Removal of Chromium Ions from Aqueous Solution using Activated *Pergularia daemia* Carbon by Batch Adsorption Method

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ABSTRACT

In this research, the stems of *Pergularia daemia* which is a kind of pick over were converted to activated carbon and were used for the removal of hexavalent chromium ion from aqueous solution. The effect of some parameters such as contact time, adsorbent dose, pH of solution, and other ionic strength of Cr (VI) onto the adsorbent. The equilibrium data were analyzed by Langmuir, and Freundlich isotherm models. Kinetic parameters were studied using following manner such as pseudo second order model, Elovich model and intraparticle diffusion model for adsorption process in addition the thermodynamic parameters such as change in free energy (∆G°), enthalpy (∆H°) and entropy (∆S°) were determined. The results revealed that in this process, the adsorption isotherm and kinetics have more conformity with Langmuir isotherm and pseudo-second-order kinetics, respectively and the thermodynamics study provide evidence about nature of adsorption process.

**Key words:** Activated *Pergularia daemia* Carbon (APDC), Chromium (VI) ion, Batch method, Adsorption isotherm, Kinetics, Thermodynamic parameters.

Introduction

The toxicity of hexavalent chromium is 500 times higher than the trivalent form due to its carcinogenicity and mutation effects. Human toxicity of Cr (VI) includes skin irritation to lung cancer, as well as kidney, liver and Gastric damage. It is therefore essential to removal of chromium from contaminated water (Aravindhan, 2006).

Several physical and chemical methods have been technologically advanced for the removal of toxic metals from aqueous solution. Physical methods, primarily adsorption on several supports were recognized to be a promising and in effect process to remove metal ions from aqueous solution completely (Arivoli, 2007). The foremost benefits of adsorption are the reusability of material, low-cost, ease of process and short time of action so it is necessary to develop in effect adsorbents for the removal of Cr (VI) ion from aqueous solution. Activated carbon is the most widely used adsorbent and can be prepared by physical activation in which carbonation of the carbonaceous material at higher temperature (>900 °C) in an inert atmosphere followed by thermal activation (Bulut, 2008).

In the present investigation the adsorption of Cr
(VI) ion on activated carbon prepared from *Pergularia daemia* by carbonization with sulphuric acid. The kinetic and equilibrium adsorption data obtained were utilized to illustrate the sample systematized. The amounts and rates of adsorption of Cr (VI) ion using above activated carbon from aqueous solution were then measured. The literature survey shows that no work has been done so for lift up the *Pergularia Daemia* as an adsorbent.

**Experimental Methods**

The Cr (VI) solution was prepared using analytical grade of K₂Cr₂O₇ obtained from Scientific Equipment Company at Trichy, and stored at room temperature. This stock solution was used to prepare dilute solutions of chromium ion by the dilution with double distilled water.

**Preparation of adsorbent**

The natural plant material of *Pergularia daemia* used in the present investigations was collected from a nearby Poompuhar. The stem was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110 °C. Afterward, carbonization of the stem was carried out by adding w/v ratio Con. H₂SO₄ to get the primary carbon. The primary carbon was activated at >900 °C for 6 hrs under optimized conditions to obtain the activated carbon (Arivoli, 2009).

**Experimental Procedure of Batch Method**

Batch adsorption method were conducted to study the influence of effective parameters such as contact time, activated carbon dosage, initial pH and other ion concentration on the removal of Cr (VI) ion using activated *Pergularia daemia* carbon (APDC). In this experiments, different concentration of Cr (VI) ion solution (10-50 mg/L) and at different temperatures (30 - 60 °C) with known pH and known amount of adsorbent (0.025 g/L) were agitated at 120rpm until the equilibrium was reached then the solution was kept to settle down and the residual concentration of Cr (VI) ion were analyzed by UV-Visible spectrophotometer at 540 nm. All experiments were carried out at normal pH for removal of Cr (VI) ion from aqueous solution. Effect of pH on Cr (VI) ion removal was studied over a pH range of 3.0-9.0 the initial pH of the solution was adjusted by addition of dil. HCl or dil. NaOH. The effect of activated carbon dosage on adsorption rate was investigated using the procedures described above except that different dosages (25-125 mg/50 ml) were used (Arivoli and Hema, 2007). The amount of adsorption at time t, qₜ(mg/g), can be determined and the percentage removal of Cr (VI) ion can be calculated using the formula in that order.

\[
q_t = V \times \frac{(C_0 - C_t)}{w} \quad \text{.. (1)}
\]

\[
\% \text{ Removal} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad \text{.. (2)}
\]

Where, qₒ is the mass of adsorbed Cr (VI) ion per unit mass of adsorbent (mg g⁻¹), (Cₒ) and (Cₜ) are the initial and actual concentration (g dm⁻³) of Cr (VI) ion at time, respectively V is the volume of the treated solution (ml), w is the mass of adsorbent (g).

**Results and Discussion**

**Influence of contact time**

To establish the equilibrium time for maximum removal and to understand the kinetics of the adsorption process, the Cr (VI) ion adsorption in the APDC adsorbent was examined as a function of contact time with results were shown in Figure 1 and the equilibrium data are given in Table 1. The figure shows that the uptake rate was initially rapid with maximum of the adsorption was complete with in 30 min., equilibrium was achieved with in 50 min. therefore, an equilibration period of 60 min. was selected for all further experiments (Arivoli andVenkatraman, 2007).

**Influence of activated carbon dosage**

The adsorption of the Cr (VI) ion on APDC was studied by varying the adsorbent dose (Arivoli and Kalpana, 2007) for 50 mg/l of Cr (VI) ion concentration. The percentage removal of Cr (VI) ions increased with increases in the APDC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites. Hence, all studies were carried out with 0.025 g of adsorbent /50 ml of the varying adsorbate solutions of 10, 25, 50, 100, 200 and 250 mg/l. The results obtained from this study are shown in Figure 2. The amount of Cr (VI) ion adsorbed per gram reduced with increase in the dosage of APDC. This reveals that the direct and equilibrium capacities of Cr (VI) ion are functions of the activated APDC dosage.
Influence of other ions

The effect of chlorine ions (Serife, 2019) on the adsorption process studied at different concentrations. The ions added to 50 mg/l of Cr (VI) ionsolutions and the contents were agitated for 60 min at 30 °C. The results had shown in the Figure 5 reveals that low concentration of Cl⁻ does not affect the percentage of adsorption of Cr (VI) ion on ABCC, because

<table>
<thead>
<tr>
<th>C₀ (Mg / L)</th>
<th>Ce (Mg / L)</th>
<th>qₑ (Mg / L)</th>
<th>Removal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>40°C</td>
<td>50°C</td>
<td>60°C</td>
</tr>
<tr>
<td>10</td>
<td>1.599</td>
<td>1.297</td>
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</tr>
<tr>
<td>20</td>
<td>4.754</td>
<td>4.324</td>
<td>3.908</td>
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<tr>
<td>30</td>
<td>9.885</td>
<td>9.424</td>
<td>8.212</td>
</tr>
</tbody>
</table>

Fig. 2. Effect of Contact Time on the Removal of Cr VI ion
[Cr VI ion]=10 mg/L; Temperature 30 °C; Adsorbent dose=0.025g/50 ml.

Influence of initial pH

Adsorption process is highly pH dependent, because adsorbent surface has different functional groups which are responsible for interaction between Cr (VI) ion and adsorbent, can be protonated or deprotonated to produce different surface charges in solution at different pH values. Therefore the effects of initial solution pH were studied in the pH range of 3-9 for removal of Cr (VI)ion from aqueous solution. The percentage removal increased around 60 % to 93 % whereas it decreased slowly after pH 6.8 that is pHₑ (Zero point charge) shown in Figure 4. The pHₑ of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for cationic Cr (VI)ion adsorption, negatively charged groups on the surface of adsorbent are necessary. At lower pH values (pH <pHₑ) the surface charge of the surface of APDC may get positively charged as a result of being surrounded by H₂O⁺ ions and thus the competitive effects of H₂O⁺ ions as well as the electrostatic repulsion between the Cr (VI) ion and the positively charged active adsorption sites on the surface of the APDC lead to a decrease in the uptake of Cr (VI) ion. In contrast at higher pH values (pH >pHₑ) the surface of APDC may acquire a negative charge leading to an increase in Cr (VI) ion uptake due to the electrostatic force of attraction. On the other hand neutral surface of adsorbent occur support for the maximum removal of Cr (VI)ion from aqueous solution, as the result initial pH value was optimized as pH 6.8.

Fig. 3. Effect of Adsorbent dose on the Removal of Cr VI ion
[Cr VI ion]= 10mg/l; Temperature 30 °C; Contact Time 60 min.

Fig. 4. Effect of Initial pH on the Removal of Cr VI ion
[Cr VI ion]= 10mg/l; Temperature 30 °C; Adsorbent dose=0.025g/50 ml.
the interaction of Cl⁻ at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases that, decreases the percentage adsorption. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions.

Adsorption Models

The adsorption equilibrium data were further analyzed into two well-known isotherm models via Freundlich and Langmuir models (Ajmani, 2019a and Ajmani, 2019b).

Freundlich model

The Freundlich model (Arshadi, 2014) which is indicative of surface heterogeneity of the adsorbent is described by the following equation.

\[ \log q_e = \log K_f + \frac{1}{n_f} \log C_e \]  \hspace{1cm} (3)

Where, K_f and 1/n_f are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between log q_e and log C_e for the adsorption of Cr (VI) ion were shown Figure 6 and its make that correlation coefficient (R²) values near 0.99 as a result temperature studied indicating that Freundlich model was applicable to the present study these values listed in Table 2.

Langmuir model

The Langmuir adsorption isotherm (Dagmawi, 2013) equation which is valid for monolayer adsorption on to a surface is given below.

\[ \frac{q_e}{C_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \]  \hspace{1cm} (4)

Where, q_m (mgg⁻¹) is the amount adsorbed at the equilibrium concentration C_e (mol L⁻¹), q_m(mgg⁻¹) is the Langmuir constant representing the maximum monolayer adsorption capacity and K_L (L mol⁻¹) is the Langmuir constant related to energy of adsorption. The plots drawn between C_e/q_e and C_e for the adsorption of Cr (VI) ion was found linear and its shown in Figure 7. The correction coefficient (R²) values confirm good agreement our experimental results the values of the monolayer capacity (q_m) and equilibrium constant (K_L) have been evaluated from the intercept and slope of these plots and given in Table 2. These facts suggest that Cr (VI) ion is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation.

\[ R_L = \frac{1}{1 + K_L C_0} \]  \hspace{1cm} (5)

Where, C_0 (mg/l) is the highest initial concentration of Cr (VI) ion and K_L (l/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

- \( R_L > 1 \) - Unfavorable adsorption
- \( 0 < R_L < 1 \) - Favorable adsorption
- \( R_L = 0 \) - Irreversible adsorption
- \( R_L = 1 \) - Linear adsorption

The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_0) and temperatures studied. The calculated R_L values are given in Table 3. The values of K_L were increased with increasing the dose of adsorbent for APDC.
High KL values indicate high adsorption affinity the monolayer saturation capacity \( q_m \) were around 68.616 mg/l for APDC.

**Thermodynamic treatment of the adsorption process**

Thermodynamic (Eliku, 2018) parameters associated with the adsorption, via standard free energy change (\( \Delta G^0 \)), standard enthalpy change (\( \Delta H^0 \)), and standard entropy change (\( \Delta S^0 \)) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant \( K_0 \) is given by the equation:

\[
\Delta G^0 = -RT\ln K_0 \quad \ldots (6)
\]

Where, \( \Delta G^0 \) is the free energy of adsorption (kJ/mol), \( T \) is the temperature in Kelvin and \( R \) is the universal gas constant (8.314 J mol/K). The adsorption distribution coefficient \( K_0 \) for the sorption reaction was determined from the slope of the plot of \( \ln(q_e/C_e) \) against \( C_e \) at different temperature. The adsorption distribution coefficient may be expressed in terms of enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) as a function of temperature, \( \ldots (7) \)

\[
\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \ldots (7)
\]

Where, \( \Delta H^0 \) is the standard heat change of sorption (kJ/mol) and \( \Delta S^0 \) is standard entropy change (kJ/mol). The value of \( \Delta H^0 \) and \( \Delta S^0 \) can be obtained from the slope and intercept of plot of \( \ln K_0 \) against \( 1/T \). The value of thermodynamic parameter calculated from equation 6 and 7 are shown in Table 4. The thermodynamic treatment of the sorption data indicates that \( \Delta G^0 \) values were negative at all temperature. The results point out that physisorption is much more favorable for the adsorption of Cr (VI) ion. The positive values of \( \Delta H^0 \) show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of Cr (VI) ion adsorption increases, this rules out the possibility of chemisorptions. The low \( \Delta H^0 \) value depicts Cr (VI) ion is physisorbed onto adsorbent APDC.

The negative \( \Delta G^0 \) values were confirming the spontaneous nature of adsorption Cr (VI) ion onto APDC. The lesser values of \( \Delta G^0 \) suggest that adsorption is physical adsorption process. The positive value of \( \Delta H^0 \) further confirms the endothermic nature of adsorption process. The positive values of \( \Delta S^0 \) in Table 4, showed increased randomness of the solid solution interface during the adsorption of Cr (VI) ion onto APDC.

**Kinetic models**

**Pseudo-second-order**

In order to investigate the mechanism of adsorption kinetic models (Garg, 2007 and Ghoneim, 2014)}
generally used to test experimental data. Pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations. The linearized form of pseudo-second order equation becomes.

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} \cdot \left( \frac{1}{q_e} \right) + \frac{1}{q_e} \cdot t
\]

Where, \( q_t \) (mg g\(^{-1} \)) is the amount of adsorbed Cr (VI) ion on the adsorbent at time \( t \), \( q_e \) the equilibrium sorption uptake and \( k_2 \) (min\(^{-1} \)) is the rate constant of pseudo-second-order adsorption. The plot \( t/q_t \) versus \( t \) gives a straight line says second order kinetic model is applicable then \( q_e \) and \( k_2 \) are determined from the slope and intercept of the plot, respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and these values shown Table 5.

**The Elovich equation**

The Elovich model (Pranay, 2015) equation is generally expressed as

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

Where \( \alpha \) is the initial adsorption rate (mg g\(^{-1} \) min\(^{-1} \)) and \( \beta \) is desorption constant (g/mg) during any one experiment. If Cr (VI) ion adsorption fits with the Elovich model, a plot of \( q_t \) Vs \( \ln (t) \) yields a linear relationship with a slope of \( (1/\beta) \) and an intercept of \( (1/\beta) \ln (\alpha/\beta) \). The Elovich model parameters \( \alpha \), \( \beta \), and correlation coefficient \( (R^2) \) are summarized in Table 5. This model indicates that the initial adsorption \( (\alpha) \) increases with temperature similar to that of initial adsorption rate \( (h) \) in pseudo-second–order kinetics models. This may be due to increase the pore or active site on the APDC adsorbent.

**Table 4. Thermodynamic Parameter for the Adsorption of Chromium VI Ion onto APDC**

<table>
<thead>
<tr>
<th>( (C_0) )</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>( \Delta G^o )</th>
<th>( DH^o )</th>
<th>( DS^o )</th>
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<tr>
<td>10</td>
<td>-4178.751</td>
<td>-4954.489</td>
<td>-6328.257</td>
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**Table 5. The Kinetic Parameters for Adsorption of Chromium VI Ion Onto APDC**

<table>
<thead>
<tr>
<th>( C_0 )</th>
<th>Temp °C</th>
<th>Pseudo second order</th>
<th>Elovich model</th>
<th>Intraparticle diffusion</th>
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<tr>
<td></td>
<td></td>
<td>( q_e )</td>
<td>( k_2 )</td>
<td>( R^2 )</td>
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Intra-particle diffusion model

Kinetic data was further analyzed using the intra-particle diffusion model (Rahman, 2015) based on the following equation.

\[ \log R = \log K_d + \alpha \log t \]  

Where, \( K_d \) is the intra-particle diffusion rate constant and \( \alpha \) is related to the thickness of the boundary layer. According to above equation a plot of \( \log R \) versus \( \log t \) gives a straight line that's says the adsorption mechanism follows the intra-particle diffusion process and the evidence of correlation co-efficient values are close to unity.

Conclusion

The adsorption of Cr (VI) ion onto APDC was highly dependent on the contact time, pH, adsorbent dosage, and other ionic strength. The adsorption data was fitted well by pseudo-second order, Elovich model, and intra particle diffusion models that are indicating chemical reaction is involved in the adsorption process. The adsorption process was found to be controlled by three steps of diffusion mechanisms. The isotherm equilibrium data fitted well with Langmuir isotherm model and the monolayer adsorption capacity was found to be 68.616 mg/g. Thermodynamic parameters are the negative values of \( \Delta G^0 \) indicated the spontaneity of Cr (VI) ion adsorption process and the positive values of \( \Delta H^0 \) and \( \Delta S^0 \) showed the endothermic nature. This study proved that it’s possible to remove Cr (VI) ion from aqueous solution using \( Pergularia daemia \) stem carbon.

References


