Adsorption of chromium(VI) ion onto activated amla dust: Adsorption isotherms and kinetics

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The adsorption efficiency of a low cost adsorbent, amla dust (Indian gooseberry, Emblica Officinalis) in removing chromium(VI) ion from aqueous solution has been investigated in batch experiments. The effects of hexavalent chromium concentration, particle size, adsorbent dosage, temperature and pH have been studied. Removal is found to be most effective at pH 4 and at the low temperature and Cr(VI) ion concentration. Therefore, the uptake capacity has been investigated in buffered solutions of pH 4 maintaining a constant ionic strength with 0.01 M NaClO₄. The batch adsorption isotherms have been studied in terms of Langmuir and Freundlich isotherm models. Adsorption of Cr(VI) on amla dust is found to follow first order kinetics. The mechanism of Cr(VI) removal on the adsorbent is complex and both the surface adsorption as well as intraparticle diffusion contribute to the rate determining step. Amla dust, the low cost adsorbent is found to be efficient in the removal of Cr(VI) ion in acidic medium, hence, the development of such materials can be applied for the removal of metal ions from industrial waste waters.

One of the heavy metal contaminants that has been a major focus in waste water management is chromium¹. Chromium(VI) ion is introduced into the environment through industrial discharges from paint and pigment, leather tanning, electroplating, glass, ceramic, photographic, textile dying and canning industries. In trace amounts, chromium is an essential element in the diet of some animals and presumably of human beings also. However, at higher concentrations all compounds of chromium are toxic. Ingestion of chromium may cause epigastric pain, nausea, vomiting and severe diarrhoea². Thus, it becomes imperative to remove chromium ion from industrial waste water before discharging into water or onto land. Widespread industrial applications and high mobility are the two primary reasons why chromate is frequently found in contaminated sites and ground water³.

Chromate ions exist in the aqueous phase in different ionic forms with total chromate concentration and pH dictating which particular chromate species will predominate³. In aqueous systems chromium exists mostly in two oxidation states; hexavalent chromium, Cr(VI) and trivalent chromium, Cr(III). While the trivalent chromium is far less toxic than hexavalent chromium and even important as a ‘glucose tolerance factor’, the existence of both Cr(VI) and Cr(III) has important effects on the overall removal of chromium from water. It has been found that chromium ions can be removed more efficiently in acidic environment with adsorption capacity increasing exponentially with decreasing pH. Some of the conventional methods² employed in the removal of Cr(VI) from waste waters are chemical precipitation, ion exchange, electrolysis and adsorption by activated carbon. Owing to operational difficulties and cost of the treatment, some new methods have been tried for a long time, one among them being adsorption on low cost adsorbents. Various low cost adsorbents reported¹ for the removal of Cr(VI) are aluminium oxide, hair, rice husk, bone powder, coconut shell and saw dust. Studies on the removal of chromium by the above activated species excepting carbon are not widely available, thus it represents an interesting field of study. In this paper, the removal of chromium(VI) by chemically activated amla dust (Indian gooseberry, Emblica Officinalis) at pH 4 is presented. The present investigation aims at studying the statics and kinetics of the adsorption of Cr(VI) with an object to explore optimum conditions for separation of the ion by adsorption methods.

Materials and Methods

All chemicals were analytical grade, purchased from Merck and all the experiments were carried out with NaClO₄ (0.01 M) as background electrolyte. The pH of the solutions were adjusted to 4 with standard
buffers. At this pH range, the chromium(VI) ions are mainly in the form of dichromate ions. Stock solutions of hexavalent chromium ion were prepared by dissolving potassium dichromate in 1 dm³ distilled water giving a concentration of 1000 mg dm⁻³ as Cr(VI). Doubly distilled water over alkaline potassium permanganate was used in the preparation of experimental solutions.

Preparation of adsorbent

Amla (Indian gooseberry, Emblica officinalis) procured locally was cut into pieces and treated with hot distilled water to remove sugar content and sundried. The raw amla sample was ground using a mortar and pestle and then sieved into several size fractions using British Standard Sieves series. A sample of each fraction, 50 g of the adsorbent was immersed in 1 dm³ of NaOH (0.5 M) at 60°C overnight, filtered and washed. Subsequently, 100 g of the above treated sample was immersed in 1 dm³ of H₂SO₄ (0.25 M) at 60°C overnight, filtered and repeatedly washed with distilled water until the supernatant solution shows a constant pH. Then the sample was oven-dried until constant weight at room temperature and stored in a desiccator. The physical characteristics of activated amla sample were determined by reported methods. For instance, specific surface area was determined by p-nitrophenol adsorption method and electrical conductivity (EC) and pH of the activated amla dust were found by soaking a known weight of (200 mg in 100 cm² of water for EC and 2 g in 100 cm³ for pH) the sample in doubly distilled water over night and agitated in a mechanical shaker for 3 h. Then the suspension was kept aside for an hour, filtered and EC was measured using a Elico model CM 185 Conductivity Bridge and pH by a Elico model LI 120 pH meter.

Adsorption isotherm and kinetics experiments

A continuous mixed batch system was employed in all Cr(VI) adsorption on amla dust. To a series of 200 cm³ glass bottles, various amounts of distilled water and solutions of potassium dichromate, sodium perchlorate and buffer were pipetted to a total volume of 50 cm³; the components were varied in each specific run. In a series of preliminary experiments, the uptake capacity of Cr(VI) on amla dust from pH 2 to 14 were carried out, which established that the removal capacity attains the maximum at pH 4. Therefore, all the experiments were conducted in aqueous solutions at a constant pH of 4, adjusting with 1 M HCl and amla particles at a dose of 1 g dm⁻³. To study the adsorption isotherms, known concentrations 80, 100, 120, 140, 160, 180, 200 and 220 mg dm⁻³ of Cr(VI) were contacted with 1 gm dm⁻³ adsorbent at 293±1 K. After 1 h of agitation in a mechanical shaker, solutions were filtered and hexavalent chromium was analysed by the pink standard procedure. Accordingly, hexavalent chromium was analysed by the pink colour complex developed between chromium ion and diphenyl carbazide in acidic solution. Absorbance was then measured at 540 nm with a Shimadzu model UV 240 spectrophotometer using 1 cm cuvette. The absorbance was converted into the respective concentration of Cr(VI) using a calibration plot.

Desorption analysis

Attempts were made to regenerate the adsorbent as well as resolubilise Cr(VI) from the spent adsorbent using HClO₄ and NaOH. Desorption studies were carried out as follows: after adsorption experiment with Cr(VI) solution of 80 mg dm⁻³, the adsorbent was separated and gently washed with distilled water to remove any unadsorbed Cr(VI). Several such adsorbent samples were resuspended in 50 cm³ of distilled water, the pH adjusted to 4 and agitated for 3 h. The suspension was kept for an hour and filtered. Then the desorbed Cr(VI) was estimated spectrophotometrically using diphenyl carbazide complexing agent. Experiments were repeated for all other concentration (100, 120, 140, 160, 180, 200 and 220 mg dm⁻³) and at varying pH of the medium (pH = 6, 8, 10 and 12). The results imply that, in addition to electrostatic forces, specific chemical interaction may also play an important role in Cr(VI) adsorption.
Results and Discussion

Characteristics of activated amla dust used in this work are summarized in Table 1. The chromium(VI) ion removal capacities at different concentrations (80, 120, 160 and 200 mg dm\(^{-3}\)) were studied as a function of time. The curves are smooth and continuous, leading to saturation, suggesting the possibility of formation of monolayer coverage of Cr(VI) on the surface of the adsorbent. The dominant Cr(VI) species at total chromium concentrations below 500 mg dm\(^{-3}\) are the oxyanions \(\text{HCrO}_4^-\), \(\text{CrO}_4^{2-}\) and \(\text{Cr}_2\text{O}_7^{2-}\). The latter species predominate in acidic environment at higher Cr(VI) concentrations. The removal efficiency of total chromium concentration at 200 mg dm\(^{-3}\) is lower than the removal at 80 mg dm\(^{-3}\), which is expected, as the adsorption capacity rate would decrease with increasing chromium concentration. It may also be assumed that the variation of ion adsorption with initial concentration is an indication of a change in adsorption process or completion of monolayer formation or setting in of a pore diffusion process. This is reflected in the poor removal efficiencies of Cr(VI) at higher concentration relative to the lower initial concentration (66.7 and 89.9% respectively). This may be due to the presence of more \(\text{Cr}_2\text{O}_7^{2-}\) at higher Cr(VI) concentrations.

The effect of the particle size of adsorbent and Cr(VI) concentration was investigated. It is seen that the adsorption density of Cr(VI) decreases with increasing particle size of adsorbent (three different particles of sizes 0.1-0.2 mm, 0.3-0.4 mm and 0.6-0.7 mm). The percent removal of Cr(VI) decreases from 89.9 to 77.4% with increase in particle size of the adsorbent. Thus, decreasing the particle size increases the external surface area, which means increasing the number of available sites for metal uptake.

The effect of adsorbent dosage on the percentage removal of Cr(VI) at various initial Cr(VI) concentration was studied. It can be observed that the percentage removal increases very sharply initially with the increase in adsorbent dosage but beyond a value of 1.0-1.4 g dm\(^{-3}\), the percentage removal reaches almost near constancy. As expected, increasing the adsorbent concentration results in a significant decrease in the equilibrium concentration of Cr(VI). A maximum removal about 74.5-92.3% is observed at an adsorbent dosage of 1.4 g dm\(^{-3}\) for 80-200 mg dm\(^{-3}\) initial Cr(VI) concentrations. It is seen that on raising the adsorbent dosage from 0.25 to 1.0 g dm\(^{-3}\) results in a smooth increase of percentage removal. Further increase in the dosage leads to a near constancy in the removal. This result is interesting in the sense that, for practical and scaling up purposes, it allows the adsorbent concentration to be increased without restriction in the kinetic behaviour. In the present study, an adsorbent dosage of 1 g dm\(^{-3}\) was used in all the other experiments, this is to prevent the agglomeration of adsorbent particles.

The chromium adsorption capacity of activated amla is found to be influenced by the temperature. Equilibrium removal for Cr(VI) ion was carried out under isothermal conditions in the temperatures 285, 293, 300 and 307 K. It is seen that uptake of Cr(VI) ion at equilibrium is dependent on temperature in the tested range. It indicates that on increasing temperature of solution from 285 to 307 K, the adsorption decreases from 74.6 mg g\(^{-1}\) (93%) to 60.8 mg g\(^{-1}\) (76%) at pH 4 and a solution concentration of 80 mg dm\(^{-3}\). The greater amount of adsorption at lower temperature may be due to strengthening of intermolecular forces. Also, at higher temperature, the escaping tendency of Cr(VI) ions from the solid to the bulk phase may result in a lower adsorption. Similar result for glucose adsorption on alumina has been obtained in a recent study. Thermodynamic parameters such as the standard free energy change \((\Delta G^\circ)\) enthalpy \((\Delta H^\circ)\) and entropy \((\Delta S^\circ)\) were determined by Eqs. (1)-(3):

\[
K_c = \frac{C_e}{C_0}
\]  

\[
\Delta G^\circ = -RT \ln K_c
\]

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

where \(K_c\) is the equilibrium constant, \(C_0\) is the amount of metal ion (mg) adsorbed on the adsorbent per litre of the solution at equilibrium and \(C_e\) is the equilibrium concentration of the metal ion in solution. The value of \(K_c\) was substituted in the Eq. (2) to evaluate \(\Delta G^\circ\):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density, g cm(^{-3})</td>
<td>0.289</td>
</tr>
<tr>
<td>Specific Surface Area, m(^2) g(^{-1})</td>
<td>0.843</td>
</tr>
<tr>
<td>Soluble substances% (w/w)</td>
<td>Nil</td>
</tr>
<tr>
<td>Moisture content% (w/w)</td>
<td>Nil</td>
</tr>
<tr>
<td>Electrical Conductivity of 0.2% solution, (\mu)S cm(^{-1})</td>
<td>0.11</td>
</tr>
<tr>
<td>pH of 2% solution</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Similarly, $\Delta H^o$ and $\Delta S^o$ were obtained from the slope and intercept of van’t Hoff plot of $\log K_c$ vs $1/T$ using the Eq. (3):

$$\log K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \quad \ldots (3)$$

Thermodynamic parameters are presented in Table 2. The standard free energy changes ($\Delta G^o$) vary with temperature from $-6.22 \text{ kJ mol}^{-1}$ to $-2.97 \text{ kJ mol}^{-1}$ at $285 \text{ K}$ to $307 \text{ K}$. The negative values of $\Delta G^o$ suggest the adsorption of Cr(VI) on amla dust is spontaneous. Such negative value in all the temperatures under study suggests that the adsorption is more spontaneous also results in increase in retention time of Cr(VI) by adsorbent. The enthalpy change ($\Delta H^o$) for adsorption of a standard adsorption process shows negative values suggesting that the adsorption is an endothermic process. Entropy change, $\Delta S^o$, was found to be $-148 \text{ JK}^{-1}\text{mol}^{-1}$, which suggests a lower degree of disorderliness in the adsorption of Cr(VI) ion on the adsorbent. That is, there is a lower degree of disorderliness in the displacement of adsorbed water molecules by the adsorbate.

**Adsorption isotherm and equilibria**

Equilibrium is described by usual isotherm equations such as [Eqs. (4) and (5)] those described by Freundlich, Langmuir or Brunauer, Emmett, and Teller or Sips\textsuperscript{15}:

- **Langmuir model**
  $$q = \frac{q_m bC_o}{1 + bC_e} \quad \ldots (4)$$

- **Freundlich model**
  $$q = k_F C_e^{1/n} \quad \ldots (5)$$

where $q_m$ is the maximum sorption capacity for monolayer coverage (mg g$^{-1}$) and $b$ is the affinity coefficient (dm$^3$ mg$^{-1}$) while $q$ (mg g$^{-1}$) and $C_e$ (mg dm$^{-3}$) represent sorption capacity and metal concentration in the solution at equilibrium respectively. Constants $k_F$ and $n$ represent Freundlich coefficients (n, dimensionless; $k_F$ mg$^{1-1/n}$ g$^{-1}$ dm$^{1/n}$).

The rearranged Langmuir equation has been used to determine the equilibrium distribution of Cr(VI) at the solid-liquid interface.

Generally, adsorption isotherm data are fitted to the rearranged Langmuir model\textsuperscript{12} Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{Q_o} + \frac{C_e}{Q_o} \quad \ldots (6)$$

where $C_e$ is the concentration of metal ion (mg dm$^{-3}$) after equilibrium, $q_e$ is the amount of metal ion (mg) adsorbed per gram of adsorbent after equilibrium, while $Q_o$ and $b$ are Langmuir constants related to adsorption capacity and energy of adsorption respectively. A typical plot of $C_e/q_e$ vs $C_e$ at 293 K, indicates the applicability of the Langmuir isotherm for the system under consideration. The values of $Q_o$ and $b$ are presented in Table 3, which includes the corresponding correlation coefficients. The essential characteristics of the Langmuir isotherms may be expressed in terms of Hall et al.\textsuperscript{16} dimensionless constant expansion factor or equilibrium parameter $R_L$. The values of $R_L$ at different initial concentrations were obtained using Eq. (7):

$$R_L = \frac{1}{1 + bC_o} \quad \ldots (7)$$

The values of $R_L$ between zero and one indicate favourable adsorption. The equilibrium parameter values were calculated from Eq. (7) and they were

<table>
<thead>
<tr>
<th>Table 2—Thermodynamic parameters and rate constant data of adsorption of Cr(VI). [Conditions: Initial [Cr(VI)] 80 mg dm$^{-3}$, adsorbent dosage 1 g dm$^{-3}$, pH 4, adsorbent particle size 0.1-0.2 mm, agitation time 1 h, temperature 293 K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>$K_c$</td>
</tr>
<tr>
<td>$\Delta G^o \text{kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^o \text{kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta S^o \text{JK}^{-1}\text{mol}^{-1}$</td>
</tr>
<tr>
<td>$10 k_{ads} \text{min}^{-1}$</td>
</tr>
</tbody>
</table>

| Model | Value |
|---|
| Langmuir | $Q_o$ mg$^{-1}$ |
| | 16.13 |
| | $b$ dm$^3$ mg$^{-1}$ |
| | 9.69 |
| | $r^2$ |
| | 0.998 |
| Freundlich | $k_F$ mg$^{1-1/n}$ g$^{-1}$ dm$^{1/n}$ |
| | 43.55 |
| | $n$ |
| | 3.61 |
| | $r^2$ |
| | 0.972 |
found to be 0.0013 to 0.0005 at 80 mg dm\(^{-3}\) respectively showing favourable adsorption.

The adsorption studied also fitted well in the linearised Freundlich adsorption model\(^{17}\). The rearranged Freundlich expression is given as Eq. (8):

\[
\log(x/m) = \log k_F + (1/n) \log C_e
\]  

where \(x\) is the amount adsorbed (mg) and \(m\) is the weight of the adsorbent (g). The Freundlich isotherm constants \(k_F\) and \(n\) are presented in Table 3. The parameters are the measure of adsorption capacity and adsorption intensity of Cr(VI) on the adsorbent. The \(n\) value presented in Table 3, represents good adsorption as suggested by McKay \textit{et al.}\(^{18}\). Therefore, the adsorbent under investigation is a better one in the removal of Cr(VI) ions.

**Adsorption kinetics**

The adsorption of Cr(VI) using plant driven product amla dust adsorbent is a fast mechanism by comparison with other adsorbents. Studies indicate that 90% of the total adsorption occurs in a time dependent on the concentration but ranging between 30-45 min. The rate of Cr(VI) adsorption by the adsorbent has been interpreted in terms of the adherence of Cr(VI) at the active sites of the adsorbent as well as its intraparticle diffusion within the pores of the adsorbent. Chromium(VI) removal by amla tends to follow the first order rate as shown by Lagergren\(^{19}\) Eq. (9):

\[
\log(q_e - q) = \log q_e - k_{ad} t/2.303
\]  

where \(q\) is the amount of Cr(VI) adsorbed (mg g\(^{-1}\)) at a definite time interval \(t\), \(q_e\) is the amount adsorbed (mg g\(^{-1}\)) at equilibrium time and \(k_{ad}\) is the rate constant of adsorption (min\(^{-1}\)). The linearity of the plot \(\log(q_e - q)\) vs time is an indication of the first order kinetics for the system under consideration. The adsorption rate constants, \(k_{ad}\) were determined to be 2.05 x 10\(^{-3}\), 1.99 x 10\(^{-4}\) and 1.71 x 10\(^{-4}\) min\(^{-1}\) at 285, 293, 300 and 307 K respectively which are presented in Table 2. It indicates that the adsorption is a temperature dependent process.

The process of adsorption onto the porous surface of adsorbent may also be associated with intraparticle diffusion. It’s occurrence and the magnitude can be determined from the plot of chromium ion adsorbed against time. Generally, in batch adsorption processes the adsorbate molecules diffuse into the interior of the porous adsorbent and the rate process usually depends upon ‘square root of \(t\)’ rather than ‘\(t\)’. The extent of adsorption of Cr(VI) as a function of square root of time at different temperatures was studied. As can be observed, the plot is linear for a wide range of contact time but does not pass through the origin, an observation, which indicates that the mechanism of Cr(VI) removal on amla is complex, therefore, both the surface adsorption as well as the intraparticle diffusion contribute to the rate-determining step\(^{20}\). The initial curved portions of the plots have been attributed to the boundary layer diffusion effect while intraparticle diffusion is responsible for the linear portions\(^{21}\). The slope of the linear portion of the graphs has been defined as a rate parameter, which characterizes the rate of adsorption in the region where intraparticle diffusion is rate controlling\(^{22}\). The intercept of the plots, amount adsorbed vs square root of time, is indicative of the extent of the boundary layer effect, that is, the larger the intercept greater is the contribution of the surface adsorption in the rate-controlling step. It appears that the boundary layer diffusion effect increases with decrease in temperature of the medium.

**Desorption studies**

Desorption studies help to elucidate the nature of adsorption, recovery of metal from waste and recycling of adsorbent. The nature of adherence of metal ions on the surface of the material may be purely physical, purely chemical or both. Desorption studies made at pH 4 shows the presence of 24-37% of desorbed Cr(VI) at various initial adsorbate concentrations (80 to 220 mg dm\(^{-3}\)). On the other hand, the desorption of Cr(VI) was found to be 42% at pH 8, 68% at pH 10 and maximum at pH 12 showing the presence of 87 to 94% of desorbed Cr(VI) for the above concentrations. Further increase in pH does not contribute significantly in the percentage desorption of Cr(VI). Therefore, it indicates that increase in pH would deprotonate the surface, hence, the alkaline adsorbent surface would abandon the negatively charged species. Desorption at higher pH is possibly due to increased solubility of Cr(VI) and abundance of hydroxyl ions, which hinders the diffusion of chromate ion towards the surface. Further, it is predicted that the higher adsorption at pH 4 indicates amla dust particles are more protonated, influencing dichromate adherence through electrostatic forces of attraction.
References
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