Continuous Fixed-Bed Column Study and Adsorption Modeling for Cadmium Removal

N. Suganthi

Department of Chemistry, L.R.G Government Arts College for Women, Tirupur 641 604, India

Abstract: Adsorption of cadmium ions from aqueous solutions using granular activated carbon prepared from Phosphoric acid treated tamarind nuts (seeds) in fixed bed column was investigated. Activated carbon granules of 300 to 800µm particle size were chosen for all studies. The effect of metal ion concentration (50-200 mg/L), feed flow rate (5-15 mL/min) and activated carbon bed height (10-20 cm) on the breakthrough characteristics of the adsorption process were determined. The results showed that the adsorption efficiency increased with increase in influent concentration, bed depth and decreased with increase in flow rate. Column adsorption data were fitted to three well established fixed bed adsorption models namely Adam’s-Bohart, Thomas and Yoon-Nelson models. The results fitted well to Thomas and Yoon-Nelson models with coefficients of correlation R² ≥ 0.9 at different working conditions. Phosphorylated tamarind nut carbon (PTNC) was proved to be suitable for adsorption of cadmium from aqueous solutions using fixed-bed adsorption column.

Keywords: Phosphorylated tamarind nut carbon, Cadmium adsorption, fixed bed modeling

1. Introduction

Industrial growth and technological advancements have introduced diverse pollutants in surface and ground water, making it unfit for consumption by human and other living organisms. Pollutants such as heavy metals, organic chemicals and synthetic dyes are of serious concern due to their potential carcinogenic and mutagenic hazards and several ailments. These chemicals in the terrestrial environment clearly pose a significant risk to the quality of soils, plants, natural waters and human health [1,2,3,4].

Heavy metals are detrimental to the environment due to its toxic effect and accumulation throughout the food chain. Cadmium is one of the toxic heavy metals with the greatest potential hazard to humans and the environment. Chronic exposure to elevated levels of cadmium is known to cause renal dysfunction, bone degeneration and liver damage [5]. Because of the toxicity and bioaccumulation, Cd(II) is considered as a priority pollutant by the US Environmental Protection Agency. The permissible limit for Cd(II) as described by WHO is 0.01 mg/dm³. The major source of Cd(II) release into the environment is through wastewater from electroplating, smelting, paint pigments, batteries, fertilizers, mining and alloy industries [6].

The removal of heavy metal contaminants is one of the most important environmental issues to be solved today. In some circumstances, conventional treatment methods such as ion-exchange, precipitation, filtration, oxidation, reduction, electrochemical recovery, membrane separation and other techniques are either ineffective or uneconomical for the removal of trace amounts of heavy metal ions [7]. However, activated carbon adsorption has been proved to be a competitive and efficient method for the removal of trace amounts of heavy metal ions from aqueous solutions [8].

Batch adsorption experiments provide certain preliminary information such as pH, optimum time, particle size and initial metal concentration for maximum adsorption which could be adopted for fixed bed column studies. In fixed-bed column, the adsorbate is continuously in contact with a given quantity of fresh adsorbent thus providing the required concentration gradients between adsorbent and adsorbate for adsorption. Fixed-bed operations are widely used in pollution control processes such as for the removal of toxic organic compounds by carbon adsorption [9]. The design and theory of fixed-bed adsorption systems focuses on establishing the shape of the breakthrough curve and its velocity through the bed. Breakthrough and bed volumes are usually employed in the evaluation of the performance of a fixed-bed column [10].

Column operations can be designed on the basis of the experimental data collected. Many mathematical models have been developed for the evaluation of efficiency and applicability of the column models for large-scale operations. In designing a column absorption process, it becomes necessary to predict the break-through curve or concentration-time profile and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. The objective of this work is to investigate the Phosphorylated tamarind nut carbon (PTNC) a novel material in fixed-bed for the removal of Cd(II) from aqueous solution. In this study the Adam’s-Bohart model, Thomas model and Yoon-Nelson model were used to analyse the behavior of PTNC in fixed-bed adsorption of cadmium.

2. Materials and Methods

2.1 Preparation of Activated Carbon

Tamarind nuts (seeds) were collected from agricultural fields of Coimbatore, Tamilnadu, India. The soil and other impurities were removed by washing with distilled water.
The seeds were washed in distilled water, dried and pulverized to 300 – 800 µm particle sizes. The material was then impregnated in orthophosphoric acid in the weight ratio of 1:1 and carbonized in the hot air oven at a temperature of 160±5 °C for 24 h. The carbonized material was then cooled to room temperature, washed with distilled water several times to remove the excess acid and dried at 100±5 °C. The carbon was then soaked in 1% sodium carbonate solution for 24 h, washed with distilled water to remove excess sodium carbonate, dried at 100±5 °C and sieved to 300 – 800 µm particle sizes. Preliminary studies were carried out with phosphorylated tamarind nut carbon soaked in 1% sodium carbonate (PTNC) and the precursors for adsorption of metals. Based on their efficiency PTNC was chosen for further studies. The physicochemical properties of Phosphorylated tamarind nut carbon (PTNC) have been previously reported [11].

2.2 Preparation of solutions

Stock solution of cadmium was prepared by dissolving accurately weighed cadmium sulphate in distilled water to the concentration of 1000 mg/L. The stock solution was diluted with distilled water to obtain working solutions of desired inlet concentrations. Before the adsorption study, Cd(II) solution of varying concentrations was adjusted to pH 7 with 0.1M HCl and 0.1M NaOH solutions. All the chemicals used for this study were of analytical reagent grade obtained from E. Merck, Ranbaxy, SD Fine and BDH.

2.3 Experimental set-up

The fixed-bed columns made of Pyrex glass tube of 2.5 cm inner diameter and 30 cm height with a Teflon stopper valve were used. At the bottom of the column, a stainless steel sieve was attached followed by a layer of glass wool. The prepared activated carbon was sieved to a particle size of 300-800 µm. A known quantity of the carbon was packed in the column to yield the desired bed height of 60, 90 and 120 mm (equivalent to 8.9, 14.6 and 19.8 g of the activated carbon). The column was then filled with glass beads in order to provide a uniform flow of the solution through the column. Cd(II) solution of concentrations (50, 100 and 200 mg/L) at pH 5.0 was allowed to pass through the carbon bed at a desired rate (5, 10, and 15 mL/min) controlled by a flow regulating valve. The schematic representation of the column is shown in Figure 1. The inflow and outflow rates were maintained at a constant rate for a particular experiment. Frequent checks were made at regular intervals to correct any alteration in the flow rates. The effluent solutions were collected at regular time intervals and the concentration of Cd(II) was analysed using atomic absorption spectrometer (Elico SL 163) at 228 nm. The experiments were carried out at temperature of 25±1 °C without any pH adjustment during the experiment.

2.4 Analysis of fixed-bed column data

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation mechanism and the dynamic response of an adsorption in fixed-bed column. The breakthrough curves show the loading behavior of metal ion to be removed from solution in a fixed-bed column and is usually expressed in terms of adsorbed Cd(II) concentration (Cad), inlet metal concentration (Ci), outlet metal concentration (Co) or normalized concentration defined as the ratio of outlet to inlet concentration (Co/Ci) as a function of time or effluent for a given bed height [12]. Effluent volume (Ve) can be calculated as:

\[
V_{eff} = \frac{Q}{t_{total}}
\]

Where \(t_{total}\) and Q are the total flow time (min) and volumetric flow rate (mL/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (Cad) mg/L versus t (min) plot can be used to find the total adsorbed Cd(II) quantity (maximum column capacity). Total adsorbed Cd(II) quantity \(q_{total}\) (mg) in the column for a given feed concentration and flow rate is calculated as:

\[
q_{total} = \frac{Q_A}{1000} = \frac{Q}{1000} \int_{t=0}^{t_{total}} C_a d. dt
\]

Equilibrium uptake \(q_{eq}\) (mg/g) or maximum capacity of the column is defined by equation (3) as the total amount of metal ion adsorbed \(q_{total}\) per gram of adsorbent (W) at the end of total flow time.

\[
q_{eq} = \frac{q_{total}}{W}
\]

For the successful design of a column adsorption process, it is important to predict the breakthrough curve for effluent parameters. Various kinetic models have been developed to predict the dynamic behavior of the column.

2.5 Theory of models for fixed-bed studies

2.5.1 The Thomas model
Thomas model is simple to use in the design of a fixed-bed adsorption column and is one of the most general and widely used methods in column performance theory [13]. This model uses Langmuir isotherm for equilibrium and second-order reversible reaction kinetics, and is suitable for adsorption process where the external and internal diffusion limitations are absent. The linearised form of Thomas model can be expressed as follows.

\[
\ln \left( \frac{C_t}{C_0} \right) = \frac{k_T q_0 M}{Q} t - \frac{k_T C_0 V}{Q}
\]  

(4)

where \( k_T \) is the Thomas rate constant (mL/min/mg); \( q_0 \) is the maximum adsorption capacity (mg/g); \( C_0 \) is the inlet Cd(II) concentration (mg/L); \( C_t \) is the outlet Cd(II) concentration (mg/L); \( M \) the total mass of the adsorbent (g), \( Q \) the volumetric flow rate (mL/min) and \( V \) is the through-put volume (ml). The values of \( k_T \) and \( q_0 \) are determined from the plot of \( \ln \left( C_t/C_0 \right) \) against \( Vt \) for a given flow rate linear regression.

2.5.2 The Adam’s – Bohart model

Adam and Bohart proposed a relationship between \( C_t/C_0 \) and \( t \) in a continuous system to describe the initial part of the breakthrough curve [14]. The expression is given in equation 5:

\[
\ln \frac{C_t}{C_0} = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{F}
\]  

(5)

where \( C_t \) is the effluent Cd(II) concentration (mg/L), \( C_0 \) is the inlet Cd(II) concentration, \( k_{AB} \) is the kinetic constant (mL/mg min), \( F \) is the linear flow rate (cm/min), \( Z \) is the bed depth of column (cm), \( N_0 \) is the saturation concentration (mg/mL) and \( t \) is time (min). Parameters describing the characteristic operations of the column (\( k_{AB} \) and \( N_0 \)) were determined using a linear plot of \( \ln \left( C_t/C_0 \right) \) against time \( (t) \). From the intercept and slope of the plot the values of \( N_0 \) and \( k_{AB} \) were determined respectively.

2.5.3 Yoon-Nelson model

Yoon and Nelson developed a model based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [15]. The linearized Yoon-Nelson model for a single component system is expressed as:

\[
\ln \left( \frac{C_t}{C_0 - C_t} \right) = k_{YN} t - \tau k_{YN}
\]  

(6)

where \( k_{YN} \) (L/min) is the rate velocity constant, \( \tau \) (min) is the time required for 50% adsorbate breakthrough. From a linear plot of \( \ln[C_t/(C_0-C_t)] \) against sampling time \( (t) \), values of \( k_{YN} \) and \( \tau \) were determined from the intercept and slope of the plot (figure not shown).

Based on Yoon-Nelson model, the amount of the adsorbate being adsorbed in a fixed bed is half of the total adsorbate entering the adsorption bed within 2\( \tau \) period [16]. For a given bed

\[
q_{YN} = \frac{q_{total(0)}}{m} = \frac{3}{2}\left( \frac{C_0 r \cdot \tau}{1000 m} \right)
\]  

(7)

From this equation, the adsorption capacity, \( q_{YN} \), varies as a function of inlet dye concentration \( (C_0) \), flow rate \( (r) \), weight of adsorbent \( (m) \) and 50% breakthrough time.

3. Results and Discussion

3.1 Effect of inlet Cd(II) concentration

The effect of variation of Cd(II) concentration from 50 to 200 mg/L used with a uniform adsorbent bed height of 90 mm and solution flow rate of 5 mL/min is shown in the breakthrough curve in Figure 2. When the initial Cd(II) concentration was increased from 50 to 200 mg/L the corresponding adsorption bed capacity appeared to increase and are presented in Table 1. The intake capacity was found to be 7.11, 13.63 and 15.12 mg/g for inlet concentrations of 50, 100 and 200 mg/L of Cd(II), respectively.

![Figure 2: Effect of inlet concentration of Cd(II) on PTNC column](image)

Higher initial Cd(II) concentrations caused a faster breakthrough as expected. A lower inlet Cd(II) concentration gave delayed breakthrough curves and the treated volume was also higher since the lower concentration gradient caused slower transport due to decreased diffusion coefficient [17]. At the highest Cd(II) concentration (200 mg/L) the PTNC bed saturated quickly leading to steep breakthrough and earlier exhaustion time. Table 1 showed that the highest uptake and low total weight of adsorbent \((m)\) and 50% breakthrough.

3.2 Effect of solution flow rate

The effect of flow rate on the adsorption of Cd(II) using PTNC was investigated by varying the flow rate (5, 10 and 15 mL/min) with a constant adsorbent bed height of 90 mm and the inlet Cd(II) concentration of 200 mg/L and are shown in Figure.3. Initially the adsorption was very rapid at lower flow rate probably associated with the
availability of reaction sites able to capture Cd(II) ions. In the later stages of the process due to the gradual occupancy of these sites, the uptake of Cd(II) becomes less effective. With increase of flow rate the breakthrough time for reaching saturation concentration decreased significantly and hence at higher flow rates breakthrough curve became steeper and the absorbed Cd(II) concentration decreased. The probable reason behind this is that, at higher flow rates the residence time of the solute in the column is insufficient for adsorption equilibrium to be reached. Thus the Cd(II) solution leaves the column before equilibrium occurs as the contact time of metal ions with PTNC is very short at higher flow rate, causing a reduction in removal efficiency [18].

![Figure 3: Effect of flow rate for the removal of Cd(II) on PTNC column](image)

The Cd(II) intake capacity was found to decrease as 14.24, 13.58 and 12.23 mg/g with inlet concentration of 200 for flow rates of 5, 10 and 15 ml/min, respectively. The sorption data were evaluated and the total quantity of metal adsorbed, maximum Cd(II) uptake and removal percentage with respect to flow rate are presented in Table 1. As seen in the Table 1, the maximum values of total adsorbed Cd(II) quantity, maximum Cd(II) uptake and Cd(II) removal percentage were obtained as 220.81 mg, 15.12 mg/g and 86.4% respectively at flow rate of 5 ml/min and the values decreased with increasing flow rate.

3.3 Effect of activated carbon bed height

Adsorption of metal ions in the fixed bed column depends upon the quantity of the adsorbent packed in the column. PTNC of weight 8.9, 14.6 and 19.8 g was added to columns to yield different bed heights of 60, 90 and 120 mm. The breakthrough curves obtained for the adsorption of Cd(II) on PTNC for different bed heights with the inlet concentration of 200 mg/L and at a constant flow rate of 5 ml/min are shown in the Figure 4. The results shown in Table 1 indicated that the breakthrough volume of the Cd(II) solution increased with increase in bed height due to the availability of more number of sorption sites(i.e the total surface area increases). The equilibrium sorption capacity decreased with increase in bed height. This shows that at smaller bed height the effluent adsorbate concentration ratio increased more rapidly than for a higher bed height. Furthermore, the bed is saturated in less time for smaller bed heights which contains less amount of adsorbent. The maximum breakthrough capacities for different bed heights of 60, 90 and 120 mm were 14.24, 15.12 and 16.21 mg/g respectively. The increase in bed height has resulted in increased uptake of Cd (II) ions. This was attributed to the fact that as the bed height increased from 60 to 120 mm, Cd (II) had more contact time with the PTNC which resulted in higher removal of metal ions from the column.

![Figure 4: Effect of bed height for the removal of Cd(II) on PTNC column](image)

3.4 Dynamic adsorption models

3.4.1 Thomas model

The column data were applied to the Thomas model to determine the Thomas rate constant k_{TH} and maximum solid-phase concentration q_{0}. The determined coefficients and relative constants were obtained using linear regression analysis according to Eq. (4) and the results are listed in Table 2. From Table 2, it was seen that values of determined coefficients (R^2) range from 0.937 to 0.993. As the inlet concentration increased the value of q_0 increased but the value of k_{TH} decreased. The reason is that the driving force for adsorption is the concentration difference between the metal ion on the adsorbent and that in the solution [12]. With increasing flow rate, the value of q_0 decreased but the value of k_{TH} increased. As the bed heights increased, the values of q_0 increased significantly while the value of k_{TH} decreased significantly. So lower flow rate, higher initial concentration and higher bed heights would increase the adsorption of Cd(II) on the carbon column. The Thomas model is suitable for adsorption process where the external and internal diffusions will not be the limiting step [19].

3.4.2 Adam's’s -Bohart model

The Adam's-Bohart adsorption model was applied to experimental data for the description of the initial part of the breakthrough curve. After applying Eq.(5) to the experimental data for all breakthrough curves, respective values of N_0 and k_{AB} were calculated and presented in Table 2 together with the correlation coefficients (R^2). From Table 2, it is seen that the values of N_0 increased with increase in concentration and bed height and decreased with flow rate. The correlation coefficient, R^2 values...
ranged from 0.891 to 0.985. Although the Adam’s-Bohart model provides a simple and comprehensive approach to running and evaluating adsorption-column tests, its validity is limited to the range of conditions used. From Table 2 the values of \( k_{\text{AB}} \) decreases with both initial concentration and flow rate increase, but it increased with bed height increase. This showed that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column [12].

3.4.3 Yoon-Nelson model

The values of \( K_{YN} \), and \( \tau \) obtained are listed in Table 3. From the results shown, the rate constant, \( K_{YN} \) increased with respect to inlet concentration. This is due to the fact that increase in initial ion concentration increases the competition between adsorbate molecules for the adsorption site, which ultimately results in increased uptake rate [20]. But the 50% breakthrough time \( \tau \) decreased with increasing (Cd(II)) inlet concentration. With increase of bed height the \( \tau \) value increased while the value of \( K_{YN} \) decreased. The values of determined coefficients \( (R^2) \) range from 0.937 to 0.993. High values of correlation coefficients indicate that Yoon and Nelson model fitted well to the experimental data. This is in agreement with the results obtained by Tsai, et al. [21]. The value of \( R^2 \) for Thomas and Yoon-Nelson model were higher than the Adam-Bohart Model. Comparing the values of \( R^2 \) and the breakthrough curves, both the Thomas and Yoon-Nelson models can be used to describe the behavior of the adsorption of Cd(II) in a fixed bed column.

### Table 1: The effect of flow rate and initial Cadmium concentration on the total adsorbed quantity of Cd(II) (\( q_{\text{total}} \)), equilibrium Cd(II) uptake (\( q_{\text{eq}} \)) and total removal percentage of Cd(II) for cadmium adsorption on PTNC

<table>
<thead>
<tr>
<th>Q (mL/min)</th>
<th>C(_0) (mg/L)</th>
<th>PTNC Bed height (mm)</th>
<th>( q_{\text{total}} ) (mg)</th>
<th>( q_{\text{eq}} ) (mg/g)</th>
<th>Removal (%)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>50</td>
<td>90</td>
<td>103.95</td>
<td>7.11</td>
<td>99.8</td>
<td>0.952</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>90</td>
<td>198.99</td>
<td>13.63</td>
<td>88.2</td>
<td>0.985</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>90</td>
<td>220.81</td>
<td>15.12</td>
<td>86.4</td>
<td>0.954</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>90</td>
<td>198.40</td>
<td>13.58</td>
<td>76.3</td>
<td>0.946</td>
</tr>
<tr>
<td>15</td>
<td>200</td>
<td>90</td>
<td>178.56</td>
<td>12.23</td>
<td>74.3</td>
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<tr>
<td>5</td>
<td>200</td>
<td>60</td>
<td>120.73</td>
<td>14.24</td>
<td>82.7</td>
<td>0.891</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>120</td>
<td>320.98</td>
<td>16.21</td>
<td>94.5</td>
<td>0.909</td>
</tr>
</tbody>
</table>

### Table 2: Adam-Bohart, Thomas and Yoon-Nelson model Parameters at different conditions using Linear Regression Analysis

<table>
<thead>
<tr>
<th>Inlet Cd(II)</th>
<th>PTNC Bed height (mm)</th>
<th>Flow rate (mL/min)</th>
<th>Adam-Bohart model Parameters</th>
<th>Thomas model Parameters</th>
<th>Yoon-Nelson model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( K_{\text{AB}} ) (L/min mg) \times 10(^3)</td>
<td>( N_0 ) (mg/L)\times 10(^3)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td></td>
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<td>( N_0 ) (mg/L)\times 10(^3)</td>
<td>( R^2 )</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>( K_{\text{YN}} ) (L/min)</td>
<td>( \tau ) (min)</td>
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<td>0.936</td>
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</table>

4. Conclusion

Tamarind nut was generated as a waste biomaterial in the agricultural sector and could be used effectively in treating water and wastewaters. From the present study, PTNC prepared by Phosphoric acid treatment of Tamarind seeds was found suitable for the removal of Cd(II) from aqueous system using fixed-bed columns. The effect of inlet Cd(II) concentration, flow rate and bed height on PTNC was investigated and the experimental breakthrough curves were obtained. Thomas, Adam-Bohart and Yoon-Nelson models were applied to the experimental data obtained from the adsorption of Cd(II) ion onto PTNC. Among these models, Thomas and Yoon-Nelson models appeared to describe the experimental results better. Thus, PTNC can be used in the fixed bed column as a potential adsorbent for removal of Cd(II) polluted aqueous solutions.

5. Future Scope

Further, studies pertaining to the removal of other toxic metal ions such as mercury, arsenic could be carried out carried out along with the removal of organics from wastewater using fixed bed columns.

References


Author Profile

N. Suganthi received B.Sc and M.Sc degree in Chemistry from PSGR Krishnamal College for Women, Bharathiar University, Coimbatore in 1998 and 2000 respectively. In 2002 she has completed M.Phil degree from Kongunadu Arts and Science College, Bharathiar University, Coimbatore. She was awarded Ph.D in Chemistry from Anna University, Chennai in 2011. At present she is working as Assistant Professor in the Department of Chemistry, L.R.G Govt Arts College for Women, Tirupur, India.

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