ABSTRACT

Granular Activated Charcoal (GAC) was prepared by using Cordia macleodii tree bark and was tested for the removal of Chromium (VI). All the experiments were carried out in batch process. To enhance its metal ions adsorption capacity, activated carbons were impregnated with the chelating agents like sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and Dioctyl sulfosuccinate sodium salt (DOSS) and were tested for the removal of Chromium (VI). Adsorption isotherms of Chromium ions in aqueous solution have been experimentally measured on both modified and unmodified charcoal. Effects of adsorbent dose, pH, contact time, initial concentration and temperature were investigated on removal of Chromium (VI). Adsorption was confirmed by SEM-EDAX and FTIR morphological analysis. The adsorption data were fitted well by Langmuir adsorption isotherm. Approximately 96.54% of hexavalent Chromium was removed at pH 2 within 3 hr. It was found that chemically modified GAC with chelating agents demonstrated better Chromium (VI) removal capabilities as compared to pure adsorbents in terms of their adsorption rate. On the basis of present studies, it can be concluded that granular activated charcoal impregnated with chelating agents has a higher Chromium (VI) adsorption capacity.

KEYWORDS: Chromium (VI), Adsorption, Impregnation, Batch study, Kinetics.

INTRODUCTION

Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. In a very small amount, they enter the body system through food, air, and water and accumulate in the body over a period of time. The presence of toxic heavy metals in water has caused several health problems with animals, plants and human beings [1-7]. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb^{2+}, Cu^{2+}, Zn^{2+}, Cr^{6+} and Co^{2+} etc [8]. There are several methods available for removal of these heavy metal ions. These methods include complexation, biosorption [9], ion-exchange, cementation [10] etc. Activated charcoal has wide applications in wastewater purification. It is effective and less expensive adsorbent for wastewater purification. Activated charcoal has a great tendency to removal metal ions by complexation with surface oxygen containing functional groups [11]. Chemical modification improves the adsorption capacity [12]. To increase the capacity of granular activated charcoal to adsorb heavy metal ions surface modification method is significantly used. Heavy metals like Cadmium, Zinc, and Chromium [13-17] are removed effectively by using surface modified activated carbon. The World Health Organisation (WHO) has set a maximum guideline concentration of 0.05 mg/L for Cr (VI) in drinking water.

The present paper deals with the study of adsorption of hexavalent Chromium by using adsorption methodology. For this study we prepare granular activated charcoal from Cordia macleodii tree bark, to enhance its adsorption capacity and make its pores free from contaminants it was treated with nitric acid and distilled water in 1:1 proportion. The surface of this activated charcoal further modified by impregnated it with Sodium dodecylbenzenesulfonate, Dioctyl sodium sulfosuccinate. Sodium dodecyl sulfate and used as adsorbent for this...
purpose. In addition, attempts are made to interpret the experimental results on the basis of interaction between the prepared adsorbent and Cr (VI) metal ions by using SEM-EDAX and FTIR technology. The objective of the study is to explore the potential of prepared GAC and modified GAC for the removal of Cr (VI) metal ions from aqueous medium.

MATERIALS AND METHODS

Preparation of Solutions

Preparation of all solutions can be done by using deionised water. Potassium dichromate (purchased from Merk) was used as a source of Cr (VI). For this purpose 2.94 gram of K₂Cr₂O₇ dissolve in 1000 ml standard volumetric flask with deionised water. The concentration of Cr (VI) was analyzed by UV-Visible spectrophotometer (model-117) using 1, 5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm [18]. The Sodium dodecylbenzenesulfonate (purchased from Sigma Aldrich), Dioctyl sodium sulfosuccinate (purchased from Acros Organics), Sodium dodecyl sulphate (purchased from Merk) was used for surface modification of activated carbon. All the solutions of these chelating agents are prepared in 0.01M concentration by dissolving it into 1000 mL volumetric flask with deionised distilled water.

Preparation of Granular Activated Charcoal (GAC)

In the present study granular activated carbon is prepared from the Cordia macleodii tree bark. Collected bark washed with deionised water several time to removes dust and mud then it was later sundried for 10 days. The dried bark is then converted into granular activated carbon (GAC) by using muffle furnace. The prepared granular activated carbon further washed with deionised water several times to remove impurities present on its surface then transferred to large petridish with a cover and kept in an oven at temperature 70°C for 48 hours then cooled in desiccators containing CaCl₂ to obtain moisture free granular activated carbon. In order to verify that this carbon was in equilibrium with the surrounding, 0.5 gram of the granular activated carbon (GAC) was weight and kept in the same desiccator and its weight monitored over a period of time until a constant weight of the carbon was obtained. The further activation was done by taking 10 gram of prepared granular activated carbon in a beaker to it 100 ml nitric acid (HNO₃) and 100 ml of water (H₂O) added and kept at room temperature for 48 hours with occasional stirring to increase porosity and make the GAC suitable for present adsorption study.

Surface modification of GAC

Surface modification can be done by taking 200 ml solution of chelating agent (0.01M) and 0.5 gram of adsorbent in reagent bottle and shaken for 3 hours at 1000 rpm at room temperature, then dried in oven. The impregnated GAC with chelating agents before and after metal ions adsorption can be analysed by SEM-EDAX, FTIR technology. The resultant loaded granulated activated charcoal with Dioctyl sodium sulfosuccinate, Sodium dodecylbenzenesulphonate, Sodium dodecyl sulfate designated as GAC-DOSS, GAC-SDBS, and GAC-SDS.

Batch study

Stock solution of Chromium (VI) was prepared by dissolving appropriate amount of K₂Cr₂O₇ in 1000 ml of double distilled water. The stock solutions were diluted with double distilled water to obtain required standard solution. The dried amount of 0.5 gram of Granular activated charcoal was taken in 250 ml reagent bottle and standard solution containing various concentration of Chromium (VI) was added and system is equilibrated by shaking the contents of the flask at room temperature. The adsorbent and adsorbate were separated by filtration and filtrate was determined by spectrophotometer at λ = 540 nm against a reagent blank. The UV-Visible spectrophotometer systronic (model 117) was used to measure the concentration of Chromium (VI). Same experiments were carried out for loaded GAC.

The amounts of percentage adsorption were computed as follows:

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

Where, in equation \(C_0\) and \(C_e\) represented the initial and equilibrium concentration (mg/L).

RESULT AND DISCUSSION

Adsoption isotherms

The adsorption isotherm gives the idea about the correlation between the amounts of adsorbed adsorbate by unit mass of adsorbent at constant temperature. In the present investigation, the adsorption of Cr (VI) metal ions onto GAC and impregnated GAC was studied by Langmuir and Freundlich models.
The Langmuir isotherm model can be given as:
\[
\frac{1}{q_e} = \frac{1}{Q^0 b} \times \frac{1}{C_e} + \frac{1}{Q^0}
\]

The Langmuir constant $Q^0$ is a measure of adsorption capacity and $b$ is the measure of energy of adsorption. In order to observe whether the adsorption is favourable or not, a dimensionless parameter ‘$R$’ obtained from Langmuir Isotherm. The values of $Q^0$ and $b$ were evaluated from the intercept and slope of linear plots of $1/q_e$ vs. $1/C_e$ respectively.

\[ R = (1 + b \times C_m)^{-1} \]

The value of $R$ indicated the type of the isotherm to be either unfavourable ($R>1$), linear ($R=1$), favourable ($0<R<1$) or irreversible ($R=0$). Where, $b$ is Langmuir adsorption constant and $C_m$ is the maximum initial solute concentration used in the Langmuir isotherm. The adsorption of Cr (VI) on Granular Activated Charcoal and loaded Granular Activated Charcoal is a favourable process as “$R$” values lies between zero to one shown in table 1.

**Freundlich Adsorption Isotherm Model**

It is most commonly used adsorption isotherm model which describes adsorption on heterogeneous surfaces with interactions among adsorbed molecules. It helps to investigate the nature of adsorption and the adsorption capacity of an adsorbent. The linear form of Freundlich isotherm model is

\[
\log q_e = \log \frac{1}{K_f} + \log C_e
\]

Where, $B$ and $K_f$ are Freundlich constant. These constants represent the adsorption capacity and the adsorption intensity respectively. $q_e$ is the amount adsorbed at equilibrium (mg/g), $C_e$ is the equilibrium concentration of adsorbate. Plot of $\log q_e$ Vs $\log C_e$ was also found to be linear. The values of $B$ and $K_f$ are calculated from the intercept and slope respectively shown in table 1.
Adsorption Kinetics

In order to examine the controlling mechanism of adsorption process, First order kinetic model, Pseudo second order kinetic and Elovich model were used to test the experimental data.

First Order Kinetics

For batch contact time process the linear form of first order kinetics equilibrium of Lagergren equation can be given as:

\[
\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t
\]

Where \( q_e \) is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g), \( q_t \) is the amount of solute adsorbed at any given time \( t \) and \( k_1 \) is the rate constant. Lagergren first order plot for the adsorption of metal ions at various initial concentrations is given in the figure 4. \( \log (q_e - q_t) \) is calculated for different agitation time (t). A graph is drawn between \( \log (q_e - q_t) \) and time \( t \). From the above equation slope is \( \left( -\frac{k_1}{2.303} \right) \) and \( y \)-intercept is \( \log q_e \). The applicability of Lagergren model suggests the formation of monomolecular layer of Cr (VI) on to surface of adsorbent.

Pseudo Second Order Kinetic Model

To describe Cr (VI) adsorption the linear form of second order kinetic equation can be written as:

\[
\frac{t}{q_t} = \frac{1}{q_e} \times t + \frac{1}{k_2 \cdot q_e^2}
\]

Here, the value of \( t/q_t \) is calculated from different agitation time’s \( t \) and a graph is drawn between \( t/q_t \) and \( t \). Here slope is \( 1/q_e \) and \( y \)-intercept is

\[
y - \text{Intercept} = \frac{1}{k_2 \cdot q_e^2}
\]

\[
k_2 = \frac{1}{y - \text{Intercept} \cdot q_e^2}
\]

Figure 5 shows Pseudo second order equation at various initial metal ions concentration. These plots shows that data had good correlation coefficients when Pseudo second order equation was employed and was possible to ascertain from them whether rate determining process is a chemical reaction. Constant value of \( K_2 \) determine, where the adsorption of metal ions obey second order kinetic model or not.

Elovich Model

Elovich rate equation is commonly used to describe the kinetics of chemisorption on porous solid adsorbents and it is also applicable to describe the sorption of heavy metal ions from aqueous solutions. The results of sorption of metal ions on to adsorbent have been represented in the form of Elovich equation.

\[
\frac{dq_t}{dt} = \alpha \exp(-\beta \cdot q_t)
\]

Where, \( \alpha \) is called initial adsorption rate in (mg/g/min) and \( \beta \) is desorption constant (g/mg).

Linear form of this equation is

\[
q_t = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln (\alpha \beta)
\]

Here, slope = \( 1/\beta \) and \( y \)-intercept = \( \frac{1}{\beta} \ln (\alpha \beta) \)

Graph is plotted between \( q_t \) versus log \( t \) and shown in figure 6. From the plot of linear relationship between the amounts of Cr (VI) metal ions adsorbed on to GAC and impregnated GAC is evaluated. Where \( q_t \) is the amount of Cr (VI) adsorbed by adsorbent at a time \( t \), \( \alpha \) is the initial Cr (VI) adsorption rate [mmol/(g min)] and \( \beta \) is the desorption constant (g/mmol).

Results show that the kinetic constants obtained from Elovich equation. It will be seen from the data that the values of \( \alpha \) and \( \beta \) varied as a function of Cr (VI) metal ions concentration. Thus on increasing the initial concentrations of Cr (VI) metal ions the value of \( \alpha \) increases and value of \( \beta \) decreases.
Scanning Electron Micrograph (SEM) analysis for the adsorption of Cr (VI)
SEM analysis also studied for the removal of Cr (VI) metal ions on the virgin granular activated charcoal and surface modified granular activated charcoal. The SEM images of GAC, GAC-Cr (VI), GAC-SDS-Cr (VI) and
GAC-SDBS-Cr (VI) are shown in figure 7 A, B, C, D respectively at 1000, 2000 and 5000 × magnifications. The SEM monograph shows the presence of tiny holes on the crystalline structure of granular activated charcoal. After adsorption of Cr (VI) onto surface modified granular activated charcoal the tiny spot becomes vanish and the surface gets change indicating the adsorption of Cr (VI) metal ions by means of physisorption.

**EDAX Analysis**

EDAX analysis performed to determine the elemental composition of the adsorbent before and after metal ions adsorption. Carbon and oxygen is the major constituent in the adsorbent. Their features can be observed at 0.2 and 0.5 keV respectively as shown in figure 8 A. Figure 8 B represent the EDAX feature of GAC-SDS following Cr (VI) adsorption. Cr (VI) broad peak appeared at 5.4 keV and for sulphur of SDS is at 2.3 keV (Data not shown). Overall the appearance of EDAX feature of Cr (VI) on the surface of adsorbent implies the ability of GAC and surface modified GAC for metal ions binding.

![Figure 7](image1.png)

*Figure 7. (A) SEM monograph of virgin GAC. (B) SEM monograph of GAC after Cr (VI) adsorption. (C) SEM monograph of impregnated GAC with SDS after Cr (VI) adsorption. (D) SEM monograph of impregnated GAC with SDBS after Cr (VI) adsorption.*

![Figure 8](image2.png)

*Figure 8. (A) EDAX spectrum of Virgin GAC, (B) EDAX spectrum of loaded GAC with SDS after Cr (VI) adsorption.*
FTIR Characterization

FTIR analysis is important to confirm the functional group present in the adsorbent. Furthermore, it provides information on binding mechanism and possible functional groups involved in the interaction with metal ions [20]. The FTIR spectra of granular activated charcoal prepared from cordia macleodii tree bark shown in figure 9 (A). Based on figure 9 (A) bands observed at 800.12 cm\(^{-1}\) due to S-O stretching. The broad band observed at 1022.28 cm\(^{-1}\) consistent with Si-O stretching vibration. The absorbance at 1390.41 cm\(^{-1}\) may be due to Al-O as a Si cage. The absorption band observed at 1541.79 cm\(^{-1}\) represents C=O stretching vibration in carboxylic chain. The absorption band appeared at 1710.09 cm\(^{-1}\) indicating C=O stretching. The band around at 2362 cm\(^{-1}\) shows the presence of carboxylate ion. Thus, the FTIR have confirmed the presence of functional group such as COO\(^{-}\), C=O on the surface of granular activated charcoal that could be the potential adsorption sites for interaction with the metal ions Cr (VI). Figure 9 (B) represents the FTIR spectrum of Cr (VI) metal ions adsorption on GAC. The intense band around 1710 cm\(^{-1}\) shifted to 1849 cm\(^{-1}\) and band around 2362 cm\(^{-1}\) reduced to 2344 cm\(^{-1}\). This attributed that the C=O and carboxylate ions were responsible for the adsorption of Cr (VI) metal ions on GAC. Figure 9 (C) indicates the FTIR spectrum of GAC loaded with DOSS for Cr (VI) adsorption were band 1710 cm\(^{-1}\) shift to 1719 cm\(^{-1}\) and 2362 reduced to 2330 cm\(^{-1}\). Here the band at 2330 cm\(^{-1}\) becomes broad indicates that the concentration of carboxylate ions increases because of loading of DOSS on GAC. Figure 9 (D) shows the FTIR spectra for GAC loaded with SDABS after Cr (VI) adsorption where band reduction observed at 1707 cm\(^{-1}\) and 2330 cm\(^{-1}\). Also for GAC loaded with SDS following Cr (VI) adsorption shown in figure 9 (E), FTIR indicates the spectrum at 1702 cm\(^{-1}\) and 2328 cm\(^{-1}\) for C=O and carboxylate ions interaction with Cr (VI) adsorption. The Cr (VI) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups. The adsorption peaks are tabulated in table 3 for GAC and loaded GAC after Cr (VI) adsorption.
Figure 9. (A) FTIR Spectra of virgin GAC. (B) FTIR spectra of GAC after Cr (VI) Adsorption. (C) FTIR spectra of GAC loaded with DOSS after Cr (VI) Adsorption. (D) FTIR spectra of GAC loaded with SDBS after Cr (VI) Adsorption. (E) FTIR spectra of GAC loaded with SDS after Cr (VI) Adsorption.
BATCH STUDY

Effect of pH

The effect of pH can be done experimentally by taking 0.5 gm of adsorbent with working volume of Cr (VI) 200 ml having initial metal ions concentration 10.1758 mg/L and the contact time of 3 hours with shaking speed 1000 rpm. The result indicates that maximum uptake capacity for Cr (VI) was found to be at pH 2 with GAC 8.6264 mg/L, GAC-DOSS 9.0 mg/L, GAC-SDBS 9.2748 mg/L, GAC-SDS 9.8242 mg/L shown in figure 10. The reason for better adsorption capacity observed at lower pH, higher adsorption of metal anions occurs due to their increased electrostatic attraction with the positively charged adsorbent surface but adsorption of metal cations decreases due to their competition with the excess H⁺ ions surrounding the binding sites of adsorbent surface.

![Figure 10. Effect of pH on Cr (VI) removal](image)

Effect of Contact time

The effect of contact time can be done by taking 0.5 gm of adsorbent with working volume of Cr (VI) 200 ml having initial metal ions concentration 10.1208 mg/L. It was observed that initially rate of adsorption is rapid up to 180 min with shaking speed 1000 rpm and then there was no further change in equilibrium concentration. Equilibrium time was found to be 300 minutes for this adsorption. The result indicates that maximum uptake capacity for Cr (VI) at pH 2 and at 180 minute with GAC 7.1318 mg/L, GAC-DOSS 7.3956 mg/L, GAC-SDBS 7.813 mg/L, GAC-SDS 8.0659 mg/L shown in figure 11.

![Figure 11. Effect of contact time on Cr (VI) removal](image)

Effect of Adsorbent dose
The effect of varying the adsorbent dosage (GAC and impregnated GAC) from 0.2–1.4 gram for adsorption of Cr (VI) from their aqueous solutions having initial concentration of 10 mg/L was studied at pH 2.0. It has been found that the percent removal of Cr (VI) increases with increase in adsorbent dose up to some extent, thereafter further increase adsorbent dose, there was no appreciable increase in percentage removal shown in figure 12. The experiments were carried out using 200 ml working volume having 10 mg/L concentration, contact time 3 hours and agitation speed 1000 rpm.

Figure 12. Effect of adsorbent dose on Cr (VI) removal

Effect of Initial Metal ions concentration

The effect of initial metal ions concentration on the adsorption of Cr (VI) metal ions onto GAC and impregnated GAC are shown in figure 13. Study were carried out by varying initial metal ions concentration from 5 to 30.2087 mg/L on GAC and impregnated GAC using adsorbent dose 0.5 gram at pH 2.0 having agitation speed 1000 rpm, contact time 3 hours. Result indicates that with increase in initial metal ions concentration percent of adsorption decreases shown in figure 13. This can be attributed to the reason that further available sites on the adsorbent were found to be limited.

Figure 13. Effect of initial metal ions concentration on Cr (VI) removal

Effect of Temperature

Effect of temperature was studied by varying the temperature from 25°C to 65°C with working volume 200 ml having the concentration 10.6813 mg/L. Study was carried out at pH 2.0 and at 1000 rpm with contact time 3 hours. Temperature directly affects of porosity of adsorbent. As the temperature increases porosity increases and...
percent of adsorption increases shown in figure 14. Also enhancement of adsorption capacity of the adsorbent at high temperature has attributed to the enlargement of pore size and activation of the adsorbent surface [21].

**Figure 14. Effect of temperature on Cr (VI) removal**

**Column study**

Column studies were carried out in a glass column of 20 mm internal diameter and 50 cm height. In the bottom side 0.5 cm thick glass wool was placed to prevent any loss of adsorbent. To this column 5 gram of adsorbent were added. Total experiment was carried out at room temperature. The flow rate was adjusted at 3 ml/min. Once the column was ready, 500 ml 21.2586 mg/L concentration of metal ions at pH 2 was taken in separating funnel attached to the respective column and allowed to flow through the column, at flow rate 3ml/min. The sample were collected after passing through the column and analyzed for metal ions content spectrophotometrically at particular wavelength. The column study result indicates that the percent removal of Cr (VI) on GAC is 56.77, GAC-DOS is 62.04, GAC-SDBS is 76.23 and for GAC-SDS is 84.26 respectively shown in figure 15.

**Figure 15. Effect of column study on Cr (VI) removal**

**Table 1. Isothermal Constants**

<table>
<thead>
<tr>
<th>System</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_o$</td>
<td>$b$</td>
</tr>
<tr>
<td>GAC-Cr (VI)</td>
<td>4.9019</td>
<td>0.0211</td>
</tr>
<tr>
<td>GAC-DOS - Cr (VI)</td>
<td>6.2300</td>
<td>0.0166</td>
</tr>
<tr>
<td>GAC-SDBS - Cr (VI)</td>
<td>7.9365</td>
<td>0.0130</td>
</tr>
<tr>
<td>GAC-SDS - Cr (VI)</td>
<td>10.1010</td>
<td>0.0102</td>
</tr>
</tbody>
</table>
In this study the removal of Cr (VI) metal ions from aqueous solutions on granular activated charcoal and impregnated granular activated charcoal were conducted by batch adsorption experiment with column study extension. The removal efficiency was controlled and studied by solution pH, Contact time, Temperature, Adsorbent dose, Initial metal ions concentration. In column study at a rate flow 3 ml/min were adjusted for the efficiency of removal of Cr (VI). The adsorption of Cr (VI) metal ions on to GAC and loaded GAC is governed by Langmuir and Freundlich isotherm. The high metal ions concentrations are used in batch experiment which indicates the presented adsorbent have a good potential of adsorption and its use significantly to lower the cost of water treatment. The result of adsorption process reveals that at pH 2 Chromium uptake capacity better. Kinetic study indicates that the rate of adsorption of Cr (VI) follows Pseudo second order and Elovich model. The FTIR spectrum confirms the adsorption of Cr (VI) metal ions. From these results it is conclude that surface modified granular activated charcoal with Dioctyl sulfosuccinate sodium salt (DOSS), sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS) can be efficiently used for the removal of Cr (VI) from the aqueous solution due to thenegatively charged groups in the hydrophilic head of the anionicsurfactant. These groups made the surface charge of the activatedcarbon more negative, resulting in more favourable conditions for Cr (VI) adsorption.

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