ICCCP 2012: 5-6 May 2012, Kuala Lumpur, Malaysia

Adsorption of Copper (II) From Aqueous Medium In Fixed-Bed Column By Kenaf Fibres

Hasfalina C.M. a,*, Maryam R. Z. a, Luqman C.A. b, Rashid M. c

a Department of Biological & Agricultural Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor Malaysia.
b Department of Chemical and Environmental Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor Malaysia.
c Malaysia-Japan International Institute of Technology, UTM International Campus, 54100 Kuala Lumpur, Malaysia.

Abstract

The adsorption of Copper (II) from aqueous solution by kenaf (Hibiscus cannabinus, L) fibres was investigated in fixed-bed column. The effect of selected operating parameters such as flow rate and bed depth was evaluated. The breakthrough data fitted well to Bed Depth Service Time (BDST) and Thomas models with high correlation coefficient, $R^2 \geq 91$. The highest bed capacity was obtained at 47.27 mg/g using 100 mg/L of initial Copper (II) and 6 mL/min flow rate. The results showed that kenaf fibres can be an effective adsorbent for Copper (II) removal.

Keywords: Adsorption of Copper (II), kenaf, fixed-bed column, breakthrough curve

1. Introduction

The contamination of wastewater by toxic heavy metals is worldwide environmental problem. Heavy metals are classified as toxic materials due to their non-biodegradability and bioaccumulation tendency in living organisms. Its excessive amount cause health problem in animals, plants and humans. These metals contaminates are leading to surface waters through different industrials activities.

A number of techniques e.g. chemical precipitation, adsorption, ion exchange, and biological treatment

have been employed. Although these techniques have been widely used, they possess limitations such as are high O&M cost and formation of byproducts [1]. Cu (II) is essential for some biosynthesis in human body and is well-known as micronutrients for animals and plants, but it is toxic at high concentration. When it is exceeding than standard level, it could cause anemia and stomach intestinal distress. It also increases the risk for lung cancer [1,2].

Recently, there is growing interest to use agriculture byproducts as an adsorbent to remove heavy metals from wastewater. It has been widely investigated as the alternative method of treatment for current costly methods. Raw and natural agricultural wastes are among the cheap adsorbents [1,3,4]. There are several different kinds of agricultural byproducts which have been used to remove heavy metals [5] such as sunflower stalks [6], Eucalyptus bark [7], rice husk [8, 9, 10, 11], wheat bran [12], mushroom biomass [13], fruit peel of orange [14,15], Ficus religiosa leaves [16] and waste tea leaves [17, 18].

Recent studies have demonstrated potential use of kenaf (Hibiscus cannabinus, L) core and bast fibres to enhance bioremediation [19], adsorption [20,21], sound absorption and thermal insulation [22]. Kenaf has shown good capacity to remove heavy metals from aqueous solution in batch studies [23, 20]. Sajab et al. [20] reported that alkali-treated kenaf core fibres exhibited the highest Cu(II) sorption at 0.38 mmol/g in batch experiments. The results of batch study however, may not be directly being applied for field applications in the wastewater treatments. Although few studies have been conducted for Cu (II) removal by using kenaf, column studies have not been studied elsewhere. Hence this present work investigated the adsorption capacity of kenaf fibres using Cu (II) in fixed-bed continuous column. The effect of bed height and flow rate on the column performance was evaluated. The breakthrough data was analyzed using Bed Depth Service Time (BDST) and Thomas models.

2. Experimental

2.1. Kenaf fibres Characterization

The BET surface areas of the kenaf fibres were analyzed using a BET analyzer. The surface morphology of the kenaf fibres was visualized using a scanning microscope (SEM, Hitachi).

2.2. Adsorbent

The kenaf (Hibiscus cannabinus, L) stalk was obtained from Institute of Tropical Forestry and Forest Products (INTROP), Malaysia. Whole stalks of kenaf were chipped into smaller size using a chipper mill. Kenaf chips were dried at ambient temperature and grounded. The kenaf particles were then rinsed with distilled water and dried overnight at 38°C and stored in a dessicator prior to use. Then the kenaf fibres were sieved using 1.0 mm stainless steel sieve to collect uniform size particles.

2.3. Adsorbate

Stock solution of Cu (II) was prepared in distilled water by dissolving copper nitrate (Cu (NO₃)₂·3H₂O) to make 1000 mg/L of solution. The working solutions were prepared daily from stock solutions by diluting to appropriate volumes. The Cu (II) concentrations in the solutions were determined using atomic absorption spectroscopy (AAS, Perkin-Elmer, 5100PC). The pH of the solution was measured using the pH meter.
2.4. Column Set-up

The PVC column was employed with the size of 10 cm diameter and 70 cm height. A known amount of adsorbent was packed in the column at the required adsorbent bed depth. Two cm thick of glass wool was placed at the bottom of the column to prevent the adsorbent media from leaching into and clogging the drainage area, as well as on the top of the adsorption column to increase the distribution of the solution onto the adsorbent surface and maintain a constant flow rate. The initial concentration of Cu (II) solutions at 100 mg/L were pumped downward into the column by peristaltic pump (Eyela Poller Pump, RP-1000). Lower concentration of metal ions solution was used to obtain a gentle breakthrough curve as industrial effluents discharge are within this range [24]. The column was operated until the concentration of metal ions in the effluents reached the value of about 99.5 mg/L. The column study was carried out at room temperature and all column experiments were performed in triplicates.

2.5. Effect of Bed Depth and Flow Rate

The adsorption media (kenaf biomass) was packed into the columns at four different depths to study the effect of bed depth such as at 15 cm (174 g), 20 cm (232 g), 25 cm (290 g), and 30 cm (348 g). Different flow rates were adjusted to study the effect of flow rate at 4 mL/min, 6 mL/min, and 9 mL/min. An initial concentration was fixed at 100 mg/L and pH 5.0. This was in accordance with the previous batch study [23]. The effluent was collected at the bottom of the column every hour until the breakthrough curve was obtained. The samples were analyzed by AAS. The statistical analysis was performed by SAS software (V.6.12).

3. Results and Discussion

The study was carried out to evaluate the effect of design parameters such as bed depth and flow rate on the shape of breakthrough time and adsorption capacity. The shape of breakthrough curves was found to be affected by the linear velocity, concentration of metal ions in the feed and the bed height [25, 26, 27, 28, 29].

3.1. Characterization of the Adsorbent

Figure 1 illustrates the SEM micrograph of kenaf fibres. The morphology of the kenaf fibres was observed to display a plate-like structure with agglomerated and irregular surface structure. The coarse surfaces of kenaf fibres indicate that it has high porosity. Pores formed on surface of kenaf fibres with the size ranging from 1 to 21 μm pores could act as active sites in adsorption.

Fig.1. Scanning Electron Micrograph (SEM) of raw kenaf fibres.
The BET surface area of raw kenaf fibres was 3.46 m²/g. The BET of kenaf fibres was much higher compared to chitosan with BET value of 1.05 m²/g [30]. This superior properties could give higher surface area to the kenaf fibres, thus provides more active sorption sites for adsorption to occur.

3.2. Effect of Bed Depth on Breakthrough Curve

Adsorption of metals in the fixed-bed column is largely depending on the quantity of adsorbent in the column. As the bed depth increased, the volume of metal solution treated and the amount of heavy metals removal increased, respectively (Table 1). It can be seen that the breakthrough time ($t_b$) and exhaustion time ($t_e$) increase with increase in bed depth. Figure 2 illustrates breakthrough curves obtained at different bed depth (15, 20, 25 and 30 cm) with a constant influent of 100 mg/L and flow rate of 6 mL/min. The slope of the S-shape from $t_b$ to $t_e$ decreased as the bed height increased from 15 to 30 cm, indicating the breakthrough curve becomes steeper as the bed height decreased.

Table 1. Experiment constant of BDST model for Cu (II) adsorption onto kenaf (C₀ =100 mg/L, pH= 5.0, flowrate = 6 mL/min)

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>qₑ (mg/g)</th>
<th>$t_b$ (hr)</th>
<th>$t_e$ (hr)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>43.733 ± 0.86</td>
<td>4.11</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>45.123 ± 0.45</td>
<td>5.322</td>
<td>28</td>
<td>0.98</td>
</tr>
<tr>
<td>25</td>
<td>46.992 ± 0.66</td>
<td>6.417</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>47.272 ± 1.49</td>
<td>8.3</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>

The adsorption capacity of Cu (II) increased slightly with an increased in bed depth from 43.733 ± 0.86 mg/g to 47.272 ± 1.49 mg/g, which could be due to increase in the surface area of the adsorbent and longer contact time. A higher bed height indicates a larger amount of binding sites available. Similar observations also have been reported by several researchers [2, 23, 27, 28, 29, 30]. The longer exhaustion time ($t_e$, the time that the effluents reach 99.5 mg/L) was observed by increasing the bed depth from 15 to 30 cm. The exhaustion time also increased from 24 to 37 hours. After breakthrough time ($t_b$, the time that the effluents reach 1.0 mg/L), the concentration of effluent of metal ions rapidly increases. The shape and gradient of the breakthrough curves were slightly different for different bed depth [26, 31].
The BDST model is one of the most commonly used to describe the heavy metals adsorption using a packed bed system [30]. The BDST equation (1) below shows a linear relationship between the bed height and breakthrough time, often called service time at the bed.

$$ t = \frac{N_0 Z}{C_0 \theta} - \frac{1}{K_a C_0} \ln\left( \frac{C_0}{C_b} - 1 \right) $$

where $t$ is service time at breakthrough point (hour), $N_0$ is adsorption capacity per volume of bed (mg/cm$^3$), $Z$ is the depth of adsorbent bed (cm), $C_0$ is influent or initial solute concentration (mg/L), $\theta$ is linear flow rate (cm/h), $K_a$ is rate constant of adsorption (L/mg.h) and $C_b$ is the effluent concentration at breakthrough point (mg/L).

The plot of service time against bed depth at a flow rate of 6 mL/min was linear indicating the validity of BDST model (Fig.3). The results of different bed depth showed the validity of BDST model to study adsorption of Cu (II) with the regression coefficient ($R^2$) of 0.98, respectively (Table 1). The value of adsorption capacity of the bed per unit of bed volume, $N_0$ and the rate constant, $K_a$ were computed from the slope and intercept of BDST plot assuming initial concentration, $C_0$ and the linear velocity, $\theta$ as constant. The rate constant, $K_a$ is a measure of the rate transfer of metal solution from the fluid phase to the solid phase. For Cu (II) the values of $N_0$ and $K_a$ were 33.575 mg/L and 0.0202 L/mg.h, respectively. The parameters obtained from BDST plot can be used to scale-up the process [23, 32].

![BDST model plot for Cu (II) adsorption onto kenaf. (C_0= 100 mg/L, pH_{Cu}= 5.0, flow rate= 6 mL/min)](image)

3.3. Effect of Flow Rate on Breakthrough Curve

The importance of the study of the effect of flow rate on adsorption is due to the industrial scale-up treatment of removal of heavy metals which could be obtained from the performance in continuous column [33]. The result of the adsorption capacity of kenaf for the removal of Cu (II) at different flow rates is shown
in Table 2. Breakthrough curves of Cu (II) are shown in Fig.4. The results showed that with the increase of flow rates, the earlier breakthrough and exhaustion times were reached. The values of adsorption capacity decreased slightly when the flow rate increased (Table 2). At the lowest flow rate of 4 mL/min, the highest bed adsorption capacity was obtained at 47.388 ± 1.56 mg/g.

The reduction in the Cu(II) uptake capacity at higher flow rates is probably due to the unavailability of sufficient retention time for solute to interact with the sorbent and the limited diffusivity of solute into the sorptive sites or pores. The same findings have been reported elsewhere [30, 31, 34, 26, 23]. The decrease of adsorption capacity from 47.388 ± 1.56 mg/g to 44.987 ± 1.65 mg/g for Cu(II) was probably due to insufficient contact time for the metal solution to interact with the adsorbent (Table 2). In this case, adsorbate left column without sufficient time to diffuse into pores of the adsorbents. Thus, it results in sharper breakthrough curves. One way to increase the residence time is to decrease the flow rate. By this way metal ions have more time to diffuse into pores of biosorbent [16].

Fig. 4. Effect of different flow rate on the breakthrough curve of Cu (II) adsorption onto kenaf at 20 cm bed depth.

Thomas model is mostly used to describe the column performance and predict of breakthrough curves. The model follows the Langmuir kinetics of adsorption-desorption with assumption of negligible axial dispersion in the column adsorption as the rate driving force obeys the second-order reversible reaction kinetics [30, 26]. The linear equation of Thomas model is given below (2):

$$\ln \left( \frac{C_0}{C} - 1 \right) = \frac{k_{Th} Q_0 M}{F} - \frac{k_{Th} C_0 V}{F}$$

(2)

where, $k_{th}$ is the Thomas rate constant (mL/ min mg), $Q_0$ is the maximum ions adsorption per weight of mass (mg/g), $M$ is the amount of adsorbent in the column (g), $V$ is volume of effluent (L), $C_0$ is the influent concentration (mg/ L), $F$ is flow rate (mL/ min), and $C$ is the effluent concentration (mg/ L).
From the slope and intercept of the plotted Thomas model (Fig.5), the values of rate, \( k_{th} \) and adsorption capacity, \( Q_0 \) were determined. The Thomas model gave a good fit of experimental data with high correlation coefficient, \( R^2 \) greater than 0.91. The values of Thomas model show that the maximum adsorption capacity did not change significantly with increasing flow rates. An increased of the flow rate in the range from 4 to 9 mL/min with the constant depth of 20 cm did not affect the adsorption capacity significantly (Table 2). As the adsorption capacity did not decrease significantly by the increased of flow rate in studied range, the flow rate of 9 mL/min can be considered as the suitable flow rate. This is because when the flow rate was increased, the volume of metal solution to be treated also increased. However, the exhaustion time reduced from 38 to 20 hours for Cu (II) removal (Fig. 4). Futalan et al. [13] in the study of sorption of Cu (II) removal from aqueous solution by chitosan reported that higher flow rates enhances the mass transfer of Cu(II) ions from the liquid film to the adsorbent surface, causing to earlier saturation of the adsorbent bed.

Table 2. Constant of Thomas model for Cu (II) adsorption onto kenaf. \((C_0 = 100 \text{ mg/L}, \text{pH} = 5.0, \text{bed depth} = 20 \text{ cm})\)

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>( K_{th} ) (L/mg h)</th>
<th>( Q_{o,calc} ) (mg/g)</th>
<th>( Q_{o,exp.} ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.00243</td>
<td>45.86349</td>
<td>47.388 ± 1.56</td>
<td>0.91</td>
</tr>
<tr>
<td>6</td>
<td>0.00375</td>
<td>45.14483</td>
<td>45.124 ± 1.25</td>
<td>0.98</td>
</tr>
<tr>
<td>9</td>
<td>0.00443</td>
<td>45.03678</td>
<td>44.987 ± 1.65</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 2 show the correlation coefficient values were varied from 0.91 to 0.98 which indicate a good agreement between the experimental data and the column data generated using the Thomas model. This is further validated by Figure 5, where it shows the predicted and experimental points at different flow rates. It clearly implies a good agreement between the experimental points and simulated plots predicted by Thomas model. The rate constant, \( K_{th} \) is observed to increase from 0.00243 to 0.00443 L/mg.h with the increase in flow rate from 4 to 9 mL/min (Table 2).

Fig. 5. Thomas model for removal of Cu (II) onto kenaf.
4. Conclusions

This study proved that kenaf has good potential to be used in adsorption of Cu(II) ions from aqueous solution in fixed bed column. Thomas and BDST models have been used successfully to evaluate the column performance. The values of $K$ and $N_0$ indicated that the adsorbent could be used for removal of single metal solutions. Further research need to be done with respect to the utilization of kenaf biomass for Cu (II) removal in the full-scale wastewater treatment plant such as sorption-desorption cycles for its regeneration and reuse.

Acknowledgements

This work was supported by Universiti Putra Malaysia. The authors would like to acknowledge Institute of Tropical Forestry and Forest Products (INTROP), Malaysia for providing the kenaf stalks.

References


