.4.3 Effect of initial Cr(VI) concentration and adsorption isotherms study
Adsortion isotherms provide significant information about the maximum adsorption capacity and nature of interaction between adsorbed ions and sorbents. It also helps in designing suitable system for removal of toxic elements from water. In the present study Langmuir-Freundlich and Dubinin-Radushkevich models were applied to study the process of adsorption.
5.4.3.1 Langmuir and Freundlich isotherm

Langmuir isotherms imply that the adsorbent surface is homogeneous with equal adsorption affinity sites, while Freundlich isotherm model assumes the presence of heterogeneous adsorption sites. The linear form of Langmuir isotherms is given by following equation no. 5.8 [3].

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

(5.8)

Where $K_L$ and $q_m$ are the Langmuir adsorption constant (L/mg) and maximum monolayer adsorption capacity (mg/g) respectively. $K_L$ represents affinity between solute and adsorbent. The other parameters are same as mentioned before in equation no. 5.1. Another constant called as separation factor $R_L$ was calculated by following equation where $C_{omax}$ is maximum initial concentration.

$$R_L = \frac{1}{1+K_L C_{omax}}$$

(5.9)

The linear form of the Freundlich isotherm model is described by equation no. 5.10 [4]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(5.10)

Where $K_F$ is Freundlich constant which is measure of adsorption capacity in mg/g and $n$ is adsorption intensity respectively. The bond energy increases proportionally with surface density as $n$ is more than one. Fig. 5.3 shows Langmuir-Freundlich isotherm plots and Table 5.2 gives different parameters calculated from the slope and intercepts of two isotherms plots.
Figure 5.3 (a) Adsorption isotherm plot (b) Langmuir and (c) Freundlich isotherm plots of Cr(VI) on the surface of Af-NPC at room temperature ($C_0 = 1$-$25$ mg/L)
Table 5.2  Langmuir and Freundlich isotherm parameters for sorption of Cr (VI) on the surface of Af-NPC at room temperature

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th></th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$ (mg/g)</td>
<td>35.335</td>
<td>$K_L$ (L/mg)</td>
<td>2.194</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.996</td>
<td>$R_L$</td>
<td>0.00113</td>
</tr>
<tr>
<td>$K_F$ (mg/g)</td>
<td>1.237</td>
<td>$n$</td>
<td>2.21</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.966</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

High regression value of about 0.996 proves that Langmuir adsorption isotherm is fitting better compared to Freundlich model for the process of adsorption of Cr(VI). Hence as per Langmuir model Cr(VI) was adsorbed on the surface of Af-NPC in the form of a monolayer without interaction between adsorbed molecules. The maximum adsorption capacity calculated by Langmuir model was 35.335 mg/g. Freundlich constant $n$ was more than 1 that is 2.21 which proves that the process of adsorption of Cr(VI) on the surface of Af-NPC is a favourable process. The value of separation factor $R_L$ 0.00113 ($0 < R_L < 1$) confirms that the adsorption is favourable and Af-NPC is a good adsorbent. At lower initial concentration (< 1mg/L) no residual Cr(VI) was detected and below 3 mg/L, residual concentration remains below permissible limit after treatment. The Af-NPC could be an efficient adsorbent for removal of hexavalent chromium due to good affinity, low cost and high adsorption capacity.

5.4.3.2 Dubinin-Radushkevich model (D-R)

D-R model was helpful in understanding nature of interaction between adsorbent and adsorbate molecules. The D-R model is expressed by following equation [5].

$$\ln q_e = \ln q_m - \beta \varepsilon^2$$  \hspace{1cm} (5.11)

Where $\beta$ (mol$^2$/J$^2$) is a constant related to mean adsorption energy and $\varepsilon$ is the Polanyi potential which is calculated by using the following expression.
\[ \varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \]  

(5.12)

Where \( T \) is the absolute temperature in Kelvin and \( R \) is the universal gas constant (8.314 J/mol K). \( C_e \) (mg/L) is the concentration of adsorbate ions at equilibrium in aqueous medium. D-R model was studied by plotting a graph of \( \ln q_e \) versus \( \varepsilon^2 \). The slope of this plot provides value of \( \beta \) (mol\(^2\)/J\(^2\)) and the intercept gives the sorption capacity \( q_m \) (mg/g). The sorption energy or mean free energy \( E \) was calculated using following equation.

\[ E = \frac{1}{(2\beta)^{\frac{1}{2}}} \]  

(5.13)

The value of mean free energy is significant in comprehending nature of process of adsorption. Value of \( E \) less than 8 kJ/mol confirm that the adsorption is physical and the value between 8-16 kJ/mol proves that the adsorption is taking place through chemisorptions [5]. Figure 5.4 gives D-R plot for adsorption of Cr(VI) on the surface of Af-NPC. Mean free energy \( E \) calculated from the plot was 5 kJ/mol. Hence based on D-R isotherm adsorption of Cr(VI) was physical on the surface of Af-NPC.

![Figure 5.4 D-R isotherm plot of adsorption of Cr(VI) on Af-NPC at room temperature (C_o = 1-25 mg/L)](image)

**Figure 5.4** D-R isotherm plot of adsorption of Cr(VI) on Af-NPC at room temperature (\( C_o = 1\text{-}25 \text{ mg/L} \))
5.4.4 Effect of interfering ions

Generally water contain various salts, presence of these salts may interfere with the removal of Cr(VI) from an aqueous medium. Fig. 5.5 shows effect of NaCl and Na₂SO₄ concentration on removal of Cr(VI) by Af-NPC. In presence of NaCl adsorption capacity of Af-NPC reduces from 26 mg/g to 13.36 mg/g with the increase in salt concentration from zero to 0.1 M and in presence of Na₂SO₄ it has reduced to 21.54 mg/g. Adsorption capacity of Af-NPC reduces for Cr(VI) due to competitive inhibition of HCrO₄⁻ ions by Cl⁻ and SO₄²⁻ ions for active sites. Cl⁻ ions reduces adsorption capacity of Af-NPC more as compared to sulphate ions. This could be due to more affinity and diffusion of Cl⁻ ions on the surface of Af-NPC than HCrO₄⁻.

![Figure 5.5 Effect of salt concentration (0-0.1M) on adsorption capacity of Af-NPC for Cr(VI) at room temperature (C₀= 15 mg/L)](image)

5.4.5 Sorbent regeneration

In the present study NaOH was used to desorbed Cr(VI) from the surface of Af-NPC. In order to analyze the reusability Af-NPC, the same sample of Af-NPC was subjected to three consecutive cycles of adsorption–desorption. It was observed that the adsorption capacity reduces only by 3% up to third cycle of adsorption (Fig. 5.6 (a)). Desorption was very fast and within 10 minutes it was possible to remove Cr(VI) from the surface of Af-NPC. By increasing strength of NaOH from 0.05 M to 0.2 M it was possible to concentrate Cr(VI) up to 30 mg/L in small volume of NaOH. The ratio of volume of initially treated solution to the volume of NaOH solution used for desorption was 7. Regeneration study reveals that Af-NPC is reusable after treatment with NaOH and
hence it has potential to be used as an effective alternate sorbent for removal of Cr(VI) from water.

**Figure 5.6** (a) % Adsorption/ desorption efficiency of Af-NPC for Cr(VI) during three consecutive cycles (b) Effect of NaOH concentration on desorption of Cr(VI). (C₀= 5 mg/L)

5.4.6 Mechanism of adsorption
In order to get an insight into the mechanism of adsorption, XPS and FTIR studies were carried out after adsorption of Cr(VI) on the surface of Af-NPC (Fig.5.7) at room temperature.
5.4.6.1 XPS analysis

XPS analysis showed presence of two characteristic peaks of Cr(VI) at 577.8 and 587.1 corresponding to Cr2p\(\frac{3}{2}\) and Cr2p\(\frac{1}{2}\) respectively confirming presence of Cr(VI) [6] on the surface of Af-NPC after adsorption as presented in Fig 5.7 (a).

5.4.6.2 FTIR analysis

Table 5.3 shows comparison of FTIR spectra before and after adsorption of Cr(VI). Shifts were seen in vibrational frequencies of oxygen containing functional groups of Af-NPC after adsorption of Cr(VI) indicating interaction of these groups in the process of adsorption.

**Table 5.3 Changes in FTIR frequencies before and after adsorption of Cr(VI) on the surface of Af-NPC**

<table>
<thead>
<tr>
<th>Vibrations</th>
<th>Af-NPC</th>
<th>Af-NPC-Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O str.</td>
<td>1711</td>
<td>1644</td>
</tr>
<tr>
<td>O-H str.</td>
<td>3399</td>
<td>3439</td>
</tr>
<tr>
<td>C-O str.</td>
<td>1112</td>
<td>1104</td>
</tr>
<tr>
<td>Cr-O</td>
<td>---</td>
<td>874.5</td>
</tr>
</tbody>
</table>

5.4.6.3. Probable mechanism

As there were no major frequency changes observed in FTIR spectra after adsorption of Cr(VI), the interaction of Cr(VI) with Af-NPC was weak. Between pH 2-6.5 the predominant Cr(VI) species is HCrO\(_4\)\(^-\) [1]. Hence probable mechanism of adsorption of Cr(VI) at room temperature and pH \(\leq 2.5\) would be first adsorption of H\(^+\) ions through oxygen containing active groups(-C=O, -O-H) of Af-NPC which create positive sites on Af-NPC followed by adsorption of HCrO\(_4\)\(^-\) ions by weak electrostatic interactions on adsorbed H\(^+\) ions. Removal of Cr(VI) decreases in presence of chloride ions and also with increase in pH confirming electrostatic interactions at room temperature. A
schematic representation of probable mechanism of adsorption is depicted in Fig. 5.7 (c).

Figure 5.7 (a) Cr 2p core levels and (b) FTIR spectrum of Af-NPC after adsorption of Cr (VI) at pH 2.5 (c) The schematic representations of possible mechanism for adsorption of Cr(VI) by Af-NPC
5.4.7 Comparison of Af-NPC with other sorbents from literature

Comparison of Af-NPC with the other adsorbents from literature with respect to adsorption capacity, equilibrium time, adsorbent dosage and surface area is presented in table 5.4. Af-NPC was found to have higher adsorption capacity and faster removal rate due to higher surface area in comparison to other adsorbents mentioned in the table 5.4.

Table 5.4 Summary of comparison of adsorption properties of Af-NPC with other adsorbents reported in the literature for Cr(VI) removal.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Adsorption capacity mg/g</th>
<th>$C_o$ (mg/L)</th>
<th>Equilibrium time (min)</th>
<th>Adsorbent dose (g/L)</th>
<th>Surface area (m$^2$/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feroxyhyte-coated maghemite nanoparticles</td>
<td>2.5</td>
<td>25.8</td>
<td>100</td>
<td>------</td>
<td>5</td>
<td>120 - 140</td>
<td>7</td>
</tr>
<tr>
<td>Mixed magnetite and maghemite</td>
<td>2</td>
<td>2.4</td>
<td>1</td>
<td>60</td>
<td>0.4</td>
<td>49</td>
<td>8</td>
</tr>
<tr>
<td>Fertilizer industry waste</td>
<td>2</td>
<td>15.24</td>
<td>100</td>
<td>70</td>
<td>4</td>
<td>388</td>
<td>9</td>
</tr>
<tr>
<td>Oxidized multiwalled carbon nanotubes</td>
<td>2.8</td>
<td>3.044</td>
<td>10</td>
<td>In hrs</td>
<td>1.25</td>
<td>197</td>
<td>10</td>
</tr>
<tr>
<td>Polymeric Fe/Zr pillared montmorillonite</td>
<td>3</td>
<td>22.35</td>
<td>120</td>
<td>120</td>
<td>2</td>
<td>145.17</td>
<td>11</td>
</tr>
<tr>
<td>Activated carbon from peanut shell</td>
<td>2-4</td>
<td>13.48</td>
<td>100</td>
<td>Several hours</td>
<td>2.5</td>
<td>95.51</td>
<td>12</td>
</tr>
<tr>
<td>Af-NPC</td>
<td>2.5</td>
<td>35.335</td>
<td>25</td>
<td>10</td>
<td>0.5</td>
<td>1013.71</td>
<td>Present study</td>
</tr>
</tbody>
</table>
5.5 Conclusion
Adsorption capacity of nanoporous carbon for Cr(VI) has increased after acid functionalization. Removal rate was very fast and adsorption equilibrium was reached within 10 min. High surface area and mesoporous nature of Af-NPC contributed for fast removal of Cr(VI) from aqueous medium. Langmuir adsorption model fitted well for adsorption data with maximum adsorption capacity of 35.335 mg/g. Af-NPC was efficient at low initial concentration and also reusable after treatment with NaOH. Weak electrostatic interactions seems to dictate the mechanism of adsorption of Cr(VI) on the surface of Af-NPC. Due to high adsorption capacity and fast removal rate synthesized Af-NPC has potential to be used as good alternative sorbent for removal of hexavalent chromium from an aqueous medium.
5.6 References:


