Activated Carbon *Merremia emarginata* (Acme) Adsorbs Hexavalent Chromium From Synthetic Aqueous Solutions

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ABSTRACT

In this study, preparation of adsorbent from *Merremia emarginata* stem and its application for the adsorption of chromium (VI) from aqueous solution was studied. The batch adsorption experiments were carried out to study the effect of contact time, adsorbent dose, effect of pH and effect of other ionic concentration on the removal of chromium (VI) by activated carbon. The equilibrium adsorption data were analyzed by Freundlich and Langmuir isotherm models. The thermodynamic parameters such as change in free energy ($\Delta G^°$), enthalpy ($\Delta H^°$) and entropy ($\Delta S^°$) were determined. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo-second order model, Elovich model and Intraparticle diffusion model the value of rate constant for adsorption process was calculated. This study indicated that activated carbon *Merremia emarginata*, which is inexpensive, has efficiency to remove chromium (VI) from aqueous solution.

Key words: Activated Carbon Merremia emarginata, (ACME), Chromium (VI) ion, Adsorption isotherm, Thermodynamic parameters, Kinetics, Equilibrium models.

Introduction

Heavy metal ions have become an ecotoxicological hazard of prime concern and increasing significance, because of their accumulation in living organisms. Chromium (VI) is considered to be a bioavailable element due to its good solubility in water, strong oxidation properties and permeability through cell membranes. Unfortunately, chromium (VI) compounds cause toxic, mutagenic and carcinogenic effects on individual organisms (Arivoli et al., 2010; Arivoli et al., 2008). Chromium (VI) is one of the most toxic and its effects are carcinogenic, mutagenic, and teratogenic to humans and animals. The removal of these toxic metals from aqueous solution has a significant effect over the past decades on the reduction and their impact on the environment (Arthur et al., 2009; Duwiejuah et al., 2017). Several physical and chemical methods have been technologically advanced for the removal of toxic metals from aqueous solution. It is more and more often observed that their permissible concentration in surface waters is exceeded several times, which is why it is extremely important to search for effective and economical methods of removing them. Adsorption is one of the more effective, reusability of
material, low-cost, ease of process, short time and eco-friendly approach. Activated carbon is the most widely used adsorbent and can be prepared from biomass (Houmei Liu et al., 2017; Jun-jie Gao et al., 2013). In this research, activated carbon prepared from *Merremia emarginata* stem, modified with concentrated H$_2$SO$_4$. Batch method static conditions, adsorption isotherms, thermodynamic parameters and adsorption kinetics were determined.

**EXPERIMENTAL**

The chemicals used in these experimental activities were all of analytical grade. The standard stock solution of chromium (1000 mg/l) was prepared by dissolving calculated amount of 99.9% analytical-grade K$_2$Cr$_2$O$_7$ in 1000 ml of distilled water. All the required solutions are made ready with analytical-grade reagents and double-distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration.

**Preparation of adsorbent**

The present work, a locally available plant, known by the local community as *Merremia emarginata*, was used as an adsorbent and this natural biomaterial is abundantly available at local area of Poompuhar. The stem of *Merremia emarginata* was washed with distilled water to remove the dirt and dust, successively dried in a hot air oven at 110 °C. Afterward, carbonization of the stem was carried out by adding w/v ratio Con. H$_2$SO$_4$ to get the primary carbon. The primary carbon was activated by thermal under mandatory conditions.

**Batch experiments**

The method of batch experiments (Kismir and Aroguz, 2011; Klimiuk et al., 2003) were conducted to study the influence of important parameters like contact time, adsorbent dose, initial pH and ionic strength on the removal of Cr (VI) ions onto activated carbon *Merremia emarginata*. For Adsorption Isotherms, Cr (VI) ion solution of different concentrations (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 120 rpm 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. The amount of adsorption at time t, qt (mg/g), can be determined using the following formula,

\[ q_t = \frac{V}{w} \left( C_0 - C_t \right) \]  (1)

Where, \( q_t \) is the mass of adsorbed Cr (VI) ion per unit mass of adsorbent (mg g$^{-1}$), \( V \) is the volume of the treated solution (ml), \( w \) is the mass of adsorbent (g), \( C_0 \) and \( C_t \) are the initial and actual concentration (g dm$^{-3}$) of Cr (VI) ion at time, respectively. The percentage of removal can be calculated as following mathematical formula,

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

**Results and Discussion**

**Effect of contact time**

The effect of contact time (Lanin et al., 2017; Li et al., 2009) on the removal of Cr (VI) on to ACME adsorbent and to determine the optimum contact time between the adsorbate and adsorbent, the experiment was carried out at room temperature and altered the contact time like 10, 20, 30, 40, 50 and 60 min. using 25 mg adsorbent dose and by optimal pH of the solution. These results were shown in Fig. 1 and the equilibrium data are given in Table 1. The Fig. 1 shows that the removal of Cr (VI) was initially rapid at that time maximum of the adsorption was complete with in 30 min; equilibrium was achieved with in 50 min. therefore all subsequent experiments were selected for 60 min.

![Fig. 1. Effect of contact time on the removal of Cr (VI) ion](image)

[Cr (VI) ion.]=10 mg/l; Temperature 30 °C; Adsorbent dose=0.025g /50 ml

**Effect of adsorbent dosage**

The effect of ACME dose was studied by varying amount of adsorbent like 10, 25, 50, 100, 200 and 250 mg the adsorbent dose (Liu et al., 2010) for 10 mg/l
of Cr (VI) ion solution. The percentage of adsorption increased with increases in the ACME dose, which is attributed to increased carbon surface area and the availability of more adsorption sites. The results obtained from this study are shown in Fig. 2, it reveals that 25 mg of adsorbent dose enough to each experiments.

![Fig. 2. Effect of Adsorbent dose on the Removal of Cr (VI) ion](image)

[Cr (VI) ion]=10mg/l; Temperature 30 °C; Contact Time 60 min

**Effect of pH**

Effect of solution pH (Maria et al., 2019) was studied in the pH range of 3-9 for removal of Cr (VI) ion from aqueous solution and keep on other parameters are constant. The percentage removal maximum at pH 6.8 that is pH zpc (Zero point charge) shown in Figure 3. The pH zpc of any adsorbent is a very important characteristic at which the surface has net electrical neutrality there is no competitive effect. The neutral surface of adsorbent occur support for the maximum removal of Cr (VI) ion from aqueous solution, as the result pH of solution was optimized as pH 6.8.

![Fig. 3. Effect of Initial pH on the Removal of Cr(VI) ion](image)

[Cr (VI) ion]=10mg/L; Contact time=60 min.; Adsorbent dose= 0.025g/50mL.

**Effect of ionic strength**

The effect of ionic strength (Soltzberg et al., 2007) was determined using different concentrations of chlorine solution such as 10, 25, 50, 100, 250 and 500 mg/l, and these results are shown in Fig. 4. Chlorine concentrations range from 10 to 25 mg when the removal capacity decreases reveals an increase in competitive adsorption. Here after increases the ionic strength of solution as well as removal capacity for that reason an electric double layer is formed on the adsorbent.

![Fig. 4. Effect of ionic strength on the removal of Cr (VI) ion](image)

[Cr (VI) ion]=10mg/L; Adsorbent dose= 0.025g/50mL.

**Adsorption isotherm Models**

The adsorption isotherm study was reveals that adsorption mechanism, the Freundlich model (Syed Qummer Zia Gilani et al., 2021) which is an indicative of surface heterogeneity of the adsorbent is described by the following equation,

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

(3)

Where, Kf and 1/nf are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between log qe and log Ce for the adsorption of Cr (VI) ion were shown Figure 5, as a result listed in Table 2.

The Langmuir adsorption isotherm (Vijayakumaran et al., 2009) equation which is valid for monolayer adsorption on to a surface is given below,

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}
\]

(4)

Where, qe (mgg-1) is the amount adsorbed at the equilibrium concentration Ce (mol L-1), qm (mgg-1)
Table 1. Equilibrium parameters for the adsorption of Cr (VI) ion onto ACME

<table>
<thead>
<tr>
<th>C₀</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>0.994</td>
<td>0.806</td>
<td>0.538</td>
</tr>
<tr>
<td>20</td>
<td>3.494</td>
<td>2.689</td>
<td>2.43</td>
</tr>
<tr>
<td>30</td>
<td>6.146</td>
<td>5.86</td>
<td>5.106</td>
</tr>
<tr>
<td>40</td>
<td>9.429</td>
<td>8.623</td>
<td>8.179</td>
</tr>
<tr>
<td>50</td>
<td>17.146</td>
<td>16.178</td>
<td>15.88</td>
</tr>
</tbody>
</table>

is the Langmuir constant representing the maximum monolayer adsorption capacity and KL (L mol⁻¹) is the Langmuir constant related to energy of adsorption. The plots drawn between Ce/qe and Ce, shown in figure 6, the feasibility of isotherm by the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor RL for the following equation.

\[
R_L = \frac{1}{1 + KLC_0}
\]

(5)

Where, Co (mg/L) is the initial concentration of Cr (VI) ion and KL (L/mg) is Langmuir isotherm constant. The parameter RL indicates the nature of shape of the isotherm accordingly.

RL> 1 - Unfavorable adsorption
0 < RL < 1 - Favorable adsorption
RL = 0 - Linear adsorption

The RL values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (Co) and temperatures studied. The calculated RL values are given in Table 3.

Table 2. Freundlich and Langmuir isotherm parameter for the adsorption of Cr (VI) ion onto ACME

<table>
<thead>
<tr>
<th>Model</th>
<th>Constant</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Kₑ (mg/g) (l/mg)⁴/n</td>
<td>18.583</td>
</tr>
<tr>
<td></td>
<td>nₑ</td>
<td>2.068</td>
</tr>
<tr>
<td></td>
<td>Rₑ</td>
<td>0.974</td>
</tr>
<tr>
<td>Langmuir</td>
<td>qₑₘ (mg/g)</td>
<td>82.696</td>
</tr>
<tr>
<td></td>
<td>Kₑ (l/mg)</td>
<td>0.237</td>
</tr>
<tr>
<td></td>
<td>Rₑ</td>
<td>0.985</td>
</tr>
</tbody>
</table>

Thermodynamic treatment of the adsorption process

Thermodynamic (Xin-jiang Hu et al., 2011) parameters studied the following equations, is physical adsorption process. The positive value of ΔH° further confirms the endothermic nature of adsorption process. The positive values of ΔS° showed increased randomness of the solid solution interface during the adsorption of Cr (VI) ion onto ACME.

\[
\Delta G^0 = -RT\ln K_v
\]

(6)

\[
\ln K_v = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

(7)

Where, ΔG₀ is the free energy of adsorption (kJ/mol), T is the temperature in (K), R is the universal gas constant (8.314 J mol/K), ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is stan-
firming the spontaneous nature of adsorption Cr (VI) ion onto ACME. The lesser values of $\Delta G^\circ$ suggest that adsorption.

### Kinetic models

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:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \quad (8)$$

Where, $q_t$ (mgg$^{-1}$) is the amount of adsorbed Cr (VI) ion on the adsorbent at time $t$, $q_e$ the equilibrium sorption uptake and $k_2$, is the rate constant of pseudo-second-order adsorption (min$^{-1}$). The plots drawn between $t/q_t$ and $t$ gives a straight line says second order kinetic model is applicable then $q_e$ and

### Table 4. Thermodynamic parameter for the adsorption of Cr (VI) ion onto ACME

<table>
<thead>
<tr>
<th>(C0)</th>
<th>30 °C</th>
<th>40 °C</th>
<th>50 °C</th>
<th>60 °C</th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-5550.905</td>
<td>-6333.656</td>
<td>-7698.83</td>
<td>-8090.241</td>
<td>21.8</td>
<td>90.3</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-3911.632</td>
<td>-4846.194</td>
<td>-5312.53</td>
<td>-6269.767</td>
<td>18.9</td>
<td>75.4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-3416.174</td>
<td>-3684.168</td>
<td>-4254.08</td>
<td>-4638.467</td>
<td>9.43</td>
<td>42.2</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-2963.232</td>
<td>-3361.318</td>
<td>-3648.22</td>
<td>-3982.104</td>
<td>7.17</td>
<td>33.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-1638.164</td>
<td>-1919.154</td>
<td>-2053.87</td>
<td>-2180.548</td>
<td>3.72</td>
<td>17.8</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5. The kinetic parameters for adsorption of Cr (VI) ion onto ACME

<table>
<thead>
<tr>
<th>C0</th>
<th>Temp °C</th>
<th>$q_e$</th>
<th>$k_2$</th>
<th>$R^2$</th>
<th>$h$</th>
<th>$q_e$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$R^2$</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>19.8804</td>
<td>0.00669</td>
<td>0.9942</td>
<td>2.6446</td>
<td>27</td>
<td>0.361</td>
<td>0.9592</td>
<td>43.1899</td>
<td>0.175</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>19.7794</td>
<td>0.00912</td>
<td>0.9965</td>
<td>3.5675</td>
<td>120</td>
<td>0.445</td>
<td>0.9592</td>
<td>52.1091</td>
<td>0.135</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>19.7595</td>
<td>0.0154</td>
<td>0.9986</td>
<td>6.0213</td>
<td>6700</td>
<td>0.667</td>
<td>0.9592</td>
<td>66.317</td>
<td>0.0844</td>
</tr>
<tr>
<td>40</td>
<td>30</td>
<td>19.764</td>
<td>0.0164</td>
<td>0.9988</td>
<td>6.4198</td>
<td>13000</td>
<td>0.703</td>
<td>0.9592</td>
<td>6.2444</td>
<td>0.0796</td>
</tr>
<tr>
<td>50</td>
<td>30</td>
<td>19.7595</td>
<td>0.0154</td>
<td>0.9986</td>
<td>6.0213</td>
<td>6700</td>
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<td>0.9592</td>
<td>66.317</td>
<td>0.0844</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
<td>19.764</td>
<td>0.0164</td>
<td>0.9988</td>
<td>6.4198</td>
<td>13000</td>
<td>0.703</td>
<td>0.9592</td>
<td>6.2444</td>
<td>0.0796</td>
</tr>
</tbody>
</table>

**Fig. 5.2.** Langmuir adsorption isotherm for the removal of Cr (VI) ion
k2 are determined from the slope and intercept of the plots respectively. The high regression value indicates the adsorption reaction exist a pseudo-second-order and these values are shown in Table 5.

The Elovich model equation is generally expressed as,

\[ q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t \]  \hspace{1cm} (8)

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 plots drawn between \( q_t \) and \( \ln(t) \) 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. Kinetic data was further analyzed using the intra-particle diffusion model based on the following equation.

\[ \log R = \log K_d + a \log t \]  \hspace{1cm} (9)

Where, kid is the intra-particle diffusion rate constant and it’s related to the thickness of the boundary layer. According to above equation a plots drawn between \( \log R \) and \( \log t \) gives a straight line that’s says the adsorption mechanism follows the intra-particle diffusion process in addition to the evidence of correlation co-efficient values are close to unity.

**Conclusion**

Due to its effectiveness in chromium ion adsorption from synthetic aqueous solution, this study advised using activated carbon *Merremia emarginata* as an alternative adsorbent for removal of heavy metal ions from the industrial effluents. The maximal monolayer adsorption capacity \( (q_m) \) was determined to be 82.696 mg/l and the isotherm equilibrium values suited the Langmuir isotherm model well. Thermodynamic parameters demonstrated that the spontaneity of the Cr (VI) ion adsorption process was represented by the negative value of \( \Delta G^\circ \), and the endothermic nature and growing randomness of the adsorption were shown by the positive values of \( \Delta H^\circ \) and \( \Delta S^\circ \). Pseudo-second order, Elovich model, and intra-particle diffusion models all performed well in fitting the adsorption data, showing that a chemical reaction is involved in the adsorption process. It was discovered that three steps of diffusion processes governed the adsorption process. This work provides proof that ACME, or activated carbon *Merremia emarginata*, was an effective and efficient way to remove Cr (VI) ions from aqueous solutions.

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**References**


