Utilisation of Agriculture Weed for the Removal of Cr(VI) from Aqueous Solution

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Abstract

The present study investigates the potential use of activated carbon prepared from Cassia tora by sulphuric acid treatment for the removal of Chromium(VI) from aqueous solution. The effects of pH, initial concentration, contact time, and carbon concentration were studied for the sorption of Cr(VI) in batch mode. The optimum pH value for Cr(VI) adsorption was determined as 2.0. The experimental results were fitted with the Freundlich, Langmuir and Redlich Peterson equations to describe the equilibrium isotherms. The Langmuir and Redlich – Peterson isotherm models were found better to describe the experimental data. The maximum adsorption capacity obtained from Langmuir equation was 72.4 mg/g. The kinetic data were then fitted with the Lagergren-first-order, pseudo-second-order and intraparticle models. Further, adsorption kinetics of Cr(VI) was studied and the rate of adsorption was found to confirm pseudo-second-order kinetics with a good correlation and intraparticle diffusion as one of the rate determining steps. Activated carbon developed from Cassia tora can be a potential alternative for Cr(VI) removal from aqueous solution.

Keywords: Adsorption, Chromium (VI), Activated carbon, Cassia tora, Isotherm, Kinetics.

1. Introduction

Release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems.1 Chromium is one of the most toxic element and its removal has become a serious health concern. It is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases. An important ore of chromium is chromite FeO.Cr2O3. It exists in three common stable valence state, chromium(0), (III) and (VI) in the order of increasing toxicity. Although many different oxidation states of chromium exist in the environment, only chromium(III) and (VI) are the most stable ones. Chromium(III) is an essential dietary nutrient. It is required to potentiate insulin for normal glucose metabolism and helps the body to use sugar, protein and fat efficiently. Trivalent and hexavalent chromium compounds are thought to be the most biologically significant. Chromium(VI) is generally considered thousand times more toxic than chromium(III).2

Chromium is used in industries like metallurgical, chemical, refractory, electroplating, leather tanning and textile.3,4 These industries are the largest source of ambient chromium in surface waters. Leaching from top soil and rocks is the most important natural source of chromium entry into the bodies of water. Solid wastes from chromate processing facilities, when disposed off improperly in landfills become a contamination of ground water, when the chromium residence time might be several years. Reports are available to indicate that workers in tanneries and chromium plating industries are found to suffer from lung cancer. Skin mucous membrane irritation and dermatitis have been observed among chrome workers.5,6 Many cases of nasal membrane inflammation, nasal septum perforation, chronic rhinitis, laryngitis and pharyngitis have been reported among chrome workers, who are exposed to chromic acid dust and mist. Asthma is often observed among chrome platers. Dermatitis, owing to chromium pollution among the workers causes the hands, arms and face red and also causes swelling with intense itching. The first case of occupational health effects from hexavalent chromium was reported in 1827 by Cumin.7 The recommended limit of chromium in potable water is 0.05 mg/L.8 Methods used for the removal of toxic metals are reverse osmosis, evaporation, ion exchange and adsorption among which adsorption is the most promising...
The objective of our investigation is to investigate the potential of *Cassia tora*, an agricultural solid waste, as a low-cost sorbent in the removal of the Cr(VI), from aqueous solution. The equilibrium and kinetics of the process are modeled on conventional theoretical methods.

2. Experimental

2.1. Preparation and Characterization of Sorbent

*Cassia tora*, collected from Tiruchirappalli, India, was dried and the stem portions chopped into small pieces. The chopped pieces were treated with concentrated sulfuric acid (Sp.gr. 1.84) in a weight ratio of 1:0.92 (CT : acid) and the resulting black product was kept in an air oven maintained at 160 ± 5 °C for 10 h, followed by washing with distilled water until it was free from excess of acid and dried at 105 ± 5 °C. The carbon adsorbent obtained was designated as CTC. The CTC was ground and the portion retained between 150 and 170 μm sieves were used. The CTC was characterized by adopting reported standard procedures and the results are summarized in Table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>16.86</td>
</tr>
<tr>
<td>Ash Content (%)</td>
<td>4.84</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>12.34</td>
</tr>
<tr>
<td>Decolorising power (mg/g)</td>
<td>44.78</td>
</tr>
<tr>
<td>pH</td>
<td>6.3</td>
</tr>
<tr>
<td>BET Surface area (m²/g)</td>
<td>56.61</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.422</td>
</tr>
<tr>
<td>Average pore diameter (Å)</td>
<td>32.63</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
<td>0.0073</td>
</tr>
<tr>
<td>Water soluble matter (%)</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Figure 1. FT – IR Spectrum of CTC

The Textural structure examination of CTC and the elemental analysis can be observed, from the SEM image recorded before and after adsorption along with their corresponding SEM-EDAX pictures as shown in Figure 2. (Figure 2(a), 2(b), 2(c) and 2(d)). The photomicrograph showing the fibrous structure reveals the surface texture and porosity of CTC. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials.

2.2. Adsorption Studies

Batch experiments was carried out by agitating the CTC with 100 ml of Cr(VI) solution (prepared from K₂Cr₂O₇) of desired concentration at pH 2.0 and at room temperature (32 ± 1°C) in an orbital shaker (300 rpm). After equilibrium was achieved, samples were withdrawn from the shaker, centrifuged and the supernatant solutions were analysed for residual Cr(VI) concentration. The residual concentration chromium concentration was determined by oxidizing Cr(III) to Cr(VI) using KMnO₄ while the amount of Cr(III) concentration by measuring the difference between the total chromium concentration and Cr(VI) concentration.

The effect of pH on Cr(VI) removal was established by adjusting 60 mg/L of Cr(VI) solutions to different pH values using dilute HCl or NaOH and agitating each with 1.0 g/L of CTC dose for 3 h. For the initial metal concentration study, a concentration range of 10–80 mg/L of

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Cr(VI) was agitated with 1.0 g/L of CTC at pH 2.0 for 3 h. The kinetics of Cr(VI) adsorption was followed with three different initial metal concentrations of 10, 20 and 30 mg/L, each agitated separately with a fixed CTC dose of 1.0 g/L for predetermined intervals of time at pH 2.0. The effect of adsorbent concentration was studied by agitating 60 mg/L of Cr(VI) solutions with a range of CTC dose, 0.1 to 1.5 g/L, after adjusting to pH 2.0 for 3 h.

2.3. Method of Experimental Data Analysis

Non-linear analysis method for analyzing the experimental data is found to be more useful than the hitherto used linear regression analysis to compare the best-fitting isotherms. When using the non-linear method, there arises no problem with transformations of non-linear isotherms to linear forms. In this study, a trial-and-error procedure, which is applicable to computer operation, is used to compare the best-fitting isotherms using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms in the solver add-in in Microsoft Excel.

3. Results and Discussion

3.1. Effect of pH

Figure 3. shows the effect of influence of initial pH on the removal of Cr(VI) by CTC. It could be observed that the removal of Cr(VI) is maximum at pH 2.0. On increasing the pH beyond 2.0, there is a progressive decrease in the Cr(VI) adsorption by CTC. The high chromium(VI) removal at low pH values is probably due to reduction of chromium(VI) to chromium(III) in accordance with the following reactions taking place at low and moderate pH values.

\[
Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O
\]
At moderate pH
\[ HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \]

The predominant anionic forms at low pH values are \( Cr_2O_7^{2-} \) and \( HCrO_4^- \) which have the tendency to oxidize the adsorbent surface thereby getting itself reduced and remains in solution as \( Cr(III) \). Therefore it is envisaged that the removal of \( Cr(VI) \) is governed by both chemical reduction \([ Cr(VI) to Cr(III) ] \) and physico-chemical adsorption \([ mainly Cr(VI) ] \). It is reported that \( Cr(III) \) adsorption is not favored at low pH values due to the formation of larger coordination sphere with water. The tendency of the adsorbent surface to reduce \( Cr(VI) \) to \( Cr(III) \) and the unfavourability of \( Cr(III) \) adsorption at low pH values explains the higher \( Cr(VI) \) removal observed where the \( Cr(VI) \) reduced to \( Cr(III) \) is not accounted. Therefore in order to find out the amount of \( Cr(VI) \) that has been reduced to \( Cr(III) \), after performing the adsorption experiments, one portion of the solution is analysed for residual \( Cr(VI) \) present in solution. This corresponds to chromium present as \( Cr(VI) \) in solution. Another portion was oxidized using \( KMnO_4 \) and this gives the amount of total chromium present in solution. On subtracting these two, the amount of \( Cr(VI) \) that has been reduced to \( Cr(III) \) can be obtained.

\[
q_e = \frac{q_m K_a C_o}{1 + K_a C_o}
\]  
\[ q_e = \frac{AC_o}{1 + BC_o^g}
\]

where, \( K_f \) and \( n \) are the Freundlich constants, and \( q_m \) and \( K_a \) are the Langmuir constants representing sorption capacity (mg/g) and energy of sorption (L/mg), respectively.

For practical design purposes in a system operating over a wide range of concentration an intermediate isotherm is often a more realistic representation of the system. Therefore, in addition to the above isotherms, one more isotherm that combine the features of Freundlich and Langmuir isotherms was considered. That isotherm model is Redlich – Peterson isotherm model and is represented as Eq.(3)

\[
q_e = \frac{AC_o}{1 + BC_o^g}
\]

It has three isotherm constants, namely, \( A \) (L/g), \( B \) (L/mg) and \( g \), which characterize the isotherm. In the above equation, constant \( g \) is the exponent, which lies between 0 and 1. If constant \( g \) is equal to one, the equation modifies to the Langmuir model. If constant \( g \) is equal to zero, then the equation changes to Henry’s law equation. In addition, Freundlich is a special case of the Redlich-Peterson isotherm when constants \( A \) and \( B \) were much bigger than one.15

The results derived from the equilibrium initial metal concentration study were modeled with the isotherms discussed above. Fitted curves of the each isotherm model with the experimental data are shown in Figure 4. and the fitting sorption parameters derived for the models are presented in Table 2. It is clear from the Table 2. that the Langmuir and Redlich – Peterson isotherm model gives a better fit of the experimental data as evident from the higher \( r^2 \) values obtained compared to other model.

Figure 3. Effect of pH on the removal of Cr(VI)

Figure 4. Fitted Isotherm models for Cr(VI) adsorption on CTC

3.2 Adsorption Isotherms

The distribution of solute between the liquid phase and the sorbent is a measure of the position of equilibrium in the sorption process and can be generally expressed by two of the most popular isotherm models, namely, Freundlich\textsuperscript{20} and Langmuir\textsuperscript{21} isotherms represented as Eq. (1) and (2), in their nonlinear forms.

\[
q_e = K_f C_e^\frac{1}{n}
\]
The Freundlich constant, n value obtained is in between 1 to 10 (1.93) which indicates the favourable adsorption of Cr(VI) on CTC. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant separation factor called equilibrium parameter \( R_L^{23} \) which is defined as, \( R_L = 1/(1 + K_a C_0) \) where \( K_a \) is the Langmuir constant and \( C_0 \) is the initial concentration. The \( R_L \) value, indicates the type of isotherm and the values obtained are in the range of 0.072–0.436, which indicate that the adsorption of Cr(VI) on CTC is favourable for the concentration range studied.

### Table 2. Parameters for the fitted isotherm models for the CTC-Cr(VI) system

<table>
<thead>
<tr>
<th>Model</th>
<th>( q_m ) (mg/g)</th>
<th>( K_a ) (L/mg)</th>
<th>( r^2 )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>72.4</td>
<td>0.127</td>
<td>0.995</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>1/n = 0.429</td>
<td>13.66</td>
<td>0.955</td>
<td></td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>( g = 0.981 )</td>
<td>( B = 0.14 )</td>
<td>( A = 9.5 )</td>
<td>( r^2 = 0.995 )</td>
</tr>
</tbody>
</table>

### 3.3. Sorption Kinetics

The agitation time experimental results showed a progressive increase in Cr(VI) uptake with time for all the initial concentrations studied. With increase in Cr(VI) concentration from 10 to 30 mg/L, the amount of Cr(VI) adsorbed at equilibrium time increased from 8.77 to 26.07 mg/g, indicating that the Cr(VI) removal by adsorption on CTC is concentration dependent. This is obvious because more efficient utilization of the adsorption capacities of the adsorbent is expected due to a greater driving force by a higher concentration gradient pressure.

The kinetic experimental results were fitted with various kinetic model equations namely, Lagergren’s pseudo first order and pseudo second order to find out which of these models best define the experimental data points. Lagergren pseudo first order\(^{24}\) equation which is expressed as: (Eq. 4)

\[
q_t = q_e \left[1 - \exp(-k_1 t)\right]
\]  

Where \( q_e \) and \( q_t \) are the amounts of Cr(VI) adsorbed at equilibrium and at time \( t \) in mg/g, respectively, and \( k_1 \) is the pseudo-first order rate constant (min\(^{-1}\)).

The pseudo second order kinetic model\(^{25,26}\) is expressed as Eq. (5)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

the initial adsorption rate is \( h = k_2q_e^2 \), then the Eq. 5 becomes

\[
\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}
\]

Where the initial adsorption rate (h), the equilibrium adsorption capacity (\( q_e \)), and the second order constants \( k_2 \) (g/mg min). The fitted curves of these kinetic models along with the experimental data are illustrated in Figure 5 and the fitted parameters of the models are presented in Table 3.

The kinetic results were also fitted with the intra particle diffusion model

\[
q_t = K_{ip} t^{1/2}
\]

where, \( K_{ip} \) is the intra particle diffusion rate constant. It was proposed by Weber and Morris\(^{27}\), to find out the process(es) through which the sorption takes place and process(es) that limits the rate of sorption. There are essentially three consecutive mass transport steps associated with the sorption of solute from the solution by porous sorbents. In a well-agitated system the initial bulk transport of solute in the solution phase, which is usually rapid because of mixing and convective flow is not taken into account. Apart from this, the removal can be considered as consisting of three steps: (i). Diffusion of solute through a hypothetical film or hydrodynamic boundary layer – film diffusion, (ii). Diffusion of solute to the interior sites through the pore-filled liquid and migration along the solid surface of the pore – intra particle or pore diffusion. (iii). Sorption onto interior sites. The third step is very rapid and does not contribute to the rate of sorption while steps (i) and (ii) are thus the major factors controlling the rate of sorption, either singly or in combination.

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**Figure 5.** Fitted kinetic model for Cr(VI) on CTC system
If intra particle diffusion is solely the rate-determining step, a linear plot passing through the origin would be obtained and the intra particle diffusion parameter, $K_p$, could be estimated from the slope of the straight line. But many authors have reported a multilinearity for such plot.28,29 Figure 6. shows the Weber – Morris plot for the present system. The initial portion of Cr(VI) uptake due to film diffusion could not be followed experimentally due to the fastness of Cr(VI) sorption and the figure depicts that boundary layer effect (film diffusion process) is important up to 5 min. This may be due to the fine particle size of CTC (150–70 μm) taken for study. The second linear portion is the gradual sorption stage attributed to intra particle diffusion effect. The third portion is final equilibrium stage where the intra particle diffusion rate starts to slow down.30 The intra particle diffusion stage does not pass through the origin indicating that intra particle diffusion is not the only rate-controlling step.28 Hence film and pore diffusion, in combination, control the rate of sorption of Cr(VI) on CTC. The rate parameter ($K_p$) for intraparticle diffusion stages were obtained from the slope of each stage and are termed as $K_{p1}$ and $K_{p2}$, respectively, listed in Table 3.

### 3.3. Effect of Carbon Concentration

Effect of CTC dose on Cr(VI) sorption was studied by varying the dose from 0.1 to 1.5 g/L, taking 60 mg/L as initial metal concentration. The amount of Cr(VI) sorption increased with increase in carbon dose and reached a maximum value after a particular dose. From the Figure. 7, it is apparent that maximum removal from 60 mg/L of Cr(VI) solution was achieved at an optimum carbon dose of 1.0 g/L. While increasing the carbon dose from 0.1 to 1.5 g/L, the sorption of metal ions per unit weight of carbon decreased from 142.85 to 32.27 mg/g. There are many factors that can contribute to this sorbent concentration effect. The first and most important factor is that sorption sites remain unsaturated during the sorption reaction. This is due to the fact that as the dose of carbon is increased, there is less commensurate increase in sorption resulting from the lower sorptive capacity utilization of the carbon.31 The second cause may be the aggregation/agglomeration of carbon particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusion path length. The particle interaction at higher carbon concentration may also help to desorb some of the loosely bound metal ions from the sorbent surface.
3.4. Desorption of Cr(VI) from Sorbent

Desorption studies will help to elucidate the nature of adsorption process and to recover the Cr(VI) from sorbent. Moreover, it also will help to regenerate the sorbent so that it can be used again to adsorb metal ions and to develop the successful sorption process. Desorption experiments were carried out by using 0.1 M NaOH for 1 h. About 80% Cr(VI) was recovered from CTC.

4. Conclusion

The results obtained show that carbon prepared from cassia tora, an inexpensive precursor, can be used for the removal of Cr(VI) from aqueous solution. The adsorption process is pH dependent and the optimum pH was 2.0. The isotherm equilibrium studies confirmed that the Langmuir and Redlich Peterson models are the best fitted models for the adsorption process of Cr(VI) by CTC. Further, the kinetic studies proved that the pseudo second order kinetic was the most applicable model. The adsorption process was found to be controlled by more than one mechanism such as the film diffusion and particle diffusion. The Proposed sorbents are efficient, environment friendly and can reduce the amount of toxic chromium ions discharged by the industries.

5. Acknowledgement

Authors are thankful to Prof. Dr. Yuh Shan Ho, for his valuable suggestion and encouragement. Authors are grateful to anonymous reviewers for their useful comments and suggestion.

6. References


Povzetek

Raziskovali smo možnosti uporabe aktivnega oglja, pridobljenega iz Cassia tora za odstranjevanje Cr(VI) iz vodne raztopine. Adsorpcijo smo izvajali pri različnih pH-pogojevih (pH, različna začetna koncentracija adsorbata in adsorbenta, kontaktni čas). Ugotovili smo, da adsorpcija poteka optimalno pri pH v redici 2.0. Eksperimentalne podatke smo analizirali z Freundlichovo, Langmuirjevo in Redlich-Petersonovo izotermo, pri čemer sta se zadnji dve izkazali boljše. Maksimalna adsorpcijska kapaciteta, dobivena s pomočjo Langmuirjeve izoterme, znaša 72.4 mg/g. Kinetično procesa smo obravnavali s hitrostnimi zakoni Lagergren-prvega reda, pri čemer sta se zadnji dve izkazali boljše. Maksimalna adsorpcijska kapaciteta, dobivena s pomočjo Langmuirjeve izoterme, znaša 72.4 mg/g. Kinetično procesa smo obravnavali s hitrostnimi zakoni Lagergren-prvega reda, pri čemer sta se zadnji dve izkazali boljše. Maksimalna adsorpcijska kapaciteta, dobivena s pomočjo Langmuirjeve izoterme, znaša 72.4 mg/g.

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