Adsorption of hexavalent chromium using activated carbon prepared from garden wastes

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ABSTRACT

This study investigated the treatment of wastewater by adsorption process through fixed-bed column using recycled garden waste. A new adsorbent was manufactured from agricultural waste using zinc chloride (ZnCl₂) as activated agent at 700°C for 1 h. The porosity characterization of the prepared activated carbon was investigated by the Branner-Emmett and Teller (BET) test. Three models, namely Yoon-Nelson, Thomas and Adam-Bohart were applied to represent the breakthrough curves of hexavalent chromium (Cr-VI) removals. The fixed-bed column study was conducted at different wastewater flow rates (6, 9 and 12 mL/min) and different bed depths (3, 5 and 7 cm). The removal efficiencies of Cr(VI) were increased from 42% to 95% with increase of activated carbon bed depth from 3 cm to 7 cm.

Keywords: Activated carbon; Garden waste; Adsorption; Landfill leachate; Heavy metals

1. Introduction

Wastewater can generally be defined as the liquid produced from different human activities such as sanitary, industrial, trading, and recreation. Depending on the type of activity, the wastewater is likely to contain heavy metals, nitrogen compounds, salts, and various types of organic matter [1]. Hence, wastewaters need to be treated before it can be discharged into the environment. Effective and affordable treatment options have to be identified in order to avoid negative impacts of such wastewater when discharged into water bodies. Adsorption is the most widely used method for treating different types of wastewater [2]. The high porosity of activated carbon (AC) makes it a good adsorbent [3–9] as one gram (1 g) of AC has a surface area of about 1000 m². This surface area allows collection of a large number of polluted molecules [10]. Activated carbon has been proven to be an effective adsorbent for many chemicals such as phenols, metal ions, detergents and others [11]. Furthermore, heavy metals among all other pollutants have been significantly associated with various diseases and disorders as aquatic pollutants [12,13]. Due to this, heavy metals should be prevented from reaching the natural environment through all feasible and effective measures [14]. In recent years, attention has been diverted towards the bio-sorption of biomaterials which are by-products of large scale industrial operations and/or agricultural waste materials [14]. Many studies have been conducted to produce cheap bio-sorbents to replace the traditional costly conventional wastewater treatment methods [15]. Blajai used microalgae namely Oscillatoria acuminata and Phormidiumirrigum as adsorbent for heavy metals from tannery effluent of Ranipet industrial area. Biosorption efficiency of Oscillatoria acuminata and Phormidiumirrigum was 90%.
and 80% respectively [16]. Most adsorption studies have been focused on the use of untreated as well as treated agricultural waste such as almond shells [17], Artocarpus heterophyllus [18], Ficus auriculata leaves [19], Spirogyra biomass-packed [20], Pistachio Shells [21], coconut shells [22,23], bamboo [24,25], sugarcane bagasse [26], and sago palm bark [4].

This study focuses on the utilization of a new agricultural waste to make activated carbon for treating wastewater through adsorption process in order to eliminate the high concentration of hexavalent chromium. Both the activation and carbonisation processes are followed simultaneously for activation. The precursor acts as oxidants and dehydrating agents in the process.

2. Materials and methods
2.1. Adsorbent preparation

The agricultural garden wastes used in the study was collected from a green area in the University Putra Malaysia (UPM) gardens in Malaysia. The sample was washed several times with water and then dried in an oven at 105°C for 24 h. The larger particles were crushed and sieved into smaller sizes less than 0.3 mm.

A horizontal chamber furnace was used for high temperature (300°C) application in the carbonization step of activated carbon preparation. In the second step of activation, the carbonized sample was activated with ZnCl₂ at an impregnation ratio of 1/1 (w/w) then dried at 100°C for 24 h. After drying, the sample was again activated for 1 h at 700°C under nitrogen flow (100 mL/min). In the chemical activation process, both the activation and carbonisation processes are carried out simultaneously. The precursor is mixed with activation agents, which acts as oxidants and dehydrating agents at low temperatures. The agent decreases the ash content of the carbonised products and increases the surface area with large porosity [27].

2.2. Adsorbent characterization

The oven-dry method (ASTM D 2867-09) was used to determine moisture content of the prepared AC sample by placing the sample into a dry and closed capsule. Then placing the capsule in a drying oven at temperature ranging from 145–155°C. After the sample is dried, it is weighted again accurately. The moisture content of the sample is expressed as the percentage difference of weight. The ash content was determined by taking weight of 0.1 mg dried sample in a crucible of known weight. The ash content remained [28].

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The BET (Brunauer, Emmett and Teller) test was used to determine the surface porosity characterizations of prepared activated carbon over a relative pressure ranged between 0.01-0.3 [29].

2.3. Surface area characterization of activated carbon

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2.4. Removal mechanism

The adsorption process is highly effective in removing ions or molecules from the aqueous solutions through the means of absorbing onto the energetically heterogeneous solid surfaces. Activated carbon is one of the commonly effective adsorbent which is used to treat hazardous and sanitary wastewater.

There are two types of adsorption, physical and chemical. In physical adsorption, no electron exchange occurs between adsorbate and adsorbent and forces such as hydrogen bonding and Van der Waals hold the adsorbate to the surface. The chemical adsorption process requires electrons transfer and sharing between the adsorbent and the adsorbed species.

2.5. Fixed-bed column models

The removal efficiency of parameter can be assessed using the following formula [30]:

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

where \( C_0 \) is initial concentration, and \( C_e \) concentration at time.

Three models, namely Thomas, Yoon-Nelson and Adam-Bohart were used to represent the Chromium removal efficiency through the fixed-bed columns of prepared AC.
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2.5.1. Thomas model

The Thomas model is represented by the following equation:

\[
\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{K_{\text{Th}} q_{\text{Th}} W}{Q} - K_{\text{Th}} C_0 t
\]

where \(K_{\text{Th}}\): Thomas rate constant (mL/min mg), \(q_{\text{Th}}\): predicted bed capacity (mg/g), \(W\): mass of the adsorbent (g), and \(Q\): feed flow rate (mL/min).

We determined the equilibrium uptake \(q_{\text{Th}}\) and Thomas rate constant, \(K_{\text{Th}}\), based on the linear regression analysis of \(\ln \left( \frac{C_0}{C_t} - 1 \right)\) vs. \(t\).

2.5.2. Yoon–Nelson model

\[
\ln \left( \frac{C_0}{C_t} - \frac{1}{C_0} \right) = \frac{k_{\text{YN}} C_o W}{Q} - k_{\text{YN}} t - \tau_{\text{YN}}
\]

where \(k_{\text{YN}}\): Yoon-Nelson velocity rate constant (1/min), and \(\tau\): time (min) needed for a 50% adsorbate breakthrough.

A linear plot of \(\ln \left( \frac{C_0}{C_t} - \frac{1}{C_0} \right)\) vs. sampling time, \(t\), was used for determining the different model parameters, \(k_{\text{YN}}\) and \(\tau\).

2.5.3. Adam's–Bohart model

\[
\ln \left( \frac{C_0}{C_t} \right) = \frac{k_{\text{AB}} C_0 W}{Q} - k_{\text{AB}} N_0 F Z
\]

where \(C_0\): inlet concentration (mg/L), \(C_t\): final concentrations (mg/L), \(k_{\text{AB}}\): adsorption rate constant (L/mg min), \(F\): linear velocity (cm/min) which can be determined through dividing the flow rate (mL/min) by column sectional area (cm²), \(N_0\): saturation concentration, (mg/L), \(t\): flow time (min), and \(Z\): bed depth of adsorbent (cm).

Fig. 1. SEM scan of raw material and activated carbon.

Fig. 2. EDX analysis of raw material and activated carbon.
3. Results and discussion

3.1. Effect of flow rate and bed depth

In this study, three different flow rates (6.0, 9.0, 12 mL/min) were used in the experimental work to investigate the effect of flow rate on the final concentration of hexavalent chromium.

Fig. 3 shows the breakthrough curve for Cr(VI) using three different bed depths (3.0, 5.0 and 7.0 cm) of activated carbon with a flow rate of 6 mL/min. While Figs. 4 and 5 show the breakthrough curves of Cr(VI) for flow rate 9 mL/min and 12 mL/min respectively. The initial concentration of Cr(VI) was 6.5 mg/L in raw sample. After adsorption treatment using activated carbon of 3 cm deep bed, the final concentration was 2.3 mg/L, while the final concentrations were decreased to 1.2 mg/L and 0.3 mg/L with the increased activated carbon bed depths of 5 cm and 7 cm, respectively. The achieved Cr(VI) removal efficiencies with the use of activated carbon beds having depths 3 cm, 5 cm, and 7 cm were 42%, 81% and 95%, respectively. These removal efficiencies were higher than other reported achievements [8] in batch adsorption treatment using garden waste as activated carbon for Cr(VI) (93%) at 5 mg/L adsorbent dose and 180 min contact time. Also, it can be seen from the figures that the increase in discharge causes negative effect on the efficiency of mass transfer which results in decreases the required time for bed saturation. Similar results have been reported by others [31–34].

The breakthrough curves of Cr(VI) for three different flow rates 6.0, 9.0 and 12 mL/min are shown in Figs. 3, 4 and 5. The increase in AC bed depth in the fixed-bed column resulted in an increase in saturation time which represents the time required for the bed to become saturated. This is as a result of availability of higher number of active sites in the surface area [35].

3.2. Modelling of the column study

The dynamic behaviour of the fixed-bed adsorption results was evaluated using the Thomas, Yoon-Nelson and the Adam’s-Bohart models.

3.3. Thomas model

The results of the Thomas model parameters, $K_{th}$ and $q_{th}$ for Cr(VI) at flow rates of 6.0, 9.0 and 12 mL/min are presented in Tables 2, 3 and 4 respectively. It can be seen from the tables that there were increase in the $K_{th}$ and $q_{th}$ values when adsorbent bed depth increased from 3 cm to 7 cm. However, for 12 mL/min flow rate $K_{th}$ decreases with the increase in bed depth.

<table>
<thead>
<tr>
<th>Adsorbent bed depth (cm)</th>
<th>$K_{th}$ (L/min mg)</th>
<th>$q_{th}$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.0475</td>
<td>18.715</td>
<td>0.882</td>
</tr>
<tr>
<td>5</td>
<td>0.0864</td>
<td>24.839</td>
<td>0.961</td>
</tr>
<tr>
<td>7</td>
<td>0.0932</td>
<td>54.710</td>
<td>0.905</td>
</tr>
</tbody>
</table>
The results of the Yoon-Nelson model parameters ($K_{YN}$ and $\tau$) are presented in Tables 5, 6 and 7 for the flow rates of 6, 9 and 12 mL/min respectively. The results show that as the bed height increases from 3 cm to 7 cm, there are increases in the $\tau$ value used in the model. Comparing the $R^2$ values for the Thomas and the Yoon-Nelson models, it can be concluded that both the models can be satisfactorily used for predicting Cr(VI) adsorption performance in a fixed-bed column.

3.5. Adam's-Bohart model

Tables 8, 9 and 10 present the constants of Bohart-Adams model based on the slopes and the intercepts of the best-fit lines. It is clear from these tables that there were decreased in the $K_{AB}$ values with the increased bed heights. The Adam-Bohart adsorption model provides a comprehensive and simple approach for conducting and evaluating the Cr(VI) removal efficiency through treatment using prepared AC.

4. Conclusions

The study was conducted to assess the effectiveness of treating Cr(VI) (hexavalent chromium) from wastewater through adsorption process using activated carbon (AC) from garden waste. The high porosity characteristic of prepared AC makes it a good adsorbent in removing heavy metals (especially Cr(VI)) from wastewater. The adsorption process was conducted using fixed-bed column with different bed depths of AC and flow rates. The final concentration
of Cr(VI) was decreased to 0.3 mg/L with a 7 cm deep adsorber bed. The removal efficiency of Cr(VI) was increased from 42 to 95% with an increase in bed depth from 3 to 7 cm. The results of breakthrough curves of Cr(VI) indicated that the increase in bed depth resulted an increase in saturation time. It can be concluded from the experimental results that the prepared activated carbon is efficient in removing pollutants such as Cr(VI) from wastewater using adsorption process because of its high adsorbent surface area.

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References


